

1st



International Chemistry Olympiad

**4 theoretical problems
2 practical problems**

THE FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 18–21 JULY 1968, PRAGUE, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A mixture of hydrogen and chlorine kept in a closed flask at a constant temperature was irradiated by scattered light. After a certain time the chlorine content decreased by 20 % compared with that of the starting mixture and the resulting mixture had the composition as follows: 60 volume % of chlorine, 10 volume % of hydrogen, and 30 volume % of hydrogen chloride.

Problems:

- 1.1 What is the composition of the initial gaseous mixture?
- 1.2 How chlorine, hydrogen, and hydrogen chloride are produced?

SOLUTION



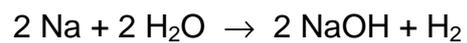
30 volume parts of hydrogen chloride could only be formed by the reaction of 15 volume parts of hydrogen and 15 volume parts of chlorine. Hence, the initial composition of the mixture had to be:

$$\text{Cl}_2: 60 + 15 = 75 \%$$

$$\text{H}_2: 10 + 15 = 25 \%$$

- 1.2 Chlorine and hydrogen are produced by electrolysis of aqueous solutions of NaCl:
- $$\text{NaCl(aq)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$



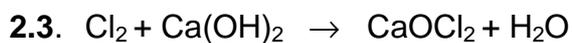
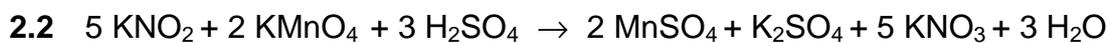
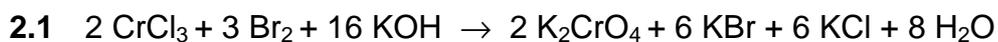


Hydrogen chloride is produced by the reaction of hydrogen with chlorine.

PROBLEM 2

Write down equations for the following reactions:

- 2.1 Oxidation of chromium(III) chloride with bromine in alkaline solution (KOH).
 - 2.2 Oxidation of potassium nitrite with potassium permanganate in acid solution (H₂SO₄).
 - 2.3 Action of chlorine on lime water (Ca(OH)₂) in a cold reaction mixture.
-

SOLUTION

PROBLEM 3

The gas escaping from a blast furnace has the following composition:

12.0 volume % of CO ₂	28.0 volume % of CO
3.0 volume % of H ₂	0.6 volume % of CH ₄
0.2 volume % of C ₂ H ₄	56.2 volume % of N ₂

Problems:

- 3.1** Calculate the theoretical consumption of air (in m³) which is necessary for a total combustion of 200 m³ of the above gas if both the gas and air are measured at the same temperature. (Oxygen content in the air is about 20 % by volume).
- 3.2** Determine the composition of combustion products if the gas is burned in a 20 % excess of air.

SOLUTION

	O ₂
3.1 2 CO + O ₂ → 2 CO ₂	14
2 H ₂ + O ₂ → 2 H ₂ O	1.5
CH ₄ + 2 O ₂ → CO ₂ + 2 H ₂ O	1.2
C ₂ H ₄ + 3 O ₂ → 2 CO ₂ + 2 H ₂ O	0.6
	17.3 parts × 5 = 86.5 parts of the air

$$\begin{array}{r}
 200 \text{ m}^3 \text{ of the gas} \dots\dots\dots 2 \times 86.5 = 173.0 \text{ m}^3 \text{ of the air} \\
 \phantom{200 \text{ m}^3 \text{ of the gas}} + 20 \% 34.6 \text{ m}^3 \\
 \hline
 207.6 \text{ m}^3 \text{ of the air}
 \end{array}$$

- 3.2** 207.6 : 5 = 41.52 parts of O₂ : 2 = 20.76 parts of O₂ for 100 m³ of the gas
 20.76 × 4 = 83.04 parts of N₂ for 100 m³ of the gas

Balance:	CO ₂	H ₂ O	N ₂	O ₂
(volume parts)	12.00	3.00	56.20	20.76
	28.00	1.20	83.04	- 17.30
	0.60	0.40		
	0.40			
	<hr/>			
	41.00	4.60	139.24	3.46

Total: $41.00 + 4.60 + 139.24 + 3.46 = 188.30$ of volume parts of the gaseous components.

$$\% \text{H}_2\text{O} = \frac{4.60}{188.30} \times 100 = 2.44$$

$$\% \text{N}_2 = \frac{139.24}{188.30} \times 100 = 73.95$$

$$\% \text{O}_2 = \frac{3.46}{188.30} \times 100 = 1.84$$

PROBLEM 4

A volume of 31.7 cm³ of a 0.1-normal NaOH is required for the neutralization of 0.19 g of an organic acid whose vapour is thirty times as dense as gaseous hydrogen.

Problem:

4.1 Give the name and structural formula of the acid.

(The acid concerned is a common organic acid.)

SOLUTION

4.1

a) The supposed acid may be: HA, H₂A, H₃A, etc.

$$n(\text{NaOH}) = c V = 0.1 \text{ mol dm}^{-3} \times 0.0317 \text{ dm}^3 = 3.17 \times 10^{-3} \text{ mol}$$

$$n(\text{acid}) = \frac{3.17 \times 10^{-3}}{\nu} \text{ mol}$$

where $\nu = 1, 2, 3, \dots$

$$n(\text{acid}) = \frac{m(\text{acid})}{M(\text{acid})}$$

$$M(\text{acid}) = \nu \times \frac{0.19 \text{ g}}{3.17 \times 10^{-3} \text{ mol}} = \nu \times 60 \text{ g mol}^{-1} \quad (1)$$

b) From the ideal gas law we can obtain:

$$\frac{\rho_1}{\rho_2} = \frac{M_1}{M_2}$$

$$M(\text{H}_2) = 2 \text{ g mol}^{-1}$$

$$M(\text{acid}) = 30 \times 2 = 60 \text{ g mol}^{-1}$$

By comparing with (1): $\nu = 1$

The acid concerned is a monoprotic acid and its molar mass is 60 g mol⁻¹.

The acid is acetic acid: CH₃-COOH

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

There are ten test tubes in the rack at your disposal (1 – 10) and each test tube contains one of aqueous solutions of the following salts: Na_2SO_4 , AgNO_3 , KI , $\text{Ba}(\text{OH})_2$, NH_4Cl , Ag_2SO_4 , $\text{Pb}(\text{NO}_3)_2$, NaOH , NH_4I , KCl .

For identification of the particular test tubes you can use mutual reactions of the solutions in the test tubes only.

Determine in which order the solutions of the salts in your rack are and write chemical equations of the reactions you used for identification of the salts.

PROBLEM 2 (Practical)

Each of the six test tubes (A – F) in the rack contains one of the following substances:

benzoic acid, salicylic acid, citric acid, tartaric acid, oxalic acid and glucose.

Determine the order in which the substances in the test tubes are placed in your rack and give chemical reactions you used for identification of the substances.

For identification of the substances the following aqueous solutions are at your disposal: HCl , H_2SO_4 , NaOH , NH_4OH , CuSO_4 , KMnO_4 , FeCl_3 , KCl , and distilled water.

2nd



International Chemistry Olympiad

**4 theoretical problems
2 practical problems**

THE SECOND INTERNATIONAL CHEMISTRY OLYMPIAD 16–20 JUNE 1969, KATOWICE, POLAND

THEORETICAL PROBLEMS

PROBLEM 1

An amount of 20 g of potassium sulphate was dissolved in 150 cm³ of water. The solution was then electrolysed. After electrolysis, the content of potassium sulphate in the solution was 15 % by mass.

Problem:

What volumes of hydrogen and oxygen were obtained at a temperature of 20 °C and a pressure of 101 325 Pa?

SOLUTION

On electrolysis, only water is decomposed and the total amount of potassium sulphate in the electrolyte solution is constant. The mass of water in the solution:

1.1 Before electrolysis (on the assumption that $\rho = 1 \text{ g cm}^{-3}$): $m(\text{H}_2\text{O}) = 150 \text{ g}$

1.2 After electrolysis:

$$m(\text{H}_2\text{O}) = m(\text{solution}) - m(\text{K}_2\text{SO}_4) = \frac{20 \text{ g}}{0.15} - 20 \text{ g} = 113.3 \text{ g}$$

The mass of water decomposed on electrolysis:

$$m(\text{H}_2\text{O}) = 150 - 113.3 = 36.7 \text{ g, i. e.}$$

$$n(\text{H}_2\text{O}) = 2.04 \text{ mol}$$



thus, $n(\text{H}_2) = 2.04 \text{ mol}$

$$n(\text{O}_2) = 1.02 \text{ mol}$$

$$V(\text{H}_2) = \frac{n(\text{H}_2)RT}{p} = \frac{2.04 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}}{101325 \text{ Pa}}$$

$$\approx 0.049 \text{ m}^3, \text{ resp. } 49 \text{ dm}^3$$

$$V(\text{O}_2) = \frac{1}{2} V(\text{H}_2) \approx 0.0245 \text{ m}^3 \approx 24.5 \text{ dm}^3$$

PROBLEM 2

A compound **A** contains 38.67 % of potassium, 13.85 % of nitrogen, and 47.48 % of oxygen. On heating, it is converted to a compound **B** containing 45.85 % of potassium, 16.47 % of nitrogen, and 37.66 % of oxygen.

Problem:

2.1 What are the stoichiometric formulas of the compounds?

2.2 Write the corresponding chemical equation.

SOLUTION

2.1 Compound **A**:

$$\text{K}_x\text{N}_y\text{O}_z \quad x : y : z = \frac{38.67}{39.1} = \frac{13.85}{14} = \frac{47.48}{16} = 0.989 : 0.989 : 2.968 = 1 : 1 : 3$$

A : KNO_3

Compound **B**:

$$\text{K}_p\text{N}_q\text{O}_r \quad p : q : r = \frac{45.85}{39.1} = \frac{16.47}{14} = \frac{37.66}{16} = 1.173 : 1.176 : 2.354 = 1 : 1 : 2$$

B : KNO_2

2.2 Equation: $2 \text{KNO}_3 \rightarrow 2 \text{KNO}_2 + \text{O}_2$

PROBLEM 3

A 10 cm³ sample of an unknown gaseous hydrocarbon was mixed with 70 cm³ of oxygen and the mixture was set on fire by means of an electric spark. When the reaction was over and water vapours were liquefied, the final volume of gases decreased to 65 cm³. This mixture then reacted with a potassium hydroxide solution and the volume of gases decreased to 45 cm³.

Problem:

What is the molecular formula of the unknown hydrocarbon if volumes of gases were measured at standard temperature and pressure (STP) conditions?

SOLUTION

The unknown gaseous hydrocarbon has the general formula: C_xH_y

$$n(\text{C}_x\text{H}_y) = \frac{0.010 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = \frac{0.010}{22.4} \text{ mol}$$

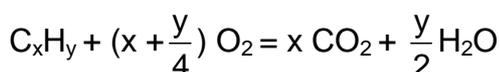
Balance of oxygen:

- Before the reaction: 70 cm³, i. e. $\frac{0.070}{22.4}$ mol

- After the reaction: 45 cm³, i. e. $\frac{0.045}{22.4}$ mol

Consumed in the reaction: $\frac{0.025}{22.4}$ mol of O₂

According to the equation:



Hence, $\frac{0.020}{22.4}$ mol of O₂ reacted with carbon and $\frac{0.020}{22.4}$ mol of CO₂ was formed

(C + O₂ = CO₂),

$\frac{0.005}{22.4}$ mol O₂ combined with hydrogen and $\frac{0.010}{22.4}$ mol of water was obtained

(2 H₂ + O₂ = 2 H₂O).

$$3 n(\text{C}) = n(\text{CO}_2) = \frac{0.020}{22.4} \text{ mol}$$

$$n(\text{H}_2) = 2 n(\text{H}_2\text{O}) = \frac{0.020}{22.4} \text{ mol}$$

$$x : y = n(\text{C}) : n(\text{H}_2) = 0.020 : 0.020 = 1 : 1$$

From the possible solutions C_2H_2 , C_3H_3 , C_4H_4 , C_5H_5 . only C_2H_2 satisfies to the conditions given in the task, i. e. the unknown hydrocarbon is acetylene.

PROBLEM 4

Calcium carbide and water are the basic raw materials in the production of:

- ethanol
- acetic acid
- ethylene and polyethylene
- vinyl chloride
- benzene

Problem:

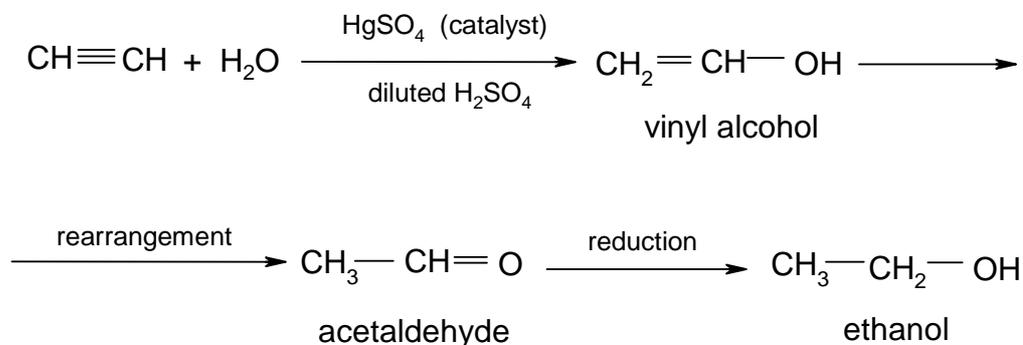
Give basic chemical equations for each reaction by which the above mentioned compounds can be obtained.

SOLUTION

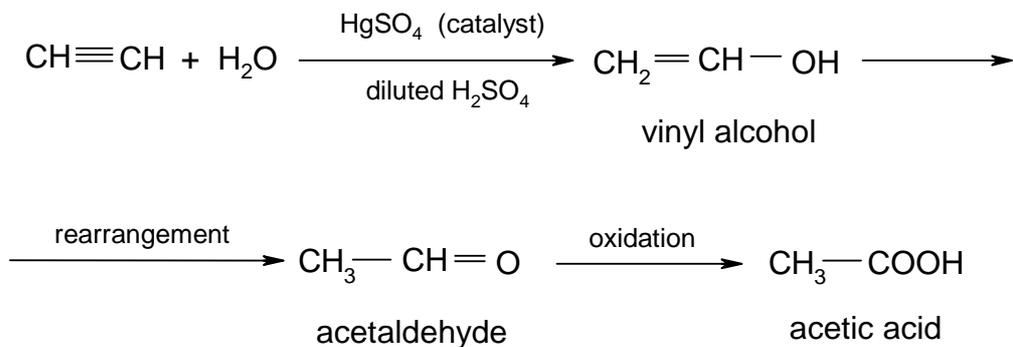
Basic reaction: $\text{CaC}_2 + 2 \text{H}_2\text{O} = \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$

From acetylene can be obtained:

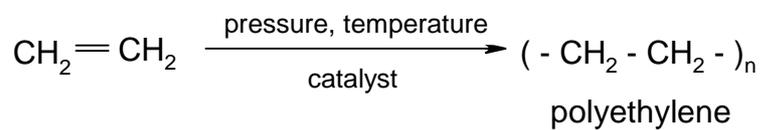
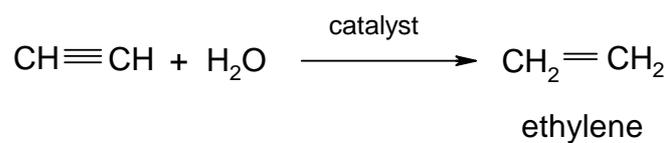
- ethanol



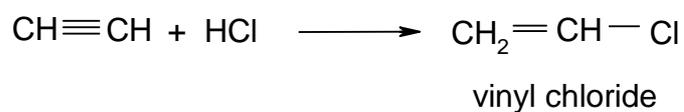
- acetic acid



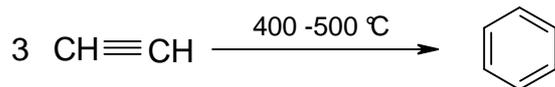
c) ethylene, polyethylene



d) vinyl chloride



e) benzene



PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**

a) Three numbered test-tubes (1-3) contain mixtures of two substances from the following pairs (4 variants):

- | | | |
|--|--|---|
| 1. ZnSO_4 - NaBr | NaCl - $\text{Ca}(\text{NO}_3)_2$ | MgSO_4 - NH_4Cl |
| 2. AlCl_3 - KBr | CaCl_2 - NaNO_3 | ZnCl_2 - $(\text{NH}_4)_2\text{SO}_4$ |
| 3. KNO_3 - Na_2CO_3 | KCl - MgSO_4 | NH_4Cl - $\text{Ba}(\text{NO}_3)_2$ |
| 4. MgCl_2 - KNO_3 | K_2CO_3 - ZnSO_4 | $\text{Al}(\text{NO}_3)_3$ - NaCl |

b) Each of the test-tubes numbered 4 and 5 contains one of the following substances: glucose, saccharose, urea, sodium acetate, oxalic acid.

Problem:

By means of reagents that are available on the laboratory desk determine the content of the individual test-tubes. Give reasons for both the tests performed and your answers and write the chemical equations of the corresponding reactions.

Note:

For the identification of substances given in the above task, the following reagents were available to competing pupils: 1 N HCl, 3 N HCl, 1 N H_2SO_4 , concentrated H_2SO_4 , FeSO_4 , 2 N NaOH, 20 % NaOH, 2 N NH_4Cl , 2 N CuSO_4 , 2 N BaCl_2 , 0,1 N AgNO_3 , 0,1 % KMnO_4 , distilled water, phenolphthalein, methyl orange. In addition, further laboratory facilities, such as platinum wire, cobalt glass, etc., were available.

PROBLEM 2 (Practical)

Allow to react 10 cm³ of a 3 N HCl solution with the metal sample (competing pupils were given precisely weighed samples of magnesium, zinc or aluminium) and collect the hydrogen evolved in the reaction in a measuring cylinder above water. Perform the task by means of available device and procedure.

In order to simplify the problem, calculate the mass of your metal sample from the volume of hydrogen on the assumption that it was measured at STP conditions.

3rd



**6 theoretical problems
2 practical problems**

THE THIRD INTERNATIONAL CHEMISTRY OLYMPIAD 1–5 JULY 1970, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

An amount of 23 g of gas (density $\rho = 2.05 \text{ g dm}^{-3}$ at STP) when burned, gives 44 g of carbon dioxide and 27 g of water.

Problem:

What is the structural formula of the gas (compound)?

SOLUTION

The unknown gas : X

$$\text{From the ideal gas law : } M(X) = \frac{\rho(X) R T}{p} = 46 \text{ g mol}^{-1}$$

$$n(X) = \frac{23 \text{ g}}{46 \text{ g mol}^{-1}} = 0.5 \text{ mol}$$

$$n(\text{CO}_2) = \frac{44 \text{ g}}{44 \text{ g mol}^{-1}} = 1 \text{ mol}$$

$$n(\text{C}) = 1 \text{ mol}$$

$$m(\text{C}) = 12 \text{ g}$$

$$n(\text{H}_2\text{O}) = \frac{27 \text{ g}}{18 \text{ g mol}^{-1}} = 1.5 \text{ mol}$$

$$n(\text{H}) = 3 \text{ mol}$$

$$m(\text{H}) = 3 \text{ g}$$

The compound contains also oxygen, since

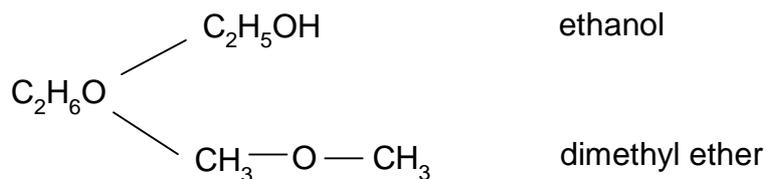
$$m(\text{C}) + m(\text{H}) = 12 \text{ g} + 3 \text{ g} = 15 \text{ g} < 23 \text{ g}$$

$$m(\text{O}) = 23 \text{ g} - 15 \text{ g} = 8 \text{ g}$$

$$n(\text{O}) = 0,5 \text{ mol}$$

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = 1 : 3 : 0,5 = 2 : 6 : 1$$

The empirical formula of the compound is $\text{C}_2\text{H}_6\text{O}$.



Ethanol is liquid in the given conditions and therefore, the unknown gas is dimethyl ether.

PROBLEM 2

A sample of crystalline soda (**A**) with a mass of 1.287 g was allowed to react with an excess of hydrochloric acid and 100.8 cm³ of a gas was liberated (measured at STP).

Another sample of different crystalline soda (**B**) with a mass of 0.715 g was decomposed by 50 cm³ of 0.2 N sulphuric acid.

After total decomposition of soda, the excess of the sulphuric acid was neutralized which required 50 cm³ of 0.1 N sodium hydroxide solution (by titration on methyl orange indicator).

Problems:

- 2.1** How many molecules of water in relation to one molecule of Na₂CO₃ are contained in the first sample of soda?
- 2.2** Have both samples of soda the same composition?

Relative atomic masses: $A_r(\text{Na}) = 23$; $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{O}) = 16$.

SOLUTION

2.1 Sample **A**: Na₂CO₃ · x H₂O

$$m(\text{A}) = 1.287 \text{ g}$$

$$n(\text{CO}_2) = \frac{pV}{RT} = 0.0045 \text{ mol} = n(\text{A})$$

$$M(\text{A}) = \frac{1.287 \text{ g}}{0.0045 \text{ mol}} = 286 \text{ g mol}^{-1}$$

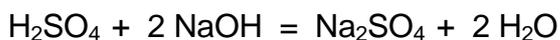
$$M(\text{A}) = M(\text{Na}_2\text{CO}_3) + x M(\text{H}_2\text{O})$$

$$x = \frac{M(\text{A}) - M(\text{Na}_2\text{CO}_3)}{M(\text{H}_2\text{O})} = \frac{(286 - 106) \text{ g mol}^{-1}}{18 \text{ g mol}^{-1}} = 10$$

Sample **A**: Na₂CO₃ · 10 H₂O

2.2 Sample **B**: $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$

$$m(\text{B}) = 0.715 \text{ g}$$



$$n(\text{NaOH}) = c V = 0.1 \text{ mol dm}^{-3} \times 0.05 \text{ dm}^3 = 0.005 \text{ mol}$$

$$\text{Excess of H}_2\text{SO}_4: n(\text{H}_2\text{SO}_4) = 0.0025 \text{ mol}$$

Amount of substance combined with sample **B**:

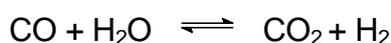
$$n(\text{H}_2\text{SO}_4) = 0.0025 \text{ mol} = n(\text{B})$$

$$M(\text{B}) = \frac{0.715 \text{ g}}{0.0025 \text{ g mol}^{-1}} = 286 \text{ g mol}^{-1}$$

Sample **B**: $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$

PROBLEM 3

Carbon monoxide was mixed with 1.5 times greater volume of water vapours. What will be the composition (in mass as well as in volume %) of the gaseous mixture in the equilibrium state if 80 % of carbon monoxide is converted to carbon dioxide?

SOLUTION

Assumption:

$$n(\text{CO}) = 1 \text{ mol}$$

$$n(\text{H}_2\text{O}) = 1.5 \text{ mol}$$

After reaction:

$$n(\text{CO}) = 0.2 \text{ mol}$$

$$n(\text{H}_2\text{O}) = 0.7 \text{ mol}$$

$$n(\text{CO}_2) = 0.8 \text{ mol}$$

$$n(\text{H}_2) = 0.8 \text{ mol}$$

$$\varphi(\text{CO}) = \frac{V(\text{CO})}{V} = \frac{0.2 \text{ mol}}{2.5 \text{ mol}} = 0.08 \text{ i.e. } 8 \text{ vol. \% of CO}$$

$$\varphi(\text{H}_2\text{O}) = \frac{V(\text{H}_2\text{O})}{V} = \frac{0.7 \text{ mol}}{2.5 \text{ mol}} = 0.28 \text{ i.e. } 28 \text{ vol. \% of H}_2\text{O}$$

$$\varphi(\text{CO}_2) = \frac{V(\text{CO}_2)}{V} = \frac{0.8 \text{ mol}}{2.5 \text{ mol}} = 0.32 \text{ i.e. } 32 \text{ vol. \% of CO}_2$$

$$\varphi(\text{H}_2) = \frac{V(\text{H}_2)}{V} = \frac{0.8 \text{ mol}}{2.5 \text{ mol}} = 0.32 \text{ i.e. } 32 \text{ vol. \% of H}_2$$

Before reaction:

$$m(\text{CO}) = n(\text{CO}) \times M(\text{CO}) = 1 \text{ mol} \times 28 \text{ g mol}^{-1} = 28 \text{ g}$$

$$m(\text{H}_2\text{O}) = 1.5 \text{ mol} \times 18 \text{ g mol}^{-1} = 27 \text{ g}$$

After reaction:

$$m(\text{CO}) = 0,2 \text{ mol} \times 28 \text{ g mol}^{-1} = 5.6 \text{ g}$$

$$m(\text{H}_2\text{O}) = 0.7 \text{ mol} \times 18 \text{ g mol}^{-1} = 12.6 \text{ g}$$

$$m(\text{CO}_2) = 0.8 \text{ mol} \times 44 \text{ g mol}^{-1} = 35.2 \text{ g}$$

$$m(\text{H}_2) = 0.8 \times 2 \text{ g mol}^{-1} = 1.6 \text{ g}$$

$$w(\text{CO}) = \frac{m(\text{CO})}{m} = \frac{5.6 \text{ g}}{55.0 \text{ g}} = 0.102 \text{ i.e. } 10.2 \text{ mass \% of CO}$$

$$w(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{m} = \frac{12.6 \text{ g}}{55.0 \text{ g}} = 0.229 \text{ i.e. } 22.9 \text{ mass \% of H}_2\text{O}$$

$$w(\text{CO}_2) = \frac{m(\text{CO}_2)}{m} = \frac{35.2 \text{ g}}{55.0 \text{ g}} = 0.640 \text{ i.e. } 64.0 \text{ mass \% of CO}_2$$

$$w(\text{H}_2) = \frac{m(\text{H}_2)}{m} = \frac{1.6 \text{ g}}{55.0 \text{ g}} = 0.029 \text{ i.e. } 2.9 \text{ mass \% of H}_2$$

PROBLEM 4

An alloy consists of rubidium and one of the other alkali metals. A sample of 4.6 g of the alloy when allowed to react with water, liberates 2.241 dm³ of hydrogen at STP.

Problems:

4.1 Which alkali metal is the component of the alloy?

4.2 What composition in % by mass has the alloy?

Relative atomic masses:

$A_r(\text{Li}) = 7$; $A_r(\text{Na}) = 23$; $A_r(\text{K}) = 39$; $A_r(\text{Rb}) = 85.5$; $A_r(\text{Cs}) = 133$

SOLUTION

4.1 M - alkali metal



$$n(\text{H}_2) = 0.1 \text{ mol}$$

$$n(\text{M}) = 0.2 \text{ mol}$$

Mean molar mass:

$$M = \frac{4.6 \text{ g}}{0.2 \text{ mol}} = 23 \text{ g mol}^{-1}$$

4.2 Concerning the molar masses of alkali metals, only lithium can come into consideration, i.e. the alloy consists of rubidium and lithium.

$$n(\text{Rb}) + n(\text{Li}) = 0.2 \text{ mol}$$

$$m(\text{Rb}) + m(\text{Li}) = 4.6 \text{ g}$$

$$n(\text{Rb}) M(\text{Rb}) + n(\text{Li}) M(\text{Li}) = 4.6 \text{ g}$$

$$n(\text{Rb}) M(\text{Rb}) + (0.2 - n(\text{Rb})) M(\text{Li}) = 4.6$$

$$n(\text{Rb}) \cdot 85.5 + (0.2 - n(\text{Rb})) \times 7 = 4.6$$

$$n(\text{Rb}) = 0.0408 \text{ mol}$$

$$n(\text{Li}) = 0.1592 \text{ mol}$$

$$\% \text{ Rb} = \frac{0.0408 \text{ mol} \times 85.5 \text{ g mol}^{-1}}{4.6 \text{ g}} \times 100 = 76$$

$$\% \text{ Li} = \frac{0.1592 \text{ mol} \times 7 \text{ g mol}^{-1}}{4.6 \text{ g}} \times 100 = 24$$

PROBLEM 5

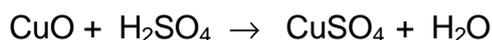
An amount of 20 g of copper (II) oxide was treated with a stoichiometric amount of a warm 20% sulphuric acid solution to produce a solution of copper (II) sulphate.

Problem:

How many grams of crystalline copper(II) sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) have crystallised when the solution is cooled to 20 °C?

Relative atomic masses: $A_r(\text{Cu}) = 63.5$; $A_r(\text{S}) = 32$; $A_r(\text{O}) = 16$; $A_r(\text{H}) = 1$

Solubility of CuSO_4 at 20 °C: $s = 20.9 \text{ g}$ of CuSO_4 in 100 g of H_2O .

SOLUTION

$$n(\text{CuO}) = \frac{m(\text{CuO})}{M(\text{CuO})} = \frac{20 \text{ g}}{79.5 \text{ g mol}^{-1}} = 0.2516 \text{ g}$$

$$n(\text{H}_2\text{SO}_4) = n(\text{CuSO}_4) = 0.2516 \text{ mol}$$

Mass of the CuSO_4 solution obtained by the reaction:

$$\begin{aligned} m(\text{solution CuSO}_4) &= m(\text{CuO}) + m(\text{solution H}_2\text{SO}_4) = \\ &= m(\text{CuO}) + \frac{n(\text{H}_2\text{SO}_4) \times M(\text{H}_2\text{SO}_4)}{w(\text{H}_2\text{SO}_4)} = 20 \text{ g} + \frac{0.2516 \text{ mol} \times 98 \text{ g mol}^{-1}}{0.20} \end{aligned}$$

$$m(\text{solution CuSO}_4) = 143.28 \text{ g}$$

Mass fraction of CuSO_4 :

a) in the solution obtained:

$$w(\text{CuSO}_4) = \frac{m(\text{CuSO}_4)}{m(\text{solution CuSO}_4)} = \frac{n(\text{CuSO}_4) \times M(\text{CuSO}_4)}{m(\text{solution CuSO}_4)} = 0.28$$

b) in saturated solution of CuSO_4 at 20°C:

$$w(\text{CuSO}_4) = \frac{20.9 \text{ g}}{120.9 \text{ g}} = 0.173$$

c) in crystalline $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$:

$$w(\text{CuSO}_4) = \frac{M(\text{CuSO}_4)}{M(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})} = 0.639$$

Mass balance equation for CuSO_4 :

$$0.28 m = 0.639 m_1 + 0.173 m_2$$

m - mass of the CuSO_4 solution obtained by the reaction at a higher temperature.

m_1 - mass of the crystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

m_2 - mass of the saturated solution of CuSO_4 at 20 °C.

$$0.28 \times 143.28 = 0.639 m_1 + 0.173 \times (143.28 - m_1)$$

$$m_1 = 32.9 \text{ g}$$

The yield of the crystallisation is 32.9 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

PROBLEM 6

Oxide of a certain metal contains 22.55 % of oxygen by mass. Another oxide of the same metal contains 50.48 mass % of oxygen.

Problem:

1. What is the relative atomic mass of the metal?
-

SOLUTION

Oxide 1: M_2O_x

$$2 : x = \frac{w(M)}{A_r(M)} : \frac{w(O)}{A_r(O)}$$

$$2 : x = \frac{0.7745}{A_r(M)} : \frac{0.2255}{16} = \frac{54.95}{A_r(M)} \quad (1)$$

Oxide 2: M_2O_y

$$2 : y = \frac{w(M)}{A_r(M)} : \frac{w(O)}{A_r(O)}$$

$$2 : y = \frac{0.4952}{A_r(M)} : \frac{0.5048}{16} = \frac{15.695}{A_r(M)} \quad (2)$$

When (1) is divided by (2):

$$\frac{y}{x} = \frac{54.95}{15.695} = 3.5$$

$$\frac{y}{x} = \frac{7}{2}$$

By substituting $x = 2$ into equation (1):

$$A_r(M) = 54.95$$

$$M = \text{Mn}$$

$$\text{Oxide 1} = \text{MnO}$$

$$\text{Oxide 2} = \text{Mn}_2\text{O}_7$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An unknown sample is a mixture of 1.2-molar H_2SO_4 and 1.47-molar HCl . By means of available solutions and facilities determine:

1. the total amount of substance (in val) of the acid being present in 1 dm^3 of the solution,
 2. the mass of sulphuric acid as well as hydrochloric acid present in 1 dm^3 of the sample.
-
-

PROBLEM 2 (Practical)

By means of available reagents and facilities perform a qualitative analysis of the substances given in numbered test tubes and write down their chemical formulas.

Give 10 equations of the chemical reactions by which the substances were proved:

5 equations for reactions of precipitation,

2 equations for reactions connected with release of a gas,

3 equations for redox reactions.

4th



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE FOURTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1972, MOSCOW, SOVIET UNION

THEORETICAL PROBLEMS

PROBLEM 1

A mixture of two solid elements with a mass of 1.52 g was treated with an excess of hydrochloric acid. A volume of 0.896 dm³ of a gas was liberated in this process and 0.56 g of a residue remained which was undissolved in the excess of the acid.

In another experiment, 1.52 g of the same mixture were allowed to react with an excess of a 10 % sodium hydroxide solution. In this case 0.896 dm³ of a gas were also evolved but 0.96 g of an undissolved residue remained.

In the third experiment, 1.52 g of the initial mixture were heated to a high temperature without access of the air. In this way a compound was formed which was totally soluble in hydrochloric acid and 0.448 dm³ of an unknown gas were released. All the gas obtained was introduced into a one litre closed vessel filled with oxygen. After the reaction of the unknown gas with oxygen the pressure in the vessel decreased by approximately ten times ($T = \text{const}$).

Problem:

1.1 Write chemical equations for the above reactions and prove their correctness by calculations.

In solving the problem consider that the volumes of gases were measured at STP and round up the relative atomic masses to whole numbers.

SOLUTION

1.1 a) Reaction with hydrochloric acid:

1.52 g – 0.56 g = 0.96 g of a metal reacted and 0.896 dm³ of hydrogen (0.04 mol) were formed.

$$\text{combining mass of the metal: } 11.2 \times \frac{0.96}{0.896} = 12 \text{ g}$$

Possible solutions:

Relative atomic mass of the metal	Oxidation number	Element	Satisfying?
12	I	C	No
24	II	Mg	Yes
36	III	Cl	No



b) Reaction with sodium hydroxide:

1.52 g – 0.96 g = 0.56 g of an element reacted, 0.896 dm³ (0.04 mol) of hydrogen were formed.

$$\text{combining mass of the metal: } 11.2 \times \frac{0.56}{0.896} = 7 \text{ g}$$

Possible solutions:

Relative atomic mass of the element	Oxidation number	Element	Satisfying?
7	I	Li	No
14	II	N	No
21	III	Ne	No
28	IV	Si	Yes



c) Combining of both elements:

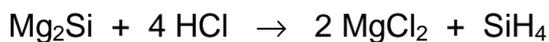
0.96 g Mg + 0.56 g Si = 1.52 g of silicide Mg_xSi_y

$$w(\text{Mg}) = \frac{0.96 \text{ g}}{1.52 \text{ g}} = 0.63 \quad w(\text{Si}) = \frac{0.56 \text{ g}}{1.52 \text{ g}} = 0.37$$

$$x : y = \frac{0.63}{24} : \frac{0.37}{28} = 2 : 1$$

silicide: Mg_2Si

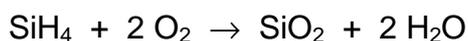
d) Reaction of the silicide with acid:



$$n(\text{Mg}_2\text{Si}) = \frac{1.52 \text{ g}}{76 \text{ g mol}^{-1}} = 0.02 \text{ mol}$$

$$n(\text{SiH}_4) = \frac{0.448 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.02 \text{ mol}$$

e) Reaction of silane with oxygen:



$$V = 1 \text{ dm}^3$$

On the assumption that $T = \text{const}$: $p_2 = \frac{n_2}{n_1} p_1$

$$n_1(\text{O}_2) = \frac{1 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.0446 \text{ mol}$$

Consumption of oxygen in the reaction: $n(\text{O}_2) = 0.04 \text{ mol}$

The remainder of oxygen in the closed vessel:

$$n_2(\text{O}_2) = 0.0446 \text{ mol} - 0.04 \text{ mol} = 0.0046 \text{ mol}$$

$$p_2 = \frac{0.0046 \text{ mol}}{0.0446 \text{ mol}} \times p_1 \approx 0.1 p_1$$

PROBLEM 2

A mixture of metallic iron with freshly prepared iron (II) and iron (III) oxides was heated in a closed vessel in the atmosphere of hydrogen. An amount of 4.72 g of the mixture when reacted, yields 3.92 g of iron and 0.90 g of water.

When the same amount of the mixture was allowed to react with an excess of a copper(II) sulphate solution, 4.96 g of a solid mixture were obtained.

Problems:

2.1 Calculate the amount of 7.3 % hydrochloric acid ($\rho = 1.03 \text{ g cm}^{-3}$) which is needed for a total dissolution of 4.72 g of the starting mixture.

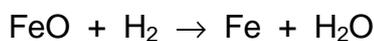
2.2 What volume of a gas at STP is released?

Relative atomic masses:

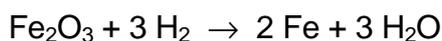
$$A_r(\text{O}) = 16; \quad A_r(\text{S}) = 32; \quad A_r(\text{Cl}) = 35.5; \quad A_r(\text{Fe}) = 56; \quad A_r(\text{Cu}) = 64$$

SOLUTION

2.1 a) Reduction by hydrogen:



$$n(\text{Fe}) = n(\text{FeO}); \quad n(\text{H}_2\text{O}) = n(\text{FeO})$$



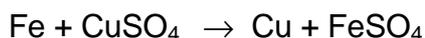
$$n(\text{Fe}) = 2 n(\text{Fe}_2\text{O}_3); \quad n(\text{H}_2\text{O}) = 3 n(\text{Fe}_2\text{O}_3)$$

The mass of iron after reduction: 3.92 g

The total amount of substance of iron after reduction:

$$n(\text{Fe}) + n(\text{FeO}) + 2 n(\text{Fe}_2\text{O}_3) = \frac{3.92 \text{ g}}{56 \text{ g mol}^{-1}} = 0.07 \text{ mol} \quad (1)$$

b) Reaction with copper(II) sulphate:



Increase of the mass: $4.96 \text{ g} - 4.72 \text{ g} = 0.24 \text{ g}$

After reaction of 1 mol Fe, an increase of the molar mass would be:

$$M(\text{Cu}) - M(\text{Fe}) = 64 \text{ g mol}^{-1} - 56 \text{ g mol}^{-1} = 8 \text{ g mol}^{-1}$$

Amount of substance of iron in the mixture:

$$n(\text{Fe}) = \frac{0.24 \text{ g}}{8 \text{ g mol}^{-1}} = 0.03 \text{ mol} \quad (2)$$

c) Formation of water after reduction:

0.90 g H₂O, i.e. 0.05 mol

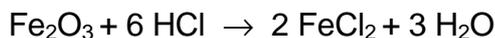
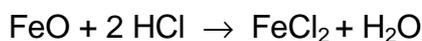
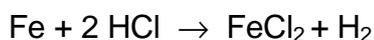
$$0.05 \text{ mol} = n(\text{Fe}) + 3 n(\text{Fe}_2\text{O}_3) \quad (3)$$

By solving equations (1), (2), and (3):

$$n(\text{FeO}) = 0.02 \text{ mol}$$

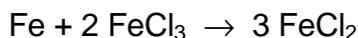
$$n(\text{Fe}_2\text{O}_3) = 0.01 \text{ mol}$$

d) Consumption of acid:



$$\begin{aligned} n(\text{HCl}) &= 2 n(\text{Fe}) + 2 n(\text{FeO}) + 6 n(\text{Fe}_2\text{O}_3) = \\ &= 0.06 \text{ mol} + 0.04 \text{ mol} + 0.06 \text{ mol} = 0.16 \text{ mol} \end{aligned}$$

A part of iron reacts according to the equation:



$$n(\text{Fe}) = 0.5 \times n(\text{FeCl}_3) = n(\text{Fe}_2\text{O}_3)$$

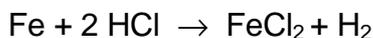
$$n(\text{Fe}) = 0.01 \text{ mol}$$

It means that the consumption of acid decreases by 0.02 mol.

The total consumption of acid: $n(\text{HCl}) = 0.14 \text{ mol}$

$$V(7.3\% \text{ HCl}) = \frac{n M}{w \rho} = \frac{0.14 \text{ mol} \times 36.5 \text{ g mol}^{-1}}{0.073 \times 1.03 \text{ g cm}^{-3}} = 68 \text{ cm}^3$$

2.2 Volume of hydrogen:



Iron in the mixture: 0.03 mol

Iron reacted with FeCl₃: 0.01 mol

Iron reacted with acid: 0.02 mol

Hence, 0.02 mol of hydrogen, i.e. 0.448 dm³ of hydrogen are formed.

PROBLEM 3

A volume of 200 cm³ of a 2-normal sodium chloride solution ($\rho = 1.10 \text{ g cm}^{-3}$) was electrolysed at permanent stirring in an electrolytic cell with copper electrodes. Electrolysis was stopped when 22.4 dm³ (at STP) of a gas were liberated at the cathode.

Problem:

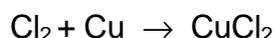
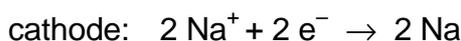
3.1 Calculate the mass percentage of NaCl in the solution after electrolysis.

Relative atomic masses:

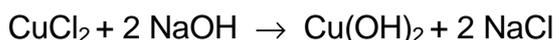
$$A_r(\text{H}) = 1; \quad A_r(\text{O}) = 16; \quad A_r(\text{Na}) = 23; \quad A_r(\text{Cl}) = 35.5; \quad A_r(\text{Cu}) = 64.$$

SOLUTION

3.1 Calculations are made on the assumption that the following reactions take place:



Because the electrolyte solution is permanently being stirred the following reaction comes into consideration:



On the assumption that all chlorine reacts with copper, the mass of NaCl in the electrolyte solution remains unchanged during the electrolysis.

$$m(\text{NaCl}) = n M = c V M = 2 \text{ mol dm}^{-3} \times 0.2 \text{ dm}^3 \times 58.5 \text{ g mol}^{-1} = 23.4 \text{ g}$$

$$V(\text{H}_2) = 22.4 \text{ dm}^3, \text{ i. e. } n(\text{H}_2) = 1 \text{ mol}$$

The amount of water is decreased in the solution by:

$$n(\text{H}_2\text{O}) = 2 \text{ mol}$$

$$m(\text{H}_2\text{O}) = 36 \text{ g}$$

Before electrolysis:

$$m(\text{solution NaCl}) = V \rho = 200 \text{ cm}^3 \times 1.10 \text{ g cm}^{-3} = 220 \text{ g}$$

$$\% \text{ NaCl} = \frac{23.4 \text{ g}}{220 \text{ g}} \times 100 = 10.64$$

After electrolysis:

$$m(\text{solution NaCl}) = 220 \text{ g} - 36 \text{ g} = 184 \text{ g}$$

$$\% \text{ NaCl} = \frac{23.4 \text{ g}}{184 \text{ g}} \times 100 = 12.72$$

PROBLEM 4

Amount of 50 g of a 4 % sodium hydroxide solution and 50 g of a 1.825 % solution of hydrochloric acid were mixed in a heat insulated vessel at a temperature of 20 °C. The temperature of the solution obtained in this way increased to 23.4 °C. Then 70 g of a 3.5 % solution of sulphuric acid at a temperature of 20 °C were added to the above solution.

Problems:

4.1 Calculate the final temperature of the resulting solution.

4.2 Determine the amount of a dry residue that remains after evaporation of the solution.

In calculating the first problem use the heat capacity value $c = 4.19 \text{ J g}^{-1} \text{ K}^{-1}$.

Relative atomic masses:

$A_r(\text{H}) = 1$; $A_r(\text{O}) = 16$; $A_r(\text{Na}) = 23$; $A_r(\text{S}) = 32$; $A_r(\text{Cl}) = 35.5$.

SOLUTION

4.1 a) $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

$$n(\text{NaOH}) = \frac{m(\text{solution NaOH}) \times w(\text{NaOH})}{M(\text{NaOH})} = \frac{50 \text{ g} \times 0.04}{40 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

$$n(\text{HCl}) = \frac{50 \text{ g} \times 0.01825}{36.5 \text{ g mol}^{-1}} = 0.025 \text{ mol}$$

unreacted: $n(\text{NaOH}) = 0.025 \text{ mol}$

b) When 1 mol of water is formed, neutralization heat is:

$$\Delta H_{\text{neutr}} = - \frac{m c \Delta t}{n(\text{H}_2\text{O})} = \frac{100 \text{ g} \times 4.19 \text{ J g}^{-1} \text{ K}^{-1} \times 3.4 \text{ K}}{0.025 \text{ mol}} = - 57\,000 \text{ J mol}^{-1}$$

c) $\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$

The temperature of the resulting solution is calculated according to the equation:

$$m_1 c_1 t_1 + m_2 c_2 t_2 = m c t$$

$$c_1 = c_2 = c$$

$$m_1 t_1 + m_2 t_2 = m t$$

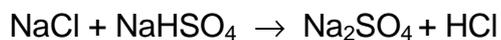
$$t = \frac{m_1 t_1 + m_2 t_2}{m} = \frac{(100 \times 23.4) + (70 \times 20.0)}{170} = 22 \text{ }^\circ\text{C}$$

- d) The temperature increase due to the reaction of NaOH with H₂SO₄ is as follows:

$$t = - \frac{n(\text{H}_2\text{O}) \Delta H_{\text{neutr}}}{m c} = - \frac{0.025 \text{ mol} \times 57\,000 \text{ J mol}^{-1}}{170 \text{ g} \times 4.19 \text{ J g}^{-1} \text{ K}^{-1}} = 2 \text{ K}$$

The final temperature of the solution: $t = 22 + 2 = 24 \text{ }^\circ\text{C}$

- 4.2 e) When the solution has evaporated the following reaction is assumed to take place:



Na₂SO₄ is the dry residue.

$$m(\text{Na}_2\text{SO}_4) = n M = 0.025 \text{ mol} \times 142 \text{ g mol}^{-1} = 3.55 \text{ g}$$

PROBLEM 5

Only one product was obtained by the reaction of bromine with an unknown hydrocarbon. Its density was 5,207 times as great as that of the air.

Problem:

5.1 Determine the structural formula of the unknown hydrocarbon.

Relative atomic masses: $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{Br}) = 80$.

SOLUTION

5.1 Relative molecular mass of the initial hydrocarbon can be calculated from the density value:

$$M_r(\text{RBr}) = 29 \times 5.207 = 151$$

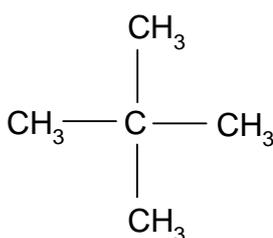
Monobromo derivative can only come into consideration because the relative molecular mass of dibromo derivative should be greater:

$$M_r(\text{RBr}_2) > 160$$

$$M_r(\text{RH}) = 151 - 80 + 1 = 72$$

The corresponding summary formula: C_5H_{12}

The given condition (the only product) is fulfilled by 2,2-dimethyl propane:



PROBLEM 6

Organic compound **A** is 41.38 % carbon, 3.45 % hydrogen and the rest is oxygen. Compound **A** when heated with ethanol in the presence of an acid yields a new substance **B** which contains 55.81 % carbon, 6.97 % hydrogen, and oxygen.

The initial compound **A** when allowed to react with hydrobromide yields product **C** which on boiling in water gives substance **D** containing 35.82 % carbon, 4.48 % hydrogen, and oxygen. An amount of 2.68 g of substance **D** required reacting with 20 cm³ of a 2 N solution of potassium hydroxide.

Problems:

6.1 Determine structural formulas of all the above mentioned substances **A**, **B**, **C** and **D**.

Use the finding that compound **A** splits off water when heated.

6.2 Write chemical equations for the above reactions.

Relative atomic masses: $A_r(\text{H}) = 1$; $A_r(\text{C}) = 12$; $A_r(\text{O}) = 16$; $A_r(\text{K}) = 39$.

SOLUTION

6.1 Stoichiometric formulas of compounds:



$$x : y : z = \frac{41.38}{12} : \frac{3.45}{1} : \frac{55.17}{16} = 1 : 1 : 1$$



$$m : n : p = \frac{55.81}{12} : \frac{6.97}{1} : \frac{37.22}{16} = 2 : 3 : 1$$



$$a : b : c = \frac{35.82}{12} : \frac{4.48}{1} : \frac{59.70}{16} = 4 : 6 : 5$$

20 cm³ of 2 N KOH correspond 0.04 / v mol of substance **D** and it corresponds to 2.68 g of substance **D**

$$v = 1, 2, 3, \dots$$

$$1 \text{ mol of compound } \mathbf{D} = v \times 67 \text{ g}$$

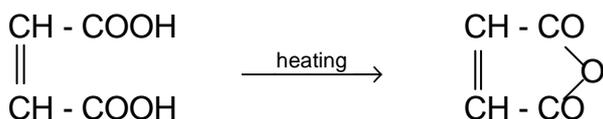
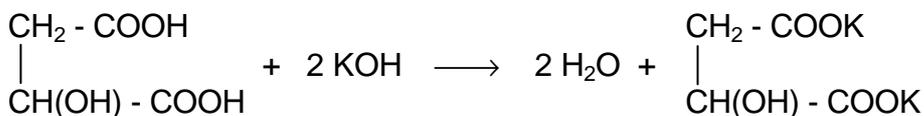
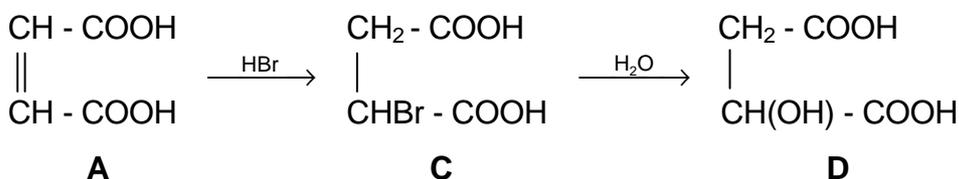
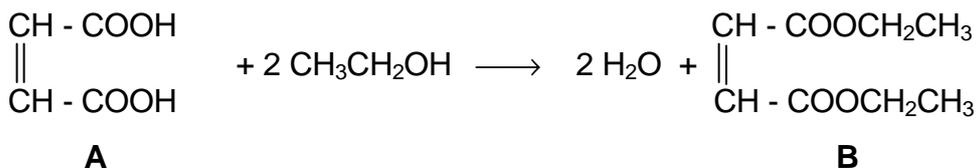
$M_r(\mathbf{D}) = 67$ or 134 or 201 , etc.

Due to both the stoichiometric formula and relative molecular mass of compound **D**, its composition is $C_4H_6O_5$.

Then molecular formulas for compounds **A**, **B**, and **C** are as follows:

A: $C_4H_4O_4$ **B**: $C_8H_{12}O_4$ **C**: $C_4H_5O_4Br$

6.2 Equations:



Compound **A**: maleic acid

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determine unknown samples in ten numbered test tubes using reagents and facilities available on the laboratory desk. Write chemical equations for the most important reactions that were used to identify each substance. In case that the reactions take place in solutions, write equations in a short ionic form.

PROBLEM 2 (Practical)

On June 10th, a mixture of formic acid with an excess of ethanol was prepared. This mixture was kept in a closed vessel for approximately one month. Determine quantitatively the composition of the mixture on the day of the competition, using only reagents and facilities available on the laboratory desk. Calculate the amounts of the acid and ethanol in per cent by mass which were initially mixed together.

5th



International Chemistry Olympiad

**6 theoretical problems
3 practical problems**

THE FIFTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1973, SOFIA, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

In nitrating a hydroxy derivative of benzene a compound is formed which contains 49.0 % by mass of oxygen. A charge of 4350 C is required for a total electroreduction of 0.458 g of the compound, efficiency being 80 %.

Problem:

1.1 Determine the stoichiometric as well as structural formulas of the compound if the product of the electrochemical reduction is an aromatic hydroxy amino derivative.

$$F \text{ (Faraday's charge)} = 96\,500 \text{ C mol}^{-1}$$

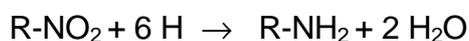
SOLUTION

1.1 a) Formula of the compound: $C_6H_xO_yN_z$

The compound is a hydroxy nitroderivative of benzene:



b) Equation of the reduction:



Combining mass of the compound:

$$E = \frac{M_r(\text{compound})}{6 z} \quad (1)$$

An amount of charge which is required for the electrochemical reduction:

$$Q = 4350 \text{ C} \times 0.8 = 3480 \text{ C}$$

Combining mass of the compound:

$$E = \frac{m}{\frac{3480 \text{ C}}{F}} = 0.458 \times \frac{96500 \text{ C}}{3480 \text{ C}} = 12.7$$

$$\text{In relation to (1): } M_r(\text{compound}) = 76.2 \times z \quad (2)$$

$$\text{c) } \% \text{ O} = \frac{y \times M_r(\text{O}) \times 100}{M_r(\text{compound})}$$

$$49 = \frac{y \times 16 \times 100}{M_r(\text{compound})}$$

$$M_r(\text{compound}) = 32.7 y$$

$$\text{d) } M_r(\text{compound}) = 6 M_r(\text{C}) + x M_r(\text{H}) + y M_r(\text{O}) + z M_r(\text{N})$$

$$M_r(\text{compound}) = 6 \times 12 + x + 16 y + 14 z$$

Taking into consideration the general formula of the unknown hydroxy derivative of benzene:

$$x = 6 - (y - 2 z) - z + y - 2 z$$

$$x = 6 - z \quad (4)$$

$$\text{Then: } M_r(\text{compound}) = 72 + 6 - z + 16 y + 14 z$$

$$M_r(\text{compound}) = 78 + 16 y + 13 z \quad (5)$$

By solving equations (2), (3), (4), and (5) we obtain:

$$\underline{M_r(\text{compound}) = 229}$$

$$x = 3$$

$$y = 7$$

$$z = 3$$

The molecular formula of the compound is: $\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ or $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$.

The compound is 2, 4, 6-trinitrophenol

PROBLEM 2

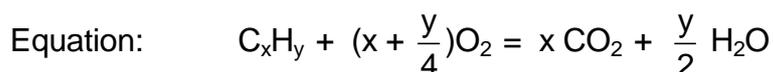
A mixture of a gaseous hydrocarbon and oxygen is in a vessel of a volume of 1 dm³ at a temperature of 406.5 K and a pressure of 101 325 Pa. There is twice as much oxygen in the mixture as is needed for the reaction with the hydrocarbon. After combustion of the hydrocarbon the pressure in the vessel (at the same temperature) is increased by 5 %.

Problem:

2.1 What hydrocarbon was in the mixture when the mass of water formed by the combustion was 0.162 g.

SOLUTION

2.1 Amounts of substances of reactants and reaction products:



$$n(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = \frac{0.162 \text{ g}}{18 \text{ g mol}^{-1}} = 0.009 \text{ mol}$$

$$n(\text{C}_x\text{H}_y) = \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{0.018}{y} \text{ mol} \quad (1)$$

$$n(\text{O}_2) = \left(x + \frac{y}{4}\right) \times \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{x + \frac{y}{4}}{y} \times 0.018 \text{ mol} \quad (2)$$

$$n(\text{CO}_2) = x \frac{0.009 \text{ mol}}{\frac{y}{2}} = \frac{x}{y} \times 0.018 \text{ mol} \quad (3)$$

Before reaction:

$$n(\text{mixture}) = \frac{pV}{RT} = \frac{101.325 \text{ kPa} \times 1 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 406.5 \text{ K}} = 0.03 \text{ mol}$$

$$n(\text{C}_x\text{H}_y) + 2 n(\text{O}_2) = 0.03 \text{ mol} \quad (4)$$

After reaction: $p = 101.325 \text{ kPa} \times 1.05 = 106.4 \text{ kPa}$

$$n(\text{mixture}) = \frac{pV}{RT} = \frac{106.4 \text{ kPa} \times 1 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 406.5 \text{ K}} = 0.0315 \text{ mol}$$

$$n(\text{CO}_2) + n(\text{O}_2) + n(\text{H}_2\text{O}) = 0.0315 \text{ mol}$$

$$n(\text{CO}_2) + n(\text{O}_2) = 0.0225 \text{ mol} \quad (5)$$

When (1), (2), and (3) are substituted in (4) and (5), an equation of two unknowns is obtained which when solved yields

$$x = 3; \quad y = 6$$

The stoichiometric formula of the unknown hydrocarbon is: C_3H_6 .

PROBLEM 3

Equal volumes (10 cm³) of 0.01-molar solutions of CH₃COOH and HClO were mixed and then diluted to a total volume of 100 cm³. Ionisation constant of CH₃COOH is equal to 1.8×10^{-5} and that for HClO is $3,7 \times 10^{-8}$.

Problems:

Calculate:

- 3.1 degree of ionisation for each of the acids in the solution,
- 3.2 degree of ionisation of HClO if the diluted solution would not contain CH₃COOH,
- 3.3 pH value for the solution containing at the same time CH₃COOH and HClO.

SOLUTION

CH₃COOH: K_1, α_1, c_1

HClO: K_2, α_2, c_2

$c_1 = c_2 = 1 \times 10^{-3} \text{ mol dm}^{-3} = c$

$$3.1 \quad K_1 = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(\alpha_1 + \alpha_2)c \times \alpha_1 c}{(1 - \alpha_1)c} = \frac{(\alpha_1 + \alpha_2) \alpha_1 c}{1 - \alpha_1} \quad (1)$$

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]} = \frac{(\alpha_1 + \alpha_2) \alpha_2 c}{1 - \alpha_2} \quad (2)$$

$K_1 \gg K_2$, therefore also $\alpha_1 \gg \alpha_2$ and $\alpha_1 + \alpha_2 \approx \alpha_1$

$$K_1(1 - \alpha_1) = \alpha_1^2 c$$

$$c \alpha_1^2 + K_1 \alpha_1 - K_1 = 0$$

$$\alpha_1 = 0,125$$

When (2) is divided by (1):

$$\frac{K_2}{K_1} = \frac{(1 - \alpha_1) \alpha_2}{(1 - \alpha_2) \alpha_1}$$

After substitution of α_1 : $\alpha_2 = 2.94 \cdot 10^{-4}$

$$3.2 \quad K_2 = \frac{\alpha_2^2 c}{1 - \alpha_2}$$

$$\alpha_2 \ll 1$$

$$K_2 = \alpha_2^2 c$$

$$\alpha_2 = 6,08 \cdot 10^{-3}$$

$$3.3 \quad [\text{H}_3\text{O}^+] = \alpha_1 c + \alpha_2 c = (\alpha_1 + \alpha_2) c = (0,125 + 2,94 \times 10^{-4}) \times 10^{-3} \approx 1,25 \times 10^{-4} \text{ mol dm}^{-3}$$

pH = 3,9

PROBLEM 4

When solutions of two unknown substances are mixed together in stoichiometric ratio, 1.25 g of a precipitate are formed which contain a salt of a bivalent metal M. The precipitate when heated to 1100 °C is decomposed to 0.70 g of a solid metal oxide MO and another gaseous oxide. After evaporation of the filtrate, a dry residue with a mass of 2.0 g remains which yields two products by thermal decomposition at 215 °C: a gaseous oxide and 0.90 g of water vapour. The total volume of the gaseous mixture is 1.68 dm³ (at STP).

Problem:

- 4.1 Determine the unknown compounds and write chemical equations for the above mentioned reactions.

SOLUTION

- 4.1 a) Dry residue: 2.0 g

H₂O: 0.90 g, i. e. 0.05 mol

Gaseous oxide A_xO_y: 1.1 g

$$n(\text{mixture}) = \frac{1.68 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.075 \text{ mol}$$

$$n(\text{A}_x\text{O}_y) = n(\text{mixture}) - n(\text{H}_2\text{O}) = 0.025 \text{ mol}$$

$$M(\text{A}_x\text{O}_y) = \frac{1.1 \text{ g}}{0.025 \text{ mol}} = 44 \text{ g mol}^{-1}$$

$$x M(\text{A}) = M(\text{A}_x\text{O}_y) - y M(\text{O})$$

Solution 1:

$$\text{If } x = 1 \text{ and } y = 1, \text{ then } M(\text{A}) = M(\text{A}_x\text{O}_y) - M(\text{O}) = (44 - 16) \text{ g mol}^{-1} = 28 \text{ g mol}^{-1}$$

A = Si. It does not satisfy the requirements of the task.

Solution 2:

$$\text{If } x = 2 \text{ and } y = 1 \text{ then } M(\text{A}) = 14 \text{ g mol}^{-1}$$

A = N and the gaseous oxide is N₂O.

Solution 3:

$$\text{If } x = 1 \text{ and } y = 2 \text{ then } M(\text{A}) = 12 \text{ g mol}^{-1}$$

A = C and the gaseous oxide is CO₂.

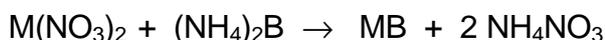
Solution 2 is correct, since it is known that gaseous N_2O is formed by thermal decomposition of NH_4NO_3 . This conclusion is supported by the following calculation:

$$M(\text{dry residue}) = \frac{2.0 \text{ g}}{0.025 \text{ mol}} = 80 \text{ g mol}^{-1} = M(\text{NH}_4\text{NO}_3)$$

Reaction of the thermal decomposition:



b) The precipitation reaction can be described by the following equation:



$$M(\text{MB}) = \frac{1.25 \text{ g}}{0.0125 \text{ mol}} = 100 \text{ g mol}^{-1}$$

$$M(\text{MO}) = \frac{0.70 \text{ g}}{0.0125 \text{ mol}} = 56 \text{ g mol}^{-1}$$

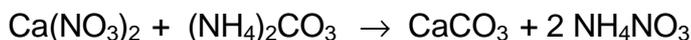
$$M(\text{M}) = M(\text{MO}) - M(\text{O}) = 56 - 16 = 40 \text{ g mol}^{-1}$$

M = Ca

Since

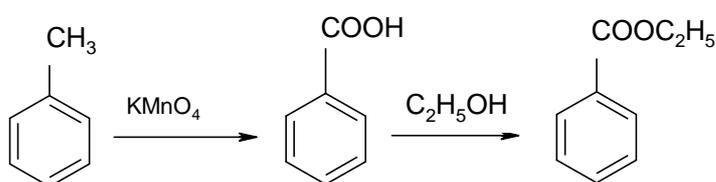
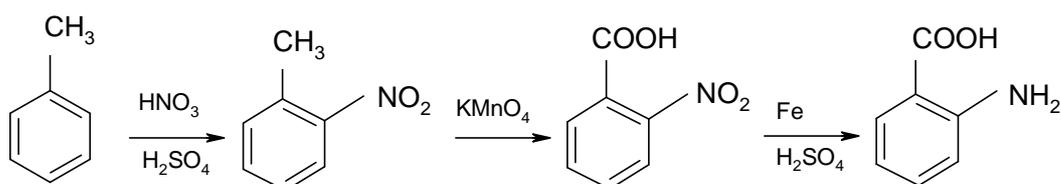
- the decomposition temperature of the precipitate is 1100 °C,
- the product of thermal decomposition is CaO,
- the molar mass of the precipitate is 100 g mol⁻¹,
- the precipitate is CaCO₃.

Reaction:

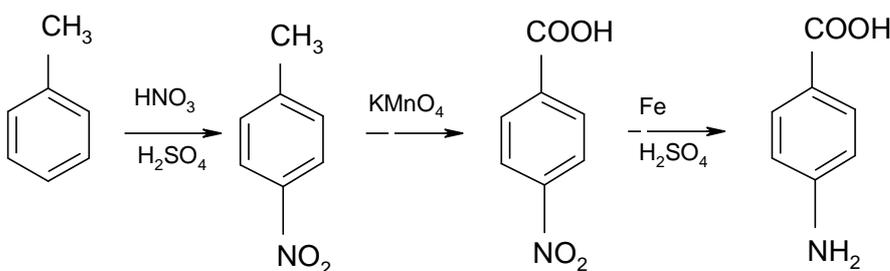
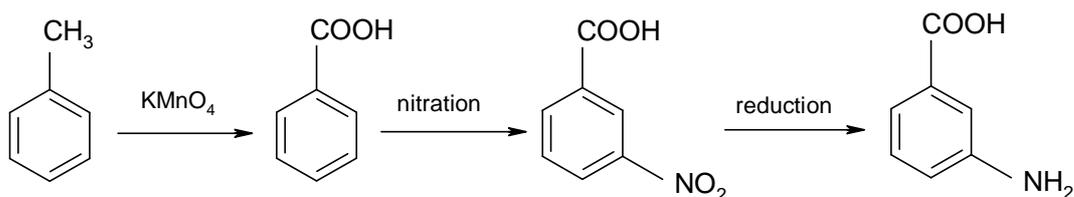


PROBLEM 5

Using your knowledge about the properties of benzene and its derivatives, write chemical equations for reactions by which ethyl ester of benzoic acid as well as o-, m-, and p-amino benzoic acids are prepared in the shortest way.

SOLUTION**a) Synthesis of ethyl ester of benzoic acid****b) Synthesis of o- and p-amino benzoic acid**

and simultaneously

**c) Synthesis of m-aminobenzoic acid**

PROBLEM 6

A gaseous mixture containing two neighbour hydrocarbons of the same homologous series was 14.4 times as dense as hydrogen. This mixture with a volume of 16.8 dm³ was hydrated and 350 g of the solution were obtained when the products of hydration were absorbed in water. Ten grams of this solution were taken and heated in the presence of silver(I) oxide which was prepared from 70 cm³ of a 1 N silver(I) nitrate solution. Unreacted Ag₂O was dissolved in an aqueous ammonia solution and a residual precipitate was filtered off. The filtrate was acidified with nitric acid and addition of an excess of sodium bromide to it resulted in 9.4 g of a precipitate.

When the mixture of the hydrocarbons that remained unreacted, was mixed with a 50 % excess of hydrogen and transmitted above a heated Pt-catalyst, its resulting volume decreased to 11.2 dm³. Volumes of gases were measured in STP conditions.

Problems:

- 6.1 What hydrocarbons were in the starting mixture?
- 6.2 Write chemical equations for the above mentioned reactions.
- 6.3 Calculate the composition of the starting mixture in % by volume.
- 6.4 How much (in %) of each hydrocarbon was hydrated?

SOLUTION

6.1 $M_r = 2 \times 14.4 = 28.8$

When reactivity of the hydrocarbons and the value of M_r are taken into consideration then the mixture can only be formed from CH \equiv CH ($M_r = 26$) and CH₃-CH \equiv CH ($M_r = 40$)

- 6.2 (1) CH \equiv CH + H₂O \rightarrow CH₃CHO
- (2) CH₃C \equiv CH + H₂O \rightarrow CH₃COCH₃
- (3) 2 AgNO₃ + 2 NH₃ + 2 H₂O \rightarrow Ag₂O + 2 NH₄NO₃
- (4) CH₃CHO + Ag₂O \rightarrow CH₃COOH + 2 Ag
- (5) Ag₂O + 4 NH₃ + H₂O \rightarrow 2 [Ag(NH₃)₂]OH

- (6) $\text{CH}_3\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{COONH}_4$
 (7) $[\text{Ag}(\text{NH}_3)_2]\text{OH} + 3 \text{HNO}_3 \rightarrow \text{AgNO}_3 + 2 \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$
 (8) $\text{CH}_3\text{COONH}_4 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 + \text{CH}_3\text{COOH}$
 (9) $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$
 (10) $\text{AgNO}_3 + \text{NaBr} \rightarrow \text{AgBr} + \text{NaNO}_3$
 (11) $\text{CH} \equiv \text{CH} + 2 \text{H}_2 \rightarrow \text{CH}_3 - \text{CH}_3$
 (12) $\text{CH}_3\text{C} \equiv \text{CH} + 2 \text{H}_2 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_3$

6.3 According to (11) and (12) and regarding the excess of hydrogen, amounts of substances before catalytic hydrogenation are as follows:

$$n(\text{mixture}) = \frac{11.2 \text{ dm}^3}{2} = 5.6 \text{ dm}^3, \text{ i. e. } 0.25 \text{ mol}$$

$$26x + 40(0.25 - x) = 28.8 \times 0.25$$

$$x = 0.2$$

$$n(\text{C}_2\text{H}_2) = 0.2 \text{ mol}$$

$$n(\text{C}_3\text{H}_4) = 0.05 \text{ mol}$$

Before hydration:

$$n(\text{mixture}) = \frac{16.8 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.75 \text{ mol}$$

$$n(\text{AgNO}_3) = cV = 1 \text{ mol dm}^{-3} \times 0.07 \text{ dm}^3 = 0.070 \text{ mol}$$

According to (3):

$$n(\text{Ag}_2\text{O}) = 0.035 \text{ mol}$$

$$n(\text{AgBr}) = \frac{9.4 \text{ g}}{188 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

According to (10), (7) and (5):

$$\text{unreacted: } n(\text{Ag}_2\text{O}) = 0.025 \text{ mol}$$

$$\text{reacted: } n(\text{Ag}_2\text{O}) = 0.035 - 0.025 = 0.010 \text{ mol}$$

Due to dilution, reacted amounts of substances are as follows:

$$n(\text{CH}_3\text{CHO}) = n(\text{C}_2\text{H}_2) = 0.35 \text{ mol}$$

	hydration	hydrogenation	total
C ₂ H ₂	0.35 mol	0.20 mol	0.55 mol
C ₃ H ₄	0.15 mol	0.05 mol	0.20 mol
			Σ = 0.75 mol

$$\text{vol. \% C}_2\text{H}_2 = \frac{0.55 \text{ mol}}{0.75 \text{ mol}} \times 100 = 73.3$$

$$\text{vol. \% C}_3\text{H}_4 = \frac{0.20 \text{ mol}}{0.75 \text{ mol}} \times 100 = 26.7$$

6.4

$$\text{vol. \% C}_2\text{H}_2 = \frac{0.35 \text{ mol}}{0.55 \text{ mol}} \times 100 = 63.64$$

$$\text{vol. \% C}_3\text{H}_4 = \frac{0.15 \text{ mol}}{0.20 \text{ mol}} \times 100 = 75.0$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The following solutions of salts are available in twelve numbered test-tubes: AgNO_3 , BaCl_2 , $(\text{NH}_4)_2\text{CO}_3$, NaCl , KI , ZnCl_2 , NH_4Cl , $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, CrCl_3 , $\text{Cr}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2$.

The numbering of the test tubes does not correspond to the order of the salts given above. Prove the content of the test tubes by means of the least number of operations. In your answer align the proper salt with each number of the test tube. Write chemical equations for the reactions.

PROBLEM 2 (Practical)

Six test tubes contain the following compounds:

Na_2CO_3	or	NaHCO_3	NiCl_2	or	CuCl_2
AgNO_3	or	$\text{Pb}(\text{NO}_3)_2$	ZnCl_2	or	$\text{Al}(\text{NO}_3)_3$
ZnSO_4	or	KI	NH_4NO_3	or	$\text{Ba}(\text{NO}_3)_2$

The numbers of the test tubes do not correspond to the order of the compounds. Prove the content of each test tube by available reagents. Describe the reactions by chemical equations.

PROBLEM 3 (Practical)

There are three test tubes marked by numbers 1, 2, and 3. Prove the content of each test-tube by means of available reagents and write the proper formula of the compound to each number. Write chemical equations for the reactions.

6th



International Chemistry Olympiad

**5 theoretical problems
3 practical problems**

THE SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1974, BUCURESTI, ROMANIA

THEORETICAL PROBLEMS

PROBLEM 1

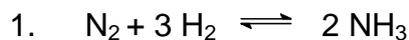
By electrochemical decomposition of water, there are in an electric circuit a voltmeter, platinum electrodes and a battery containing ten galvanic cells connected in series, each of it having the voltage of 1.5 V and internal resistance of 0.4 Ω . The resistance of the voltmeter is 0.5 Ω and the polarisation voltage of the battery is 1.5 V. Electric current flows for 8 hours, 56 minutes and 7 seconds through the electrolyte. Hydrogen obtained in this way was used for a synthesis with another substance, thus forming a gaseous substance **A** which can be converted by oxidation with oxygen via oxide to substance **B**.

By means of substance **B** it is possible to prepare substance **C** from which after reduction by hydrogen substance **D** can be obtained. Substance **D** reacts at 180 $^{\circ}\text{C}$ with a concentration solution of sulphuric acid to produce sulphanilic acid. By diazotization and successive copulation with p-N,N-dimethylaniline, an azo dye, methyl orange is formed.

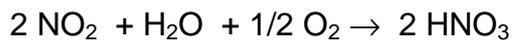
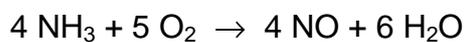
Problems:

1. Write chemical equations for all the above mentioned reactions.
2. Calculate the mass of product **D**.
3. Give the exact chemical name for the indicator methyl orange. Show by means of structural formulas what changes take place in dependence on concentration of H_3O^+ ions in the solution.

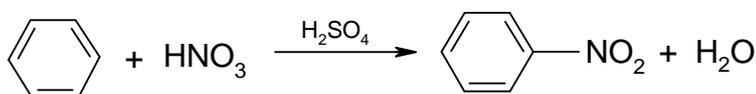
Relative atomic masses: $A_r(\text{N}) = 14$; $A_r(\text{O}) = 16$; $A_r(\text{C}) = 12$; $A_r(\text{H}) = 1$.

SOLUTION

(A)



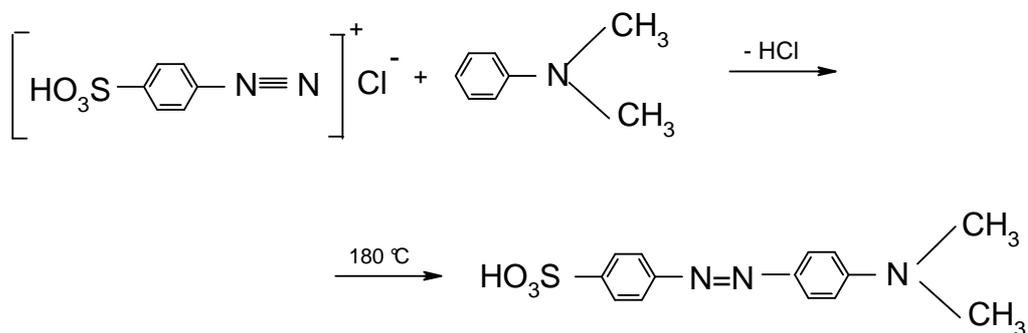
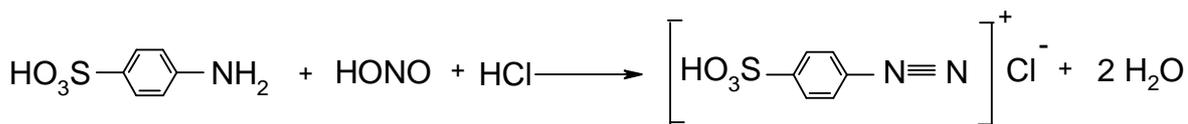
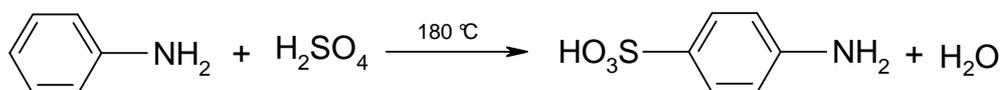
(B)



(C)



(D)



4'-dimethyl amino 4-azo benzene sulphonic acid

$$2. \quad m = \frac{M}{F z} I t$$

$$F = 96500 \text{ C mol}^{-1}$$

$$I = \frac{b E_b - E_p}{R_v + b R_i} = \frac{(10 \times 1.5 \text{ V}) - 1.5 \text{ V}}{0.5 \Omega + (10 \times 0.4 \Omega)} = 3 \text{ A}$$

b - number of batteries,

E_b - voltage of one battery,

E_p - polarisation voltage,

R_v - resistance of voltmeter,

R_i - internal resistance of one battery

$$m(\text{H}_2) = \frac{1 \text{ g mol}^{-1}}{96500 \text{ C mol}^{-1}} \times 3 \text{ A} \times 32167 \text{ s} = 1 \text{ g}$$

From equations:

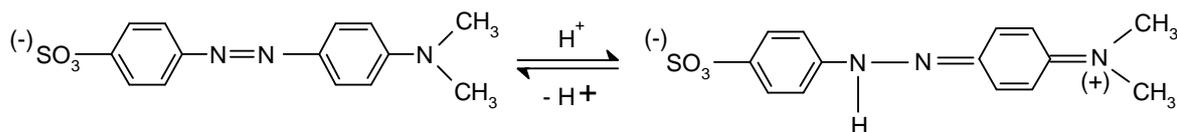
$$1 \text{ g H}_2 \text{ i. e. } 0.5 \text{ mol H}_2 \text{ corresponds } \frac{1}{3} \text{ mol NH}_3 \dots \frac{1}{3} \text{ mol HNO}_3 \dots \frac{1}{3} \text{ mol C}_6\text{H}_5\text{NO}_2$$

$$\dots \frac{1}{3} \text{ mol C}_6\text{H}_5\text{NH}_2 \quad (\mathbf{D})$$

The mass of product **D**:

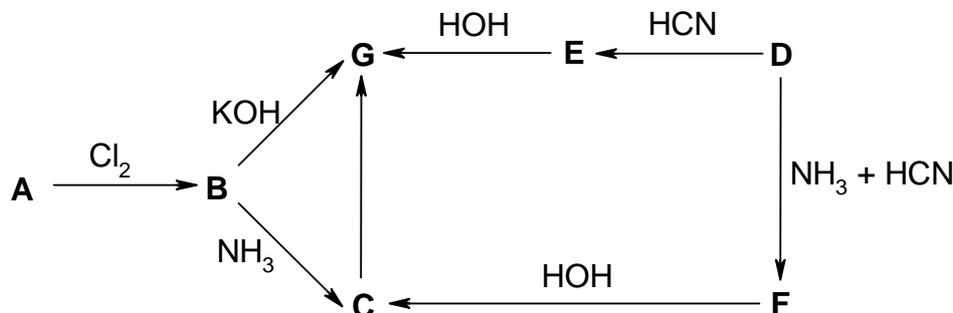
$$m = n M = 31 \text{ g C}_6\text{H}_5\text{NH}_2$$

3.



PROBLEM 2

Substance **G** can be prepared by several methods according to the following scheme:



Compound A is 48.60 mass % carbon, 8.10 % hydrogen, and 43.30 % oxygen. It reacts with a freshly prepared silver(I) oxide to form an undissolved salt. An amount of 1.81 g of silver(I) salt is formed from 0.74 g of compound **A**.

Compound D contains 54.54 mass % of carbon, 9.09 % of hydrogen, and 36.37 % of oxygen. It combines with NaHSO₃ to produce a compound containing 21.6 % of sulphur.

Problems:

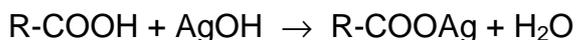
- Write summary as well as structural formulas of substances **A** and **D**.
- Write structural formulas of substances **B**, **C**, **E**, **F**, and **G**.
- Classify the reactions in the scheme marked by arrows and discuss more in detail reactions **B** → **G** and **D** → **E**.
- Write structural formulas of possible isomers of substance **G** and give the type of isomerism.

Relative atomic masses:

$$A_r(\text{C}) = 12; \quad A_r(\text{H}) = 1; \quad A_r(\text{O}) = 16; \quad A_r(\text{Ag}) = 108; \quad A_r(\text{Na}) = 23; \quad A_r(\text{S}) = 32.$$

SOLUTION

- Compound A:

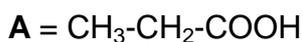


$$\text{A: } (\text{C}_x\text{H}_y\text{O}_z)_n$$

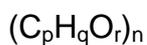
$$x : y : z = \frac{48.60}{12} : \frac{8.10}{1} : \frac{43.30}{16} = 1 : 2 : 0.67$$

If $n = 3$, then the summary formula of substance **A** is: C₃H₆O₂.

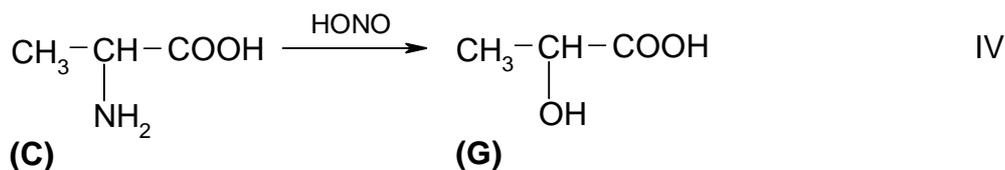
$$M(\mathbf{A}) = 74 \text{ g mol}^{-1}$$



Compound D:

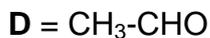
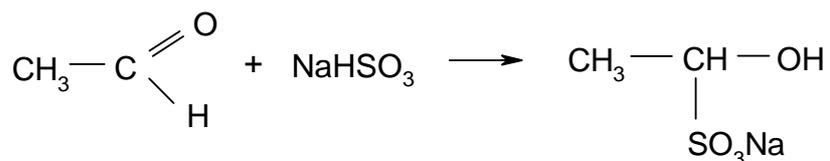


$$p : q : r = \frac{54.54}{12} : \frac{9.09}{1} : \frac{36.37}{16} = 1 : 2 : 0.5$$



If $n = 2$, then the summary formula of substance **D** is: $\text{C}_2\text{H}_4\text{O}$.

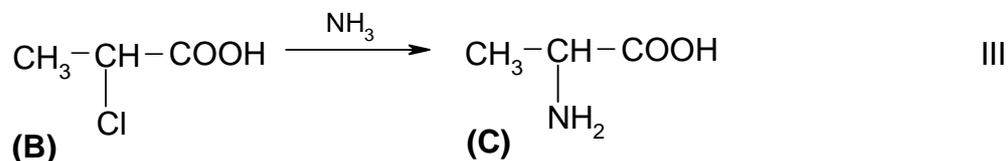
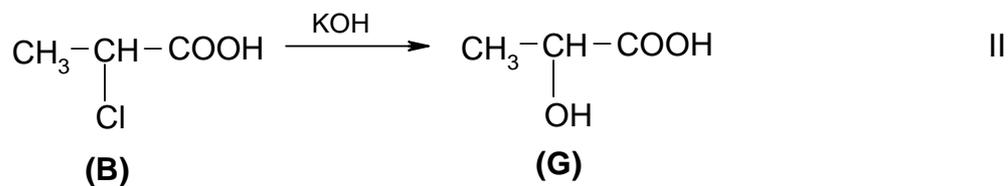
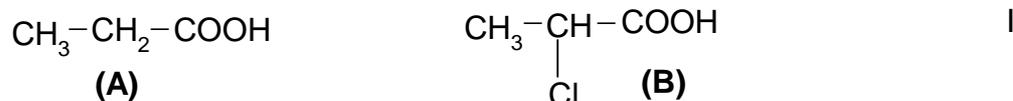
$$M(\mathbf{D}) = 44 \text{ g mol}^{-1}$$

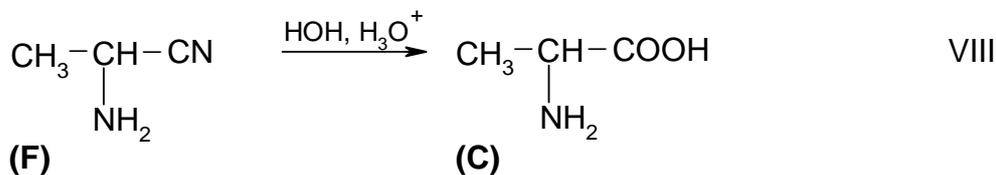
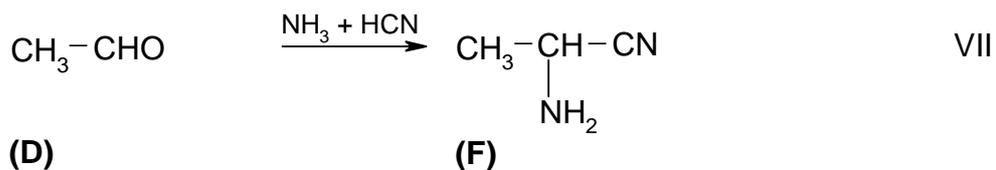
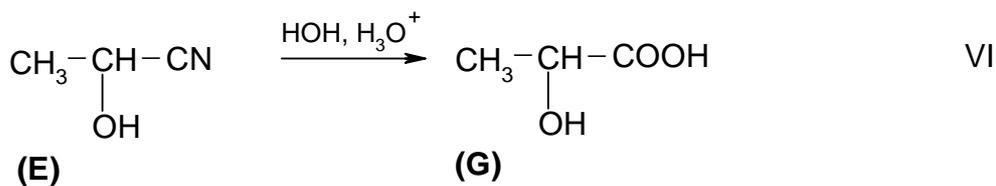
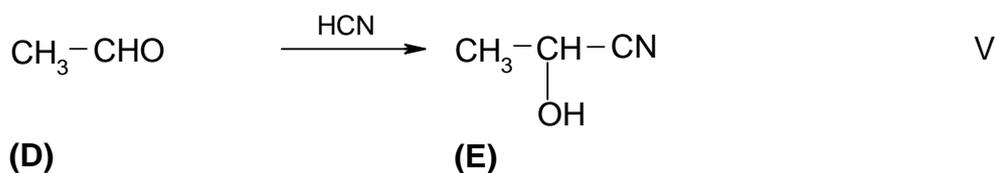
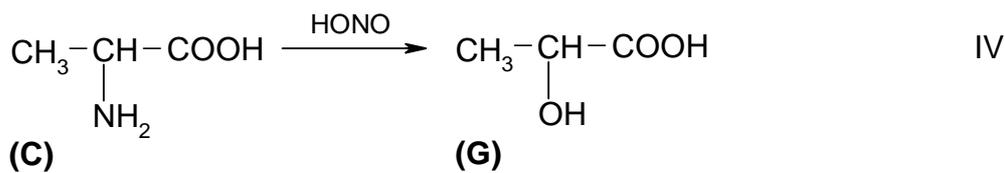


Reaction:

The reduction product contains 21.6 % of sulphur.

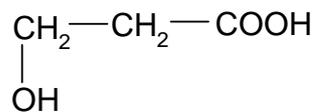
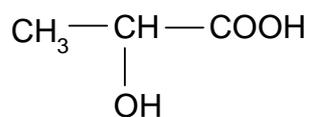
2.



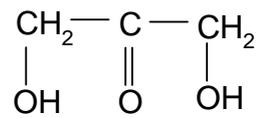
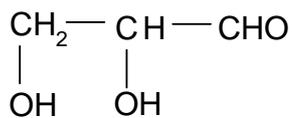
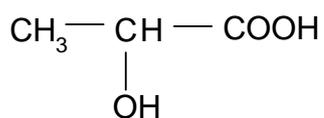


3. I - substitution reaction
 II - substitution nucleophilic reaction
 III - substitution nucleophilic reaction
 IV - substitution reaction
 V - additive nucleophilic reaction
 VI - additive reaction, hydrolysis
 VII - additive reaction
 VIII - additive reaction, hydrolysis

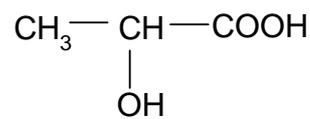
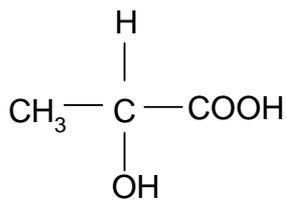
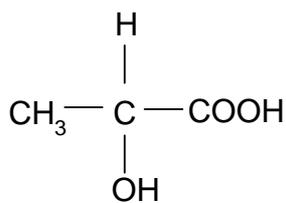
4.



position isomerism



structural isomerism



d(+)
stereoisomerism
(optical isomerism)

l(-)

racemic mixture

PROBLEM 3

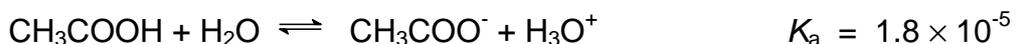
The following 0.2 molar solutions are available:



Problems:

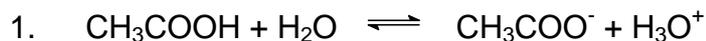
- Determine the concentration of H₃O⁺ ions in solution **C**.
- Determine pH value in solution **A**.
- Write an equation for the chemical reaction that takes place when substances **B** and **E** are allowed to react and mark conjugate acid-base pairs.
- Compare acid-base properties of substances **A**, **B**, and **C** and determine which one will show the most basic properties. Explain your decision.
- Write a chemical equation for the reaction between substances **B** and **G**, and explain the shift of equilibrium.
- Write a chemical equation for the reaction between substances **C** and **E**, and explain the shift of equilibrium.
- Calculate the volume of **D** solution which is required to neutralise 20.0 cm³ of **H** solution.
- What would be the volume of hydrogen chloride being present in one litre of **A** solution if it were in gaseous state at a pressure of 202.65 kPa and a temperature of 37 °C?

Ionisation constants:



Relative atomic masses:

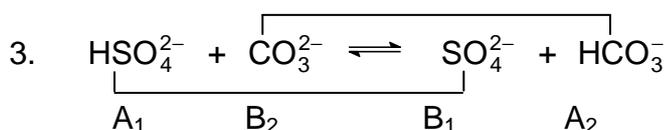
$$A_r(\text{Na}) = 23; \quad A_r(\text{S}) = 32; \quad A_r(\text{O}) = 16.$$

SOLUTION

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}_3\text{O}^+]^2}{c}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c} = \sqrt{1.8 \times 10^{-5} \times 0.2} = 1.9 \times 10^{-3} \text{ mol dm}^{-3}$$

$$2. \quad \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.2 = 0.7$$

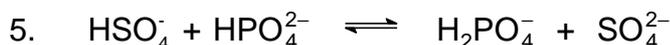


4. By comparison of the ionisation constants we get:

$$K_a(\text{HCl}) > K_a(\text{HSO}_4^-) > K_a(\text{CH}_3\text{COOH})$$

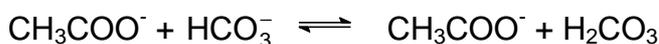
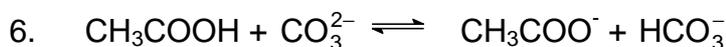
Thus, the strength of the acids in relation to water decreases in the above given order.

CH_3COO^- is the strongest conjugate base, whereas Cl^- is the weakest one.



$$K_a(\text{HSO}_4^-) \gg K_a(\text{HPO}_4^{2-})$$

Equilibrium is shifted to the formation of H_2PO_4^- and SO_4^{2-} .



$$K_a(\text{CH}_3\text{COOH}) > K_a(\text{H}_2\text{CO}_3) > K_a(\text{HCO}_3^-)$$

Equilibrium is shifted to the formation of CH_3COO^- and H_2CO_3 .

$$7. \quad n(\text{H}_2\text{SO}_4) = c V = 0.2 \text{ mol dm}^{-3} \times 0.02 \text{ dm}^3 = 0.004 \text{ mol}$$

$$V(0.2 \text{ molar NaOH}) = \frac{n}{c} = \frac{0.008 \text{ mol}}{0.2 \text{ mol dm}^{-3}} = 0.04 \text{ dm}^3$$

$$8. \quad V(\text{HCl}) = \frac{n R T}{p} = \frac{0.2 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310 \text{ K}}{202.65 \text{ kPa}} = 2.544 \text{ dm}^3$$

PROBLEM 4

A mixture contains two organic compounds, **A** and **B**. Both of them have in their molecules oxygen and they can be mixed together in arbitrary ratios. Oxidation of this mixture on cooling yields the only substance **C** that combines with NaHSO_3 . The ratio of the molar mass of the substance being formed in the reaction with NaHSO_3 to that of substance **C**, is equal to 2.7931.

The mixture of substances **A** and **B** is burned in the presence of a stoichiometric amount of air (20 % O_2 and 80 % of N_2 by volume) in an eudiometer to produce a mixture of gases with a total volume of 5.432 dm^3 at STP. After the gaseous mixture is bubbled through a $\text{Ba}(\text{OH})_2$ solution, its volume is decreased by 15.46 %.

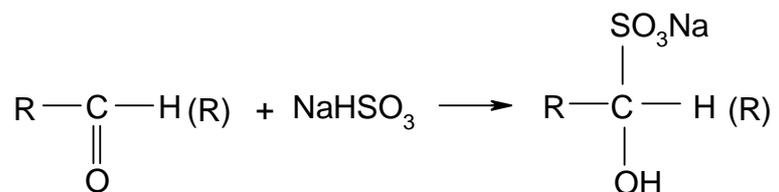
Problems:

- 4.1 Write structural formulas of substance **A** and **B**.
 4.2 Calculate the molar ratio of substances **A** and **B** in the mixture.

$$A_r(\text{C}) = 12; \quad A_r(\text{O}) = 16; \quad A_r(\text{S}) = 32; \quad A_r(\text{Na}) = 23.$$

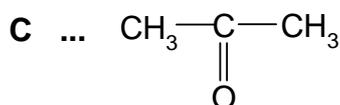
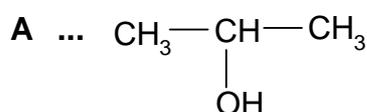
SOLUTION

4.1

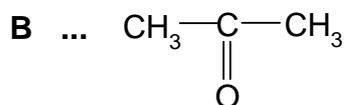


$$M_r(\text{C}) \quad M_r(\text{NaHSO}_3) = 104 \quad M_r(\text{C}) + 104$$

$$\frac{M_r(\text{C}) + 104}{M_r(\text{C})} = 2.7931 \quad M_r(\text{C}) = 58$$

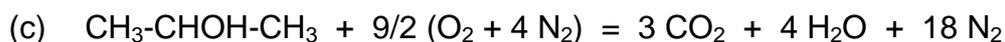


4.2 At STP conditions the gaseous mixture can only contain CO₂ and N₂. Carbon dioxide is absorbed in a barium hydroxide solution and therefore:



(a) $V(\text{CO}_2) = 5.432 \text{ dm}^3 \times 0.1546 = 0.84 \text{ dm}^3$

(b) $V(\text{N}_2) = 5.432 \text{ dm}^3 - 0.84 \text{ dm}^3 = 4.592 \text{ dm}^3$



Let us mark the amounts of substances as:

$$n(\text{CH}_3\text{-CHOH-CH}_3) = x$$

$$n(\text{CH}_3\text{-CO-CH}_3) = y$$

From equations (a), (c) and (d):

(e) $(3x \times 22.4) + (3y \times 22.4) = 0.84$

From equations (b), (c) and (d):

(f) $(18x \times 22.4) + (16y \times 22.4) = 4.592$

In solving equations (e) and (f) we get:

$$x = 0.0025 \text{ mol} \quad y = 0.01 \text{ mol}$$

$$\frac{x}{y} = \frac{1}{4}$$

PROBLEM 5

A mixture of two metals found in Mendelejev's periodical table in different groups, reacted with 56 cm³ of hydrogen on heating (measured at STP conditions) to produce two ionic compounds. These compounds were allowed to react with 270 mg of water but only one third of water reacted. A basic solution was formed in which the content of hydroxides was 30 % by mass and at the same time deposited a precipitate with a mass that represented 59.05 % of a total mass of the products formed by the reaction. After filtration the precipitate was heated and its mass decreased by 27 mg.

When a stoichiometric amount of ammonium carbonate was added to the basic solution, a slightly soluble precipitate was obtained, at the same time ammonia was liberated and the content of hydroxides in the solution decreased to 16.81 %.

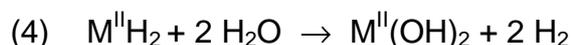
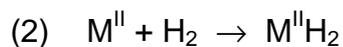
Problem:

5.1 Determine the metals in the starting mixture and their masses.

SOLUTION

Ionic hydrides are formed by combining of alkali metals or alkaline earth metals with hydrogen. In relation to the conditions in the task, there will be an alkali metal (M^I) as well as an alkaline earth metal (M^{II}) in the mixture.

Equations:

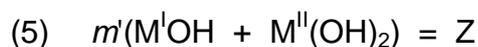


reacted: 0.09 g H₂O, i. e. 0.005 mol

unreacted: 0.18 g H₂O, i. e. 0.01 mol

Since all hydroxides of alkali metals are readily soluble in water, the undissolved precipitate is M^{II}(OH)₂, however, it is slightly soluble in water, too.

Thus, the mass of hydroxides dissolved in the solution:



Therefore:

$$30 = \frac{Z}{Z + 0.18} \times 100 \quad Z = 0.077 \text{ g}$$

$$(6) \quad m'(M^I\text{OH} + M^{II}(\text{OH})_2) = 0.077 \text{ g}$$

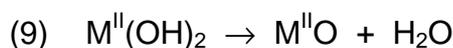
It represents 40.95 % of the total mass of the hydroxides, i. e. the total mass of hydroxides is as follows:

$$(7) \quad m'(M^I\text{OH} + M^{II}(\text{OH})_2) = \frac{0.077 \text{ g} \times 100}{40.95} = 0.188 \text{ g}$$

The mass of solid $M^{II}(\text{OH})_2$:

$$(8) \quad 0.188 \text{ g} - 0.077 \text{ g} = 0.111 \text{ g}$$

Heating:



Decrease of the mass: 0.027 g (H_2O)

$$(10) \quad \text{Mass of } M^{II}\text{O}: 0.084 \text{ g}$$

In relation to (8), (9), and (10):

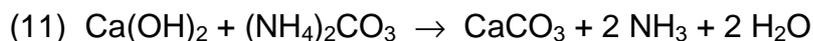
$$\frac{M_r(M^{II}\text{O})}{M_r(M^{II}\text{O}) + 18} = \frac{0.084}{0.111}$$

$$M_r(M^{II}\text{O}) = 56 \text{ g mol}^{-1}$$

$$M_r(M^{II}) = M_r(M^{II}\text{O}) - M_r(\text{O}) = 56 - 16 = 40$$

$$\underline{M^{II} = \text{Ca}}$$

Precipitation with $(\text{NH}_4)_2\text{CO}_3$:



According to (5) and (6) the mass of the solution was:

$$0.18 \text{ g} + 0.077 \text{ g} = 0.257 \text{ g}$$

After precipitation with $(\text{NH}_4)_2\text{CO}_3$:

$$16.81 = \frac{m(\text{M}^I\text{OH})}{m(\text{solution})} \times 100$$

Let us mark as n' the amount of substance of $\text{Ca}(\text{OH})_2$ being present in the solution.

$$M(\text{Ca}(\text{OH})_2) = 74 \text{ g mol}^{-1}$$

Taking into account the condition in the task as well as equation (11), we get:

$$16.81 = \frac{(0.077 - 74 n') \times 100}{0.257 - 74 n' + 2 n' \times 18}$$

$$n' = 5 \times 10^{-4} \text{ mol}$$

The total amount of substance of Ca(OH)₂ (both in the precipitate and in the solution):

$$(12) \quad n(\text{Ca(OH)}_2) = \frac{0.111 \text{ g}}{74 \text{ g mol}^{-1}} + 5 \times 10^{-4} \text{ mol} = 0.002 \text{ mol} \quad (\text{i. e. } 0.148 \text{ g})$$

According to equations (3) and (4):

$$n(\text{H}_2\text{O}) = 0.004 \text{ mol} \quad (\text{for } \text{M}^{\text{II}}\text{H}_2)$$

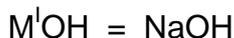
$$n(\text{H}_2\text{O}) = 0.001 \text{ mol} \quad (\text{for } \text{M}^{\text{I}}\text{H})$$

$$n(\text{M}^{\text{I}}\text{OH}) = 0.001 \text{ mol}$$

According to equations (7) and (11):

$$m(\text{M}^{\text{I}}\text{OH}) = 0.188 \text{ g} - 0.148 \text{ g} = 0.04 \text{ g}$$

$$M(\text{M}^{\text{I}}\text{OH}) = \frac{m(\text{M}^{\text{I}}\text{OH})}{n(\text{M}^{\text{I}}\text{OH})} = \frac{0.04 \text{ g}}{0.001 \text{ mol}} = 40 \text{ g mol}^{-1}$$



Composition of the mixture:

$$0.002 \text{ mol Ca} + 0.001 \text{ mol Na}$$

or

$$0.080 \text{ g Ca} + 0.023 \text{ g Na}$$

PRACTICAL PROBLEMS**PROBLEM 1 (practical)**

Test tubes with unknown samples contain:

- a salt of carboxylic acid,
- a phenol,
- a carbohydrate,
- an amide.

Determine the content of each test tube using reagents that are available on the laboratory desk.

PROBLEM 2 (practical)

Determine cations in solutions No 5, 6, 8 and 9 using the solution in test tube 7.

Without using any indicator find out whether the solution in test tube 7 is an acid or a hydroxide.

SOLUTION

Test tube: No 5 - NH_4^+ ; No 6 - Hg^{2+} ; No 7 - OH^- ; No 8 - Fe^{3+} ; No 9 - Cu^{2+}

PROBLEM 3 (practical)

The solution in test tube No 10 contains two cations and two anions.

Prove those ions by means of reagents that are available on the laboratory desk.

SOLUTION

The solution in test tube No 10 contained: Ba^{2+} , Al^{3+} , Cl^- , CO_3^{2-}

7th



**8 theoretical problems
4 practical problems**

THE SEVENTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1975, VESZPRÉM, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

How many grams of alum $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ are crystallised out from 320 g $\text{KAl}(\text{SO}_4)_2$ solution saturated at 20 °C if 160 g of water are evaporated from the solution at 20 °C?

(The solution saturated at 20 °C contains 5.50 % of $\text{KAl}(\text{SO}_4)_2$ by mass.)

Relative atomic masses:

$A_r(\text{K}) = 39.10$; $A_r(\text{Al}) = 26.98$; $A_r(\text{S}) = 32.06$; $A_r(\text{O}) = 16.0$; $A_r(\text{H}) = 1.01$

SOLUTION

Let us mark

x - mass of crystallised alum,

y - mass of the saturated solution of $\text{AlK}(\text{SO}_4)_2$ which remains after crystallisation

Mass fraction of $\text{KAl}(\text{SO}_4)_2$ in the crystalhydrate is equal to 0.544.

Then: $320 = x + y + 160$

i. e. $y = 160 - x$

Mass balance equation for $\text{AlK}(\text{SO}_4)_2$:

$320 \times 0.055 = x \cdot 0.544 + (160 - x) \cdot 0.055$

$x = 18.0 \text{ g}$

PROBLEM 2

An alloy prepared for experimental purposes contains aluminium, zinc, silicon, and copper. If 1000 mg of the alloy are dissolved in hydrochloric acid, 843 cm³ of hydrogen (0 °C, 101.325 kPa) are evolved and 170 mg of an undissolved residue remain. A sample of 500 mg of the alloy when reacted with a NaOH solution produces 517 cm³ of hydrogen at the above conditions and in this case remains also an undissolved fraction.

Problem:

2.1 Calculate the composition of the alloy in % by mass.

Relative atomic masses:

$$A_r(\text{Al}) = 26.98; \quad A_r(\text{Zn}) = 65.37; \quad A_r(\text{Si}) = 28.09; \quad A_r(\text{Cu}) = 63.55.$$

SOLUTION

2.1 HCl dissolves: Al, Zn

NaOH dissolves: Al, Zn, Si

$$\frac{0.843 \text{ dm}^3}{22.414 \text{ dm}^3 \text{ mol}^{-1}} = 37.61 \text{ mmol H}_2 \quad (\text{Al, Zn})$$

$$\frac{2 \times 0.517 \text{ dm}^3}{22.414 \text{ dm}^3 \text{ mol}^{-1}} = 46.13 \text{ mmol H}_2 \quad (\text{Al, Zn, Si})$$

The difference of 8.52 mmol H₂ corresponds to 4.26 mmol Si

$$\underline{\text{Si:}} \quad m(\text{Si}) = 4.26 \text{ mmol} \times 28.09 \text{ g mol}^{-1} = 119.7 \text{ mg}$$

$$\% \text{ Si} = \frac{119.7 \text{ mg}}{1000 \text{ mg}} \times 100 = 11.97$$

$$\underline{\text{Cu:}} \quad m(\text{Si} + \text{Cu}) = 170 \text{ mg}$$

$$m(\text{Cu}) = 170 \text{ mg} - 119.7 \text{ mg} = 50.3 \text{ mg (in 1000 mg of the alloy)}$$

$$\% \text{ Cu} = 5.03$$

Al: $m(\text{Zn} + \text{Al}) = 1000 \text{ mg} - 170 \text{ mg} = 830 \text{ mg}$

$x \text{ mg Al}$ gives $\frac{3}{2} \times \frac{x}{26.98} \text{ mmol H}_2$

$(830 - x) \text{ mg Zn}$ gives $\frac{830 - x}{65.37} \text{ mmol H}_2$

$$\frac{3}{2} \times \frac{x}{26.98} + \frac{830 - x}{65.37} = 37.61 \text{ mmol H}_2$$

$x = 618.2 \text{ mg Al}$ (in 1000 mg of the alloy)

$\% \text{ Al} = 61.82$

Zn: $m(\text{Zn}) = 830 \text{ mg} - 618.2 \text{ mg} = 211.8 \text{ mg}$ (in 1000 mg of the alloy)

$\% \text{ Zn} = 21.18$

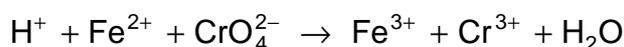
PROBLEM 3

A sample of 1500 mg of an alloy that contains silver, copper, and chromium is dissolved and the solution containing Ag^+ , Cu^{2+} , and Cr^{3+} ions, is diluted to exactly 500 cm^3 . One tenth of the volume of that solution is taken for further procedure:

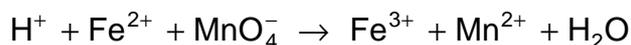
After elimination of silver and copper, chromium is oxidised in it according to the following unbalanced equation:



Then 25.00 cm^3 of a 0.100 molar Fe(II) salt solution are added. The following reaction (written in an unbalanced form) is taking place:



According to the unbalanced equation:



a volume of 17.20 cm^3 of a 0.020-molar KMnO_4 solution is required for an oxidation of the Fe(II) salt which remains unoxidized in the solution.

In another experiment, a volume of 200 cm^3 of the initial solution is electrolysed. Due to secondary reactions, the efficiency of the electrolysis is 90 % for metals under consideration. All three metals are quantitatively deposited in 14.50 minutes by passing a current of 2 A through the solution.

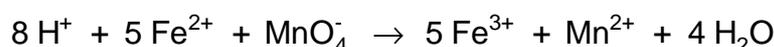
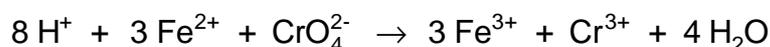
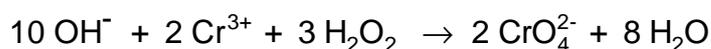
Problem:

3.1 Balance the three chemical equations and calculate the composition of the alloy in % by mass.

Relative atomic masses: $A_r(\text{Cu}) = 63.55$; $A_r(\text{Ag}) = 107.87$; $A_r(\text{Cr}) = 52.00$

SOLUTION

3.1 Equations:



Content of Cr:

$$17.20 \times 0.020 = 0.344 \text{ mmol KMnO}_4$$

$$5 \times 0.344 = 1.72 \text{ mmol Fe}^{2+}$$

$$\text{Reacted: } 25 \times 0.1 - 1.72 = 0.78 \text{ mmol Fe}^{2+}$$

It corresponds:

$$\frac{0.78}{3} = 0.26 \text{ mmol Cr in 150 mg of the alloy}$$

$$m(\text{Cr}) = 2.6 \text{ mmol} \times 52 \text{ g mol}^{-1} = 135.2 \text{ mg in 1500 mg of the alloy}$$

$$\underline{\% \text{ Cr} = 9.013}$$

Content of Cu and Ag:

$$Q = 40.575 \text{ mF} / 1500 \text{ mg} \quad (1087.4 \text{ mAh})$$

$$Q_{\text{Cr}} = 2.6 \times 3 = 7.8 \text{ mF} \quad (209 \text{ mAh})$$

$$Q_{(\text{Cu}+\text{Ag})} = 40.575 - 7.8 = 32.775 \text{ mF} \quad (878.4 \text{ mAh})$$

(F = Faraday's charge)

$$m(\text{Cu} + \text{Ag}) = m(\text{alloy}) - m(\text{Cr}) = 1500 - 135.2 = 1364.8 \text{ mg}$$

$$\text{For deposition of copper: } \frac{2x}{63.55} \text{ mF}$$

$$\text{For deposition of silver: } \frac{1364.8 - x}{107.87} \text{ mF}$$

$$32.775 = \frac{2x}{63.55} + \frac{1364.8 - x}{107.87}$$

$$x = 906.26$$

$$m(\text{Cu}) = 906.26 \text{ mg in 1500 mg of the alloy}$$

$$m(\text{Ag}) = 458.54 \text{ mg in 1500 mg of the alloy}$$

$$\underline{\% \text{ Cu} = 60.4} \quad \underline{\% \text{ Ag} = 30.6}$$

PROBLEM 4

The pH value of a solution containing 3 % by mass of formic acid ($\rho = 1.0049 \text{ g cm}^{-3}$) is equal to 1.97.

Problem:

4.1 How many times should the solution be diluted to attain a tenfold increase in the value of ionisation degree?

Relative atomic masses: $A_r(\text{H}) = 1.01$; $A_r(\text{C}) = 12.01$; $A_r(\text{O}) = 16$.

SOLUTION

$$4.1 \quad c_1 = \frac{n_1}{V} = \frac{1004.9 \text{ g} \times 0.03}{45.03 \text{ g mol}^{-1} \times 1 \text{ dm}^3} = 6.55 \times 10^{-1} \text{ mol dm}^{-3}$$

$$\text{pH} = 1.97; [\text{H}^+] = 1.0715 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\alpha_1 = \frac{[\text{H}^+]}{c_1} = 0.01636 \quad (1.636 \%)$$

Calculation of c_2 after dilution (two alternative solutions):

a) α_1 – before dilution; α_2 – after dilution

$$K_a = \frac{\alpha_1 c_1}{1 - \alpha_1} \quad (1)$$

$$K_a = \frac{\alpha_2^2 c_2}{1 - \alpha_2} = \frac{(10 \alpha_1)^2 c_2}{1 - 10 \alpha_1} \quad (2)$$

From equations (1) and (2):

$$\frac{c_1}{c_2} = \frac{100 (1 - \alpha_1)}{1 - 10 \alpha_1} = 117.6$$

$$b) \quad K_a = \frac{[\text{H}^+]^2}{c - [\text{H}^+]} = \frac{(1.0715 \times 10^{-2})^2}{0.655 - 1.0715 \times 10^{-2}} = 1.78 \times 10^{-4}$$

$$c_2 = \frac{K_a (1 - 10 \alpha_1)}{(10 \alpha_1)^2} = 5.56 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\frac{c_1}{c_2} = \frac{6.55 \times 10^{-1} \text{ mol dm}^{-3}}{5.56 \times 10^{-3} \text{ mol dm}^{-3}} = 117.8$$

PROBLEM 5

A certain aldehyde **B** is subsequent to an aldehyde **A** in the homologous series of aldehydes. An amount of 19 g of aldehyde **B** is added to 100 g of an aqueous solution containing 23 mass % of aldehyde **A**. Addition of AgNO_3 in ammonia solution to 2 g of the aldehydes solution results in a precipitation of 4.35 g of silver.

Problems:

5.1 Determine by calculation what aldehydes were used.

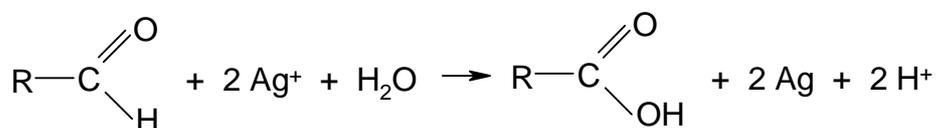
5.2 Give the structural formulas of the aldehydes.

Relative atomic masses:

$$A_r(\text{C}) = 12.01; \quad A_r(\text{O}) = 16.00; \quad A_r(\text{H}) = 1.01; \quad A_r(\text{Ag}) = 107.87$$

SOLUTION

5.1 Equation:



$$n(\text{Ag}) = \frac{4.35 \text{ g}}{107.87 \text{ g mol}^{-1}} = 0.04033 \text{ mol}$$

$$n(\text{A}) + n(\text{B}) = 0.02017 \text{ mol}$$

$$\frac{m(\text{A})}{M(\text{A})} + \frac{m(\text{B})}{M(\text{A}) + 14} = 0.02017 \text{ mol} \quad (1)$$

$$m(\text{A}) = \frac{23 \text{ g}}{119 \text{ g}} \times 2 \text{ g} = 0.39 \text{ g}$$

$$m(\text{B}) = \frac{19 \text{ g}}{119 \text{ g}} \times 2 \text{ g} = 0.32 \text{ g}$$

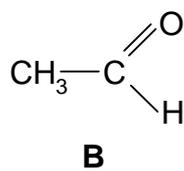
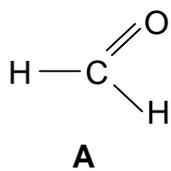
According to equation (1):

$$M(\text{A}) = 30 \text{ g mol}^{-1}$$

$$M(\text{B}) = 44 \text{ g mol}^{-1}$$

5.2 A = formaldehyde, methanal

B = acetaldehyde, ethanal



PROBLEM 6

The equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ is at 600 °C equal to 70.0

Problems:

6.1 How much iodine (in %) is converted till the equilibrium is reached if the reactants are mixed in:

- 1 : 1 molar ratio at 600 °C;
- 2 : 1 molar ratio at 600 °C (the amount of hydrogen is twice as great as that of iodine).

6.2 How many moles of hydrogen should be mixed with one mole of iodine when 99 % of iodine is to be converted to hydrogen iodide till the equilibrium is reached at 600 °C?

SOLUTION

6.1a) (two alternative solutions)

$$\text{i) } [\text{H}_2] = [\text{I}_2] = c - x$$

$$[\text{HI}] = 2x$$

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{4x^2}{(c-x)^2}$$

$$\sqrt{K} = \frac{2x}{c-x}$$

$$x = \frac{\sqrt{70} \cdot c}{2 + \sqrt{70}} \quad \frac{x}{c} = 0.807 \quad 80.7 \%$$

$$\text{ii) } [\text{H}_2] = [\text{I}_2] = c - c\alpha$$

$$[\text{HI}] = 2c\alpha$$

$$K = \frac{4\alpha^2 c^2}{(1-\alpha)^2 c^2} = \frac{4\alpha^2}{(1-\alpha^2)^2}$$

$$\sqrt{K} = \frac{2\alpha}{1-\alpha}$$

$$\alpha = 0.807, \text{ i. e. } 80.7 \%$$

6.1b) (two alternative solutions)

$$\text{i) } [\text{H}_2] = 2c - x \quad [\text{I}_2] = c - x$$

$$[\text{HI}] = 2x$$

$$K = \frac{4x^2}{(2c - x)(c - x)}$$

$$x = 0.951c \quad \frac{x}{c} = 0.951 \text{ i. e. } 95.1 \%$$

$$\text{ii) } [\text{H}_2] = 2c - c\alpha \quad [\text{I}_2] = c - c\alpha$$

$$[\text{HI}] = 2c\alpha$$

$$K = \frac{4c^2\alpha^2}{(2 - \alpha)(1 - \alpha)c^2}$$

$$\alpha = 0.951 \text{ i. e. } 95.1 \%$$

$$\mathbf{6.2} \quad [\text{H}_2] = xc - 0.99c \quad [\text{I}_2] = c - 0.99c$$

$$[\text{HI}] = 1.98c$$

$$K = \frac{1.98^2 c^2}{c^2 (1 - 0.99)(x - 0.99)} = \frac{1.98^2}{0.01(x - 0.99)}$$

$$x = 6.59 \text{ mol H}_2$$

PROBLEM 7

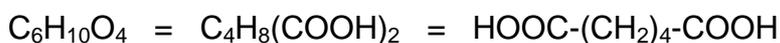
A certain saturated hydrocarbon **A** is transformed by a catalytic oxidation partly into a secondary alcohol **B**, and partly into a ketone **C**. The ketone when oxidised with nitric acid in the presence of catalyst yields a compound **D** with a formula of $C_6H_{10}O_4$. From compound **D** when heated in the presence of acetic anhydride, a ketone **E** is formed, its formation being accompanied by evolution of CO_2 and H_2O . Compounds **E** and **C** have similar structures but compound **E** contains one methylene group less than ketone **C**. Compound **D** is one of the starting materials in the production of an important polycondensation synthetic fibre.

Problem:

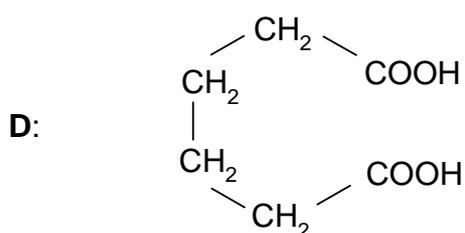
7.1 Write the structural formulas of compounds **A**, **B**, **C**, **D**, and **E**.

SOLUTION

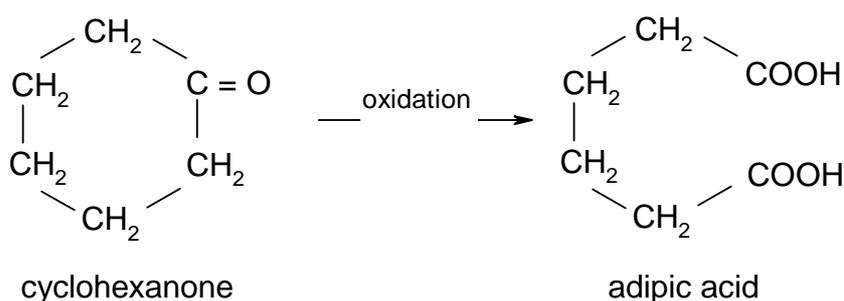
7.1 In general: ketone $\xrightarrow{\text{oxidation}}$ carboxylic acid

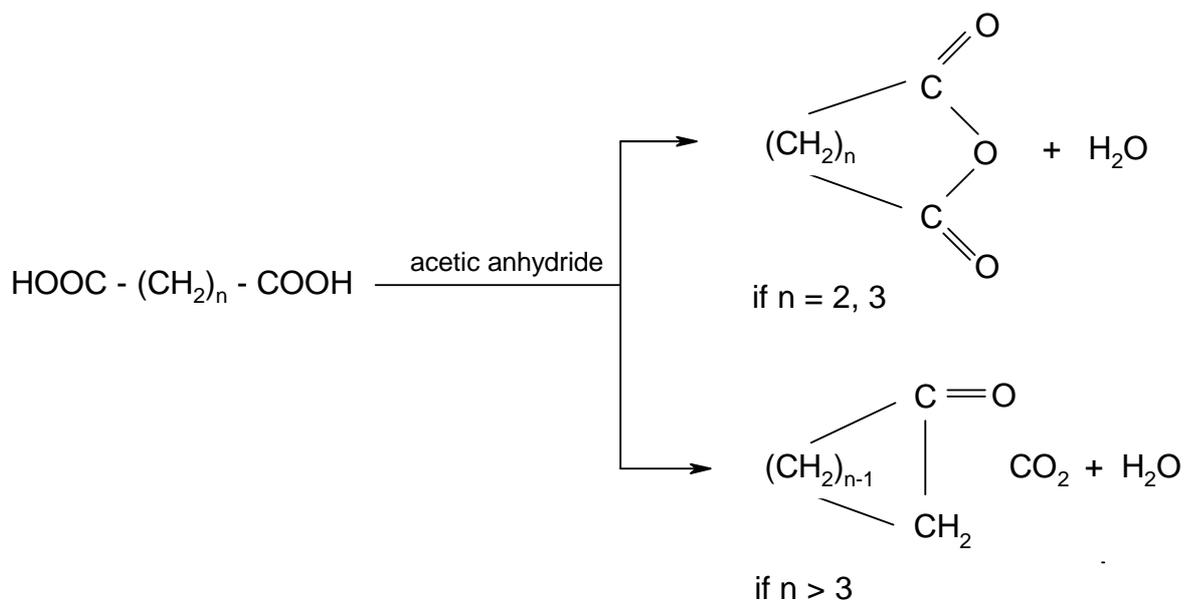
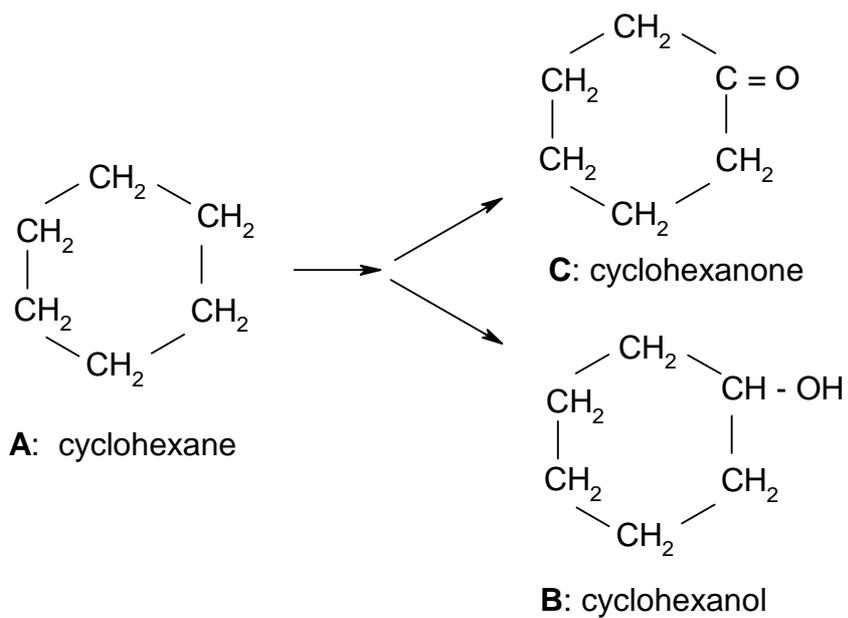


Product **D** is adipic acid which is a basic material in the production of nylon.



Compound C is cyclohexanone, because:





Compound E: cyclopentanone

PROBLEM 8

- a) Mark by the "+" in a corresponding window those molecules for which the assertions written on the left side of the Table, are true.

Assertion	Molecule			
	C ₂ H ₄	N ₂ H ₄	H ₂ O ₂	H ₂ F ₂
There is a covalent bond between two equal atoms				
The molecule contains a double bond				
The molecule is planar				
The molecule is polar				
There is also a hydrogen bond in the molecule				
It has basic properties in relation to water				

- b) The following assertion and Table are incomplete. Fill in the dotted places by a missing word and the missing formulas, respectively.

Assertion: The electronic structures of the molecules (ions) being placed in the Table one under the other are

CH ₄	C ₂ H ₆	CO ₃ ²⁻	C ₂ O ₄ ²⁻
NH ₄ ⁺	N ₂ H ₆ ²⁺	NO ₂ ⁺	N ₂

SOLUTION

a)

Assertion	Molecule			
	C ₂ H ₄	N ₂ H ₄	H ₂ O ₂	H ₂ F ₂
There is a covalent bond between two equal atoms	+	+	+	
The molecule contains a double bond	+			
The molecule is planar	+			+
The molecule is polar		+	+	+
There is also a hydrogen bond in the molecule				+
It has basic properties in relation to water		+		

b) **Assertion:** The electronic structures of the molecules (ions) being placed in the Table under the other are **isoelectronic**.

CH ₄	C ₂ H ₆	CO ₃ ²⁻	CO ₂	C ₂ O ₄ ²⁻	C ₂ ²⁻
NH ₄ ⁺	N ₂ H ₆ ²⁺	NO ₃ ⁻	NO ₂ ⁺	N ₂ O ₄	N ₂

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Aqueous solutions of the following compounds: AgNO_3 , HCl , Ag_2SO_4 , $\text{Pb}(\text{NO}_3)_2$, NH_3 and NaOH are available in numbered bottles. Allow to react each of them with others and align the numbers of the bottles with formulas of the compounds.

Attention! The use of any other reagent is not permitted. In performing the reactions do not use the whole volume of the solutions. A few cm^3 of the solution should remain in each bottle after your work is finished. It is advisable to make a draft at first but only those solutions will be evaluated by the jury that will be written in the Table.

Write your observations into the squares of the Table below the diagonal using the following uniform symbols:

white precipitate : ↓

coloured precipitate: ↓↓

formation of a complex soluble in water: []

evolution of a gas: ↑

Write into the corresponding squares above the diagonal the chemical formulas of the precipitate, the complex ion or gas which are formed by the corresponding reactions.

Write into the last line of the Table the final results obtained on the basis of your experiments.

Number of sample	1	2	3	4	5	6
1						
2						
3						
4						
5						
6						
Formula of compounds						

PROBLEM 2 (practical)

A solid compound is in each of the numbered test-tubes. It might be chloride, iodide, oxide, hydroxide, sulphide, sulphate or carbonate, each combined with one of the following cations: Ag^+ , Pb^{2+} , Cu^{2+} , Cd^{2+} , Sb(V) , Sn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Cr^{3+} , Al^{3+} , Zn^{2+} , Ba^{2+} .

Problem:

Write the chemical formula for each solid compound given as a sample. You can use only reagents that are available on your laboratory desk.

Attention! In carrying out reactions do not use the whole quantity of the sample. A small portion of the sample is to remain in each test tube. Only those results will be evaluated that will be written in the Table below.

Table:

Compound			
Number of sample	Formula	Number of sample	Formula
1		6	
2		7	
3		8	
4		9	
5			

PROBLEM 3 (practical)

Three samples are found in sealed ampoules. All of them are aromatic compounds: a hydrocarbon, a phenol, and an aldehyde.

Determine the group of compounds to which your numbered samples belong, using only the reagents which are at your disposal.

Attention! Be careful when opening the ampoules. The identification of the samples based upon physical characteristics only (colour, smell), is not sufficient. Only those results will be taken into account that will be written in the Table below.

Table:

No of sample	Reagent	Observation	Type of compound
1			
2			
3			

PROBLEM 4 (practical)

A crystalline sodium carbonate loses a part of water when stored for a long time, i. e. its water content is not constant. After a long storage it has an average content of crystal water.

A solution of Na_2CO_3 is in the test-tube and the mass of $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$ used in its preparation is marked on the test-tube.

Determine the content of crystal water per mole of sodium carbonate in the sample. Make calculations with an accuracy of 0.01 mol.

Procedure:

Transfer the solution from the test tube quantitatively into a 100 cm^3 volumetric flask and dilute it up to the mark with distilled water free of carbon dioxide (having been boiled and cooled to room temperature). Measure 10.00 cm^3 of the solution into a 100 cm^3 Erlenmeyer flask and dilute it to about 30 cm^3 with the above mentioned distilled water. Add 2 – 3 drops of methyl orange indicator and titrate with a 0.1-molar HCl volumetric solution to a colour transition of the indicator. On boiling for 1 – 2 minutes the carbon dioxide dissolved in the solution is expelled. If the colour of the solution changes to yellow, cool it and titrate again to the colour transition of the indicator. Calculate the carbonate content in the sample from the total consumption of the 0.1-molar HCl solution.

$$A_r(\text{Na}) = 22.99; \quad A_r(\text{C}) = 12.01; \quad A_r(\text{O}) = 16.00; \quad A_r(\text{H}) = 1.01.$$

8th



International Chemistry Olympiad

**7 theoretical problems
3 practical problems**

THE EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD 10–19 JULY 1976, HALLE, GERMAN DEMOCRATIC REPUBLIC

THEORETICAL PROBLEMS

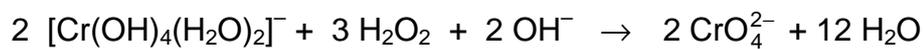
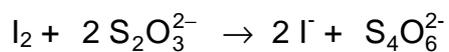
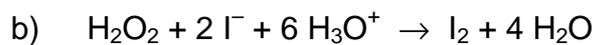
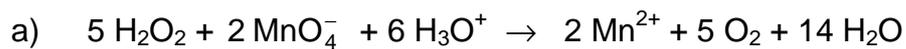
PROBLEM 1

- 1.1 Explain by means of generally used international symbols and formulas which compounds are named as peroxy compounds. Write summary formulas for six of them.
- 1.2 Write chemical equations for two methods of quantitative determination of the content of peroxide in calcium(II) peroxide.
- 1.3 By means of chemical equations express the following chemical reactions:
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ dissolved in water, is mixed with an excess of sodium hydroxide solution. A clear green solution is formed. The colour of the solution changes to yellow when an aqueous hydrogen peroxide solution is added.
 - If an aqueous solution of a violet manganese compound is mixed with a hydrogen peroxide solution, the resulting solution is decolourised and a gas is released from it.

SOLUTION

- 1.1 Peroxy compounds contain the functional group: O_2^{2-}
Examples: H_2O_2 , Na_2O_2 , BaO_2 , H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{C}_2\text{O}_6$, CrO_5 , $[\text{VO}_2]^{3+}$
- 1.2 Calcium(II) peroxide is decomposed by an aqueous solution of a suitable acid, and H_2O_2 which is liberated, is determined by:
- manganometric method,
 - iodometric method.

Equations:

b) Equation is given in 2a.

PROBLEM 2

A sample of 2.3793 g of crystallohydrate of the type $M_xA_y \cdot z H_2O$, where M is a metal, reacted with an excess of $SOCl_2$. Gaseous products formed by the reaction were introduced into a barium chloride solution containing hydrochloric acid and hydrogen peroxide. Small quantities of $SOCl_2$ carried by the gaseous products were removed by freezing out. The mass of the precipitate that is deposited from the solution, was 14.004 g. It was found to contain 13.74 mass % of sulphur.

In another experiment, 1.1896 g of the initial substance were dissolved in water and the solution was diluted to a volume of 100 cm^3 . One fifth of this solution required to react with 10 cm^3 of a 0.2-molar $AgNO_3$ solution. The mass of the precipitate formed by the titration was 0.28664 g. (The end point of the titration was determined by the conductometric method.)

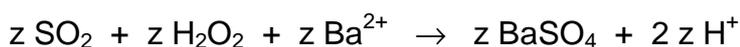
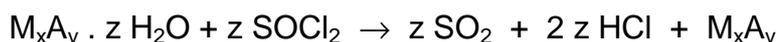
Problems:

- 2.1** Calculate the summary formula of the crystallohydrate. (Use the relative atomic mass values given in the attached Periodical Table of Elements.)
- 2.2** If you know that the sample can contain a maximum of seven moles of water per one mole of the crystallohydrate, give an example of another possible hydrate that cannot come into consideration due to the given limitation.

SOLUTION

- 2.1 a)** The content of sulphur confirms that the precipitate is $BaSO_4$.

Reactions:

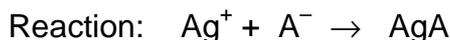


$$n(BaSO_4) = \frac{m(BaSO_4)}{M(BaSO_4)} = \frac{14.004 \text{ g}}{233.4 \text{ g mol}^{-1}} = 0.06 \text{ mol}$$

Amount of substance of H_2O in the hydrate:

$$n(H_2O) = 0.06 \text{ mol}$$

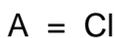
b) Amount of substance of A⁻ in the sample:



$$n(\text{Ag}^+) = c V = 0.2 \text{ mol dm}^{-3} \times 0.01 \text{ dm}^3 = 0.002 \text{ mol}$$

$$n(\text{AgA}) = 0.002 \text{ mol}$$

$$M(\text{AgA}) = \frac{m(\text{AgA})}{n(\text{AgA})} = \frac{0.28664 \text{ g}}{0.002 \text{ mol}} = 143.32 \text{ g mol}^{-1}$$



The precipitate being formed by the titration is AgCl, thus the hydrate is a chloride.

$$\frac{1.1896}{5} \text{ g, i. e. } 0.23792 \text{ g of the hydrate contain } 0.002 \text{ mol Cl}^-$$

$$2.3792 \text{ g of the hydrate contain } 0.02 \text{ mol Cl}^-.$$

The molar ratio of Cl⁻ to H₂O in the hydrate:

$$n(\text{Cl}^-) : n(\text{H}_2\text{O}) = 0.02 : 0.06 = 1 : 3$$

Assumption:

i) MCl . 3 H₂O

$$n(\text{Cl}^-) = 0.02 \text{ mol}$$

$$n(\text{MCl} \cdot 3 \text{ H}_2\text{O}) = 0.02 \text{ mol}$$

$$M(\text{MCl}_3 \cdot 3 \text{ H}_2\text{O}) = \frac{2,3793 \text{ g}}{0,02 \text{ mol}} = 118.965 \text{ g mol}^{-1}$$

$$\begin{aligned} M(\text{M}) &= M(\text{MCl} \cdot 3 \text{ H}_2\text{O}) - M(\text{Cl}) - 3 M(\text{H}_2\text{O}) = \\ &= 118.965 - 35.453 - 54.046 = 29.466 \text{ g mol}^{-1} \end{aligned}$$

Elements with similar molar masses are non-metals, therefore the first assumption is not suitable.

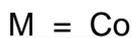
ii) MCl₂ . 6 H₂O

$$n(\text{Cl}^-) = 0.02 \text{ mol}$$

$$n(\text{MCl}_2 \cdot 6 \text{ H}_2\text{O}) = 0.01 \text{ mol}$$

$$M(\text{MCl}_2 \cdot 6 \text{ H}_2\text{O}) = \frac{2,3793 \text{ g}}{0,01 \text{ mol}} = 237.93 \text{ g mol}^{-1}$$

$$\begin{aligned} M(\text{M}) &= M(\text{MCl}_2 \cdot 6 \text{ H}_2\text{O}) - 2 M(\text{Cl}) - 6 M(\text{H}_2\text{O}) = \\ &= 237.93 - 70.906 - 108.092 = 58.932 \text{ g mol}^{-1} \end{aligned}$$



The second assumption satisfies the conditions of the task.

The formula of the hydrate is: **CoCl₂ · 6 H₂O**

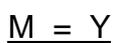


$$n(\text{Cl}^-) = 0.02 \text{ mol}$$

$$n(\text{MCl}_3 \cdot 9 \text{H}_2\text{O}) = \frac{0.02}{3} \text{ mol}$$

$$M(\text{MCl}_3 \cdot 9 \text{H}_2\text{O}) = 356.895 \text{ g mol}^{-1}$$

$$\begin{aligned} M(\text{M}) &= M(\text{MCl}_3 \cdot 9 \text{H}_2\text{O}) - 3 M(\text{Cl}) - 9 M(\text{H}_2\text{O}) = \\ &= 356.895 - 106.359 - 162.138 = 88.398 \text{ g mol}^{-1} \end{aligned}$$



2.2 The hydrate YCl₃ · 9 H₂O as well as the other hydrate SnCl₄ · 12 H₂O cannot come into account because of the limitation in the task (a maximum of seven moles of H₂O per one mole of the hydrate).

PROBLEM 3

A sample of 5 g of a technical iron(II) sulphide FeS, which contains 5 % metallic iron reacted with hydrochloric acid.

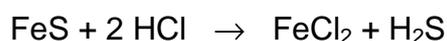
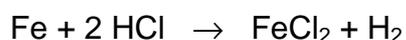
Problems:

3.1 Calculate the volume of the gaseous products at STP conditions.

3.2 What is the composition (in volume %) of the gaseous mixture?

SOLUTION

3.1 Reactions:



$$n(\text{Fe}) = \frac{m(\text{Fe})}{M(\text{Fe})} = \frac{0.25 \text{ g}}{55.85 \text{ g mol}^{-1}} = 4.48 \times 10^{-3} \text{ mol}$$

$$n(\text{FeS}) = \frac{m(\text{FeS})}{M(\text{FeS})} = \frac{4.75 \text{ g}}{87.91 \text{ g mol}^{-1}} = 5.40 \times 10^{-2} \text{ mol}$$

$$V(\text{H}_2) = n(\text{H}_2) \times V_0 = 4.48 \times 10^{-3} \text{ mol} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} = \underline{0.1 \text{ dm}^3}$$

$$V(\text{H}_2\text{S}) = n(\text{H}_2\text{S}) \times V_0 = 5.40 \times 10^{-2} \text{ mol} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} = \underline{1.21 \text{ dm}^3}$$

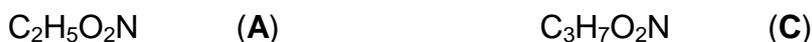
3.2 Composition of the gaseous mixture:

$$\frac{0.1 \text{ dm}^3}{1.31 \text{ dm}^3} \times 100 = 7.63 \text{ volume \% of H}_2$$

$$\frac{1.21 \text{ dm}^3}{1.31 \text{ dm}^3} \times 100 = 92.37 \text{ volume \% of H}_2\text{S}$$

PROBLEM 4

Four often occurring natural substances have the following summary (empirical) formulas:



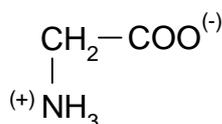
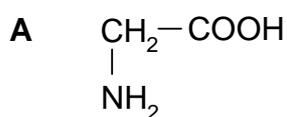
The given substances when allowed to react with an alkali hydroxide solution yield alkali salts. However, in a neutral or acidic solution the reaction takes place on the nitrogen atom.

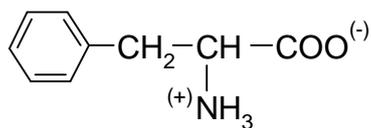
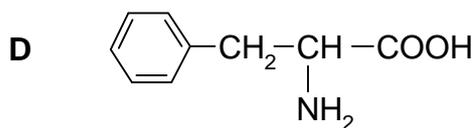
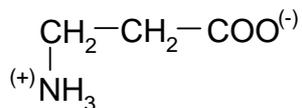
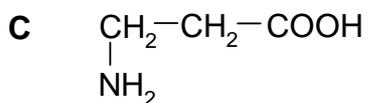
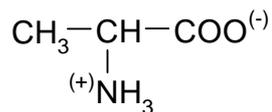
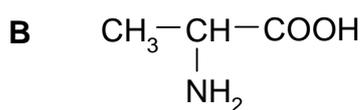
Problems:

- 4.1 Write structural formulas for the compounds **A**, **B**, **C**, and **D**.
- 4.2 Which of the given substances are optically active and which ones are inactive?
- 4.3 Write the formula of the functional group which is typical of certain natural substances and which is contained also in the product formed by the reaction of two molecules of compound **A**. Give the name of the natural substances to which belongs the above mentioned product.
- 4.4 A cyclic organic compound being of technical importance contains also the functional group mentioned in passage 3.
 - a) Write the structural formula of this cyclic compound.
 - b) Write the characteristic part of the structural formula of a macromolecular substance that can be obtained from the mentioned compound.
 - c) Write the characteristic part of the structural formula of an isomeric macromolecular substance that is also technically important.
 - d) Give the name for the group of compounds to which belong the above mentioned macromolecular substances.

SOLUTION

4.1





4.2 **A** - optically inactive

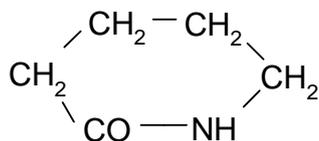
B - optically active

C - optically inactive

D - optically active

4.3 - NH - CO - peptides

4.4 a)



b) - CO - (CH₂)₅ - NH -

c) - NH - (CH₂)₆ - NH - CO - (CH₂)₄ - CO -

d) polyamides

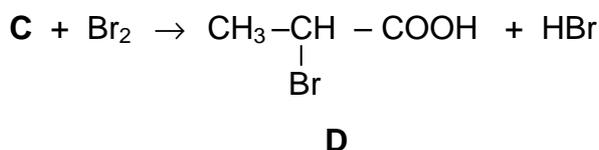
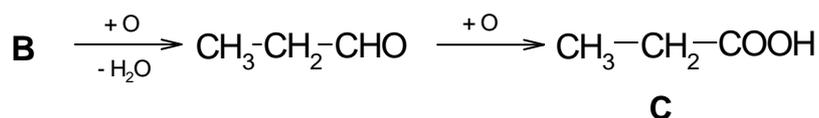
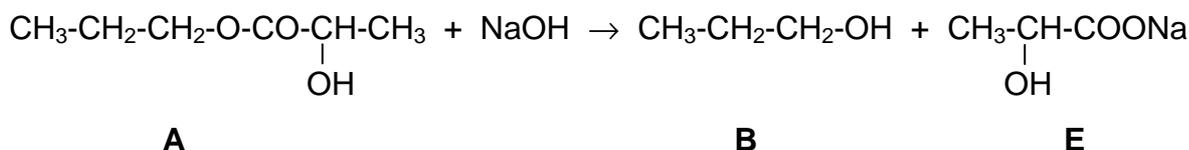
PROBLEM 5

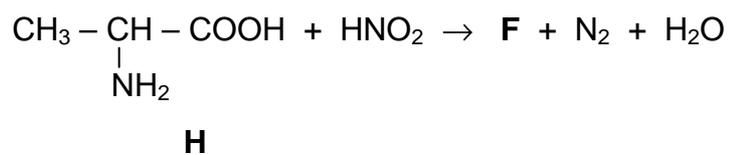
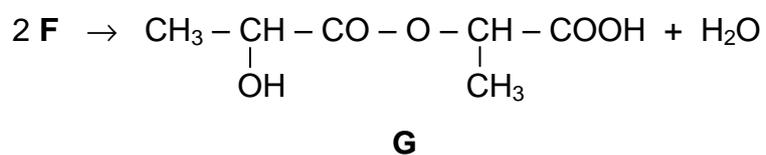
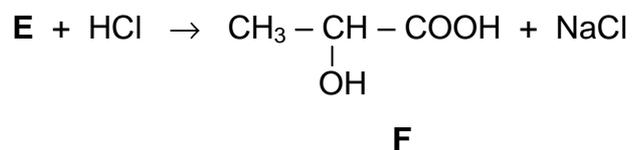
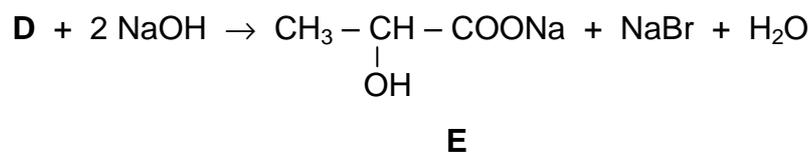
- a) Compounds **B** and **E** are formed when an organic substance **A** (summary formula $C_6H_{12}O_3$) reacts with a sodium hydroxide solution (saponification).
- b) Substance **B** can be oxidised in a two-step process to a substance **C**.
- c) Substance **C** when reacted with bromine yields a substitution product **D** which can be hydrolysed by the reaction with sodium hydroxide solution to produce a substance **E**.
- d) Substance **E** when allowed to react with a stoichiometric amount of hydrochloric acid gives a compound **F** (40.0 % C, 6.66 % H, the rest is oxygen).
- e) Substance **F** is an important product of metabolism in biological processes.
- f) Compound **F** when allowed to stand, splits off one mole of water from two moles of the substance that results in the formation of an unstable compound **G**.
- g) Substance **F** can also be obtained from a compound **H** containing nitrogen, by one-step reaction with nitrous acid. Assuming the quantitative course of the reaction, 4.5 g of substance **F** are formed from 4.45 g of substance **H**.

Problems:

5.1 Write all equations for the above mentioned chemical reactions.

5.2 Give structural formulas of the organic compounds **A – H**.

SOLUTION



PROBLEM 6

Temperature in a larger room should be measured by means of a gaseous thermometer. A glass tube with the internal volume of 80 cm³ was for this purpose filled with nitrogen at a temperature of 20 °C and a pressure of 101.325 kPa. The tube was then slowly and steadily moved throughout the room. Due to the thermal expansion the gas at the higher temperature escapes from the tube and is captured above the liquid whose vapour pressure is negligible. The total volume of the gas escaped from the tube was 35 cm³ at a temperature of 20 °C and a pressure of 101.325 kPa.

Problems:

- 6.1 How many moles of nitrogen were used to fill the glass tube?
- 6.2 How many moles of nitrogen escaped from the tube at the higher temperature?
- 6.3 Calculate the average temperature in the room under investigation if the thermal expansion of the glass tube is assumed to be negligible.
- 6.4 Does anything change if instead of pure nitrogen, a mixture containing 50 volume % of nitrogen and 50 volume % of hydrogen is used?

SOLUTION

6.1 Filling of the tube:

$$n_1(\text{N}_2) = \frac{p V_1}{R T} = \frac{101.325 \text{ kPa} \times 0.080 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}} = 3.33 \times 10^{-3} \text{ mol}$$

6.2 Escaped from the tube:

$$n_2(\text{N}_2) = \frac{p V_2}{R T} = \frac{101.325 \text{ kPa} \times 0.035 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}} = 1.46 \times 10^{-3} \text{ mol}$$

Remained in the tube:

$$n_3(\text{N}_2) = n_1 - n_2 = 1.87 \times 10^{-3} \text{ mol}$$

- 6.3 Temperature at which the amount of substance of nitrogen (n_3) takes a volume of V_1 (the mean temperature in the room under investigation):

$$T = \frac{p V_1}{R n_3} = \frac{101.325 \text{ kPa} \times 0.080 \text{ dm}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1.87 \times 10^{-3} \text{ mol}} = 521 \text{ K}$$

$$\underline{t = 248 \text{ }^\circ\text{C}}$$

6.4 No change can occur in comparison with the preceding experiment.

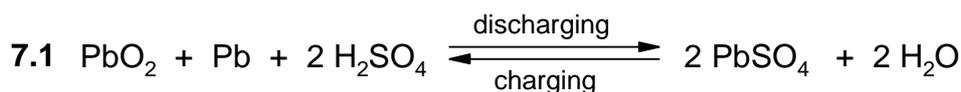
PROBLEM 7

The density of a sulphuric acid solution in a charged lead accumulator should be equal to $\rho = 1.28 \text{ g cm}^{-3}$ which corresponds to the solution containing 36.87 % of H_2SO_4 by mass. In a discharged lead accumulator it should not decrease under the value of $\rho = 1.10 \text{ g cm}^{-3}$ which corresponds to the 14.35 % solution of sulphuric acid.

(Faraday's constant F is equal to 26.8 Ah mol^{-1} .)

Problems:

- 7.1 Write the equation for a total electrochemical reaction that takes place in the lead accumulator when it is charged and discharged.
- 7.2 Calculate the masses of H_2O and H_2SO_4 being consumed or formed according to the equation in No 1.
- 7.3 Calculate the mass of H_2SO_4 that is required to be added to a led accumulator with a capacity of 120 Ah if the content of H_2SO_4 is to be in the range as given in the task.
- 7.4 Calculate the difference in volumes of the sulphuric acid solutions in a charged and a discharged lead accumulator with a capacity of 120 Ah.

SOLUTION

$$7.2 \quad n(\text{H}_2\text{SO}_4) = 2 \text{ mol} \qquad n(\text{H}_2\text{O}) = 2 \text{ mol}$$

$$m(\text{H}_2\text{SO}_4) = 196 \text{ g} \qquad m(\text{H}_2\text{O}) = 36 \text{ g}$$

$$\text{Discharging: } \Delta m(\text{H}_2\text{SO}_4) = -196 \text{ g}$$

$$\Delta m(\text{H}_2\text{O}) = +36 \text{ g}$$

$$\text{Charging: } \Delta m(\text{H}_2\text{SO}_4) = +196 \text{ g}$$

$$\Delta m(\text{H}_2\text{O}) = -36 \text{ g}$$

7.3 The mass of H_2SO_4 required:

$$26.8 \text{ Ah corresponds to } 98 \text{ g } \text{H}_2\text{SO}_4$$

$$120 \text{ Ah corresponds to } 438.8 \text{ g } \text{H}_2\text{SO}_4$$

Analogously:

26.8 Ah corresponds to 18 g H₂O

120 Ah corresponds to 80.6 g H₂O

Discharged lead accumulator:

mass of H ₂ SO ₄ solution	–	m
mass of H ₂ SO ₄	–	m_1
mass fraction of H ₂ SO ₄	–	$w_1 = 0.1435$
density of H ₂ SO ₄ solution	–	$\rho_1 = 1.10 \text{ g cm}^{-3}$

Charged lead accumulator:

mass of H ₂ SO ₄ formed	–	$m_2 = 438.8 \text{ g}$
mass of H ₂ O consumed	–	$m_3 = 80.6 \text{ g}$
mass fraction of H ₂ SO ₄	–	$w_2 = 0.3687$
density of the H ₂ SO ₄ solution	–	$\rho_2 = 1.28 \text{ g cm}^{-3}$

Because:

$$w_1 = \frac{m_1}{m} \quad (\text{a})$$

$$w_2 = \frac{m_1 + m_2}{m + m_2 - m_3} \quad (\text{b})$$

We get a system of equations (a) and (b) which are solved for m_1 and m :

$$m_1 = 195.45 \text{ g}$$

$$m = 1362 \text{ g}$$

7.4 Volume of the electrolyte V_1 in a discharged lead accumulator:

$$V_1 = \frac{m}{\rho_1} = \frac{1362 \text{ g}}{1.10 \text{ g cm}^{-3}} = 1238.2 \text{ cm}^3$$

Volume of the electrolyte V_2 in a charged lead accumulator:

$$V_2 = \frac{m + m_2 - m_3}{\rho_2} = \frac{1720.2 \text{ g}}{1.28 \text{ g cm}^{-3}} = 1343.9 \text{ cm}^3$$

Difference in the volumes:

$$\Delta V = V_2 - V_1 = 1343.9 - 1238.2 = 105.7 \text{ cm}^3$$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A sample contains two of the following cations: Ag^+ , Pb^{2+} , Fe^{2+} , Cr^{3+} , Co^{2+} , Al^{3+} , Mn^{2+} , and one of the following anions: SO_4^{2-} , Cl^- , NO_3^- .

Prove the cations and anions in the sample by means of the following reagents:

2 N-HCl, concentrated H_2SO_4 , 2 N- H_2SO_4 , 2 N- HNO_3 , 2 N- CH_3COOH , NaOH, NH_4OH , H_2O_2 , Na_2CO_3 , $\text{KNO}_3/\text{Na}_2\text{CO}_3$, NH_4SCN , $\text{Na}_2\text{B}_4\text{O}_7$, NaF, $\text{C}_2\text{H}_5\text{OH}$, BaCl_2 , AgNO_3 , NH_4Cl , $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, alizarin B.

Write the results into the attached table in the following way:

- a) into the column "Reagent" write the formula of the reagent which was needed to prove whether the cation or anion is present or absent in the sample;
- b) into the column "+/—" mark the presence or absence of an ion, proved in the sample, by the sign "+" and "–", respectively.

PROBLEM 2 (practical)

A solution contains sodium oxalate and oxalic acid.

Determine how many milligrams of sodium oxalate and oxalic acid are contained in the solution under investigation.

The following solutions are at your disposal: KMnO_4 ($c = 0.01972 \text{ mol dm}^{-3}$), NaOH ($c = 0.1019 \text{ mol dm}^{-3}$), concentrated H_2SO_4 , and a solution of phenolphthalein.

PROBLEM 3 (practical)

Four unknown organic aliphatic compounds of a general formula $A-CH_2-B$ are numbered from 1 to 4, and given as samples. Some of them may be in an aqueous solution.

Perform the following experiments:

1. Determine the pH value of the solution.
2. Allow the sample to react with hydrochloric acid.
3. Reaction with alkali hydroxide (basic hydrolysis – 5 minutes boiling under a reverse cooler) and a subsequent proof of halides.

Moreover, the following data are at your disposal:

- a) One of the compounds under investigation forms an intra-molecular anhydride.
- b) The content of carbon and hydrogen (in mass %) as well as the relative molecular mass are known for the same compound, the data being given, however, in an arbitrary order which does not correspond to the numbering of samples.

Determine the functional groups A and B for each substance using results of your experiments as well as the available data.

Write your results into the attached table; mark positive results with sign "+" whereas the negative ones with sign "-".

9th



8 theoretical problems
3 practical problems

THE NINTH INTERNATIONAL CHEMISTRY OLYMPIAD 4–14 JULY 1977, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

Compare three salts of a composition $M_2S_2O_x$ where x are three different small integers and M is an alkali metal. To each of the three salts apply some of the following assertions:

- The O–O bond is characteristic for the anion.
- The S–S bond is characteristic for the anion.
- The S–O–S bond is characteristic for the anion.
- It is formed by thermal decomposition of hydrogen sulphate.
- It is formed by anodic oxidation of hydrogen sulphate.
- It is formed by the reaction of an aqueous solution of sulphite with sulphur.
- Its aqueous solution dissolves silver bromide.
- Neutralisation of its aqueous solution with hydroxide MOH yields sulphate M_2SO_4 .
- In aqueous solution, it is able to oxidise $Mn(II)$ salt to permanganate.

Problems:

- 1.1 Fill in the correct x values in the formulas given in the Table and indicate in the corresponding square by appropriate letters those assertions that may be applied to each of the given salts:

$M_2S_2O_{\square}$					
$M_2S_2O_{\square}$					
$M_2S_2O_{\square}$					

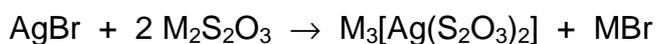
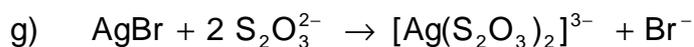
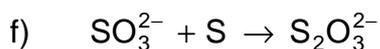
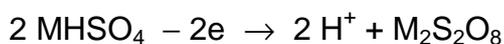
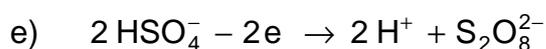
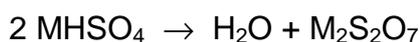
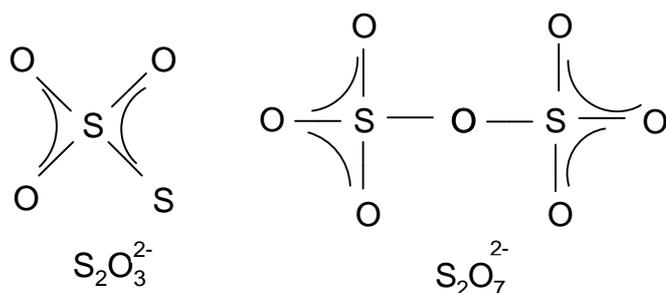
- 1.2 Write structural formulas of the anions of the above three salts and assign σ -bonds and π -bonds in them.
- 1.3 Write the chemical equations expressing the processes involved in the assertions under the letters d, e, f, g, h, i.

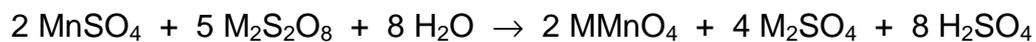
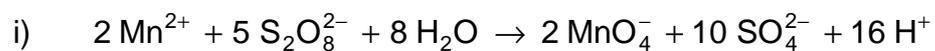
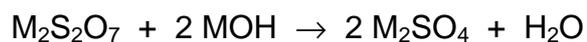
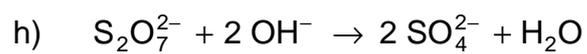
SOLUTION

1.1

$M_2S_2O_3$	b	f	g		
$M_2S_2O_7$	c	d	h		
$M_2S_2O_8$	a	e	i		

1.2





PROBLEM 2a

Note: The International Jury did not choose Task 2a for the competition but the alternative Task 2b.

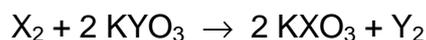
Attention

Make sure to open only the correct envelopes.

You lose points for an incorrectly opened envelope.

Return unopened envelopes together with your solution.

Halogen X reacts with an aqueous solution of another halogen compound KYO₃ according to the equation:



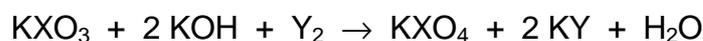
1. The atomic number of halogen X is greater than that of halogen Y. (If you find this answer correct open envelope 1.)
2. The atomic number of halogen X is smaller than that of halogen Y. (If you find this assertion correct open envelope 2.)

Choose the correct answer 1 or 2, open the correct envelope and continue in the solution according to the text in the opened envelope.

Text in envelope 1:

Your answer is correct. Continue.

Compound KXO₃ is oxidised in alkaline solution by halogen Y forming a compound KX^{VII}O₄ whereas halogen Y is reduced to halide KY:



An aqueous solution of potassium halide KY yields with AgNO₃ solution a white precipitate AgY insoluble in water but readily soluble in aqueous ammonia solution.

3. Halogen Y is fluorine (envelope 3).
4. Halogen Y is chlorine (envelope 4).
5. Halogen Y is bromine (envelope 5).

Choose the correct answer 3, 4 or 5, open the corresponding envelope and carry on according to the instructions inside.

Text in envelope 2:

Your answer is incorrect. Choose envelope 1.

Text in envelope 3:

Your answer is incorrect. Choose answers 4 or 5.

Text in envelope 4:

Your answer is correct. Choose the final correct answer by indicating the correct alternative 6 or 7:



Text in envelope 5:

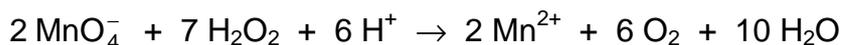
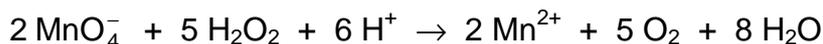
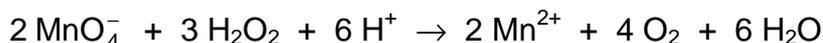
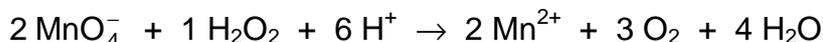
Your answer is incorrect. Choose answers 3 or 4.

SOLUTION

The correct answers are as follows: 1, 4, 7.

PROBLEM 2b

The reaction of permanganate ions with hydrogen peroxide in an acidic solution gives Mn(II) salt and at the same time oxygen is released:



Problems:

1. The possible ratios of the reactants in the above equations express:

- a) all equations
- b) only some of the equations
- c) only one equation
- d) none

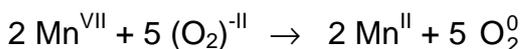
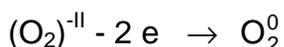
Indicate the correct assertion by a cross in the corresponding square and explain your decision.

2. Which of the reactants is an oxidising agent and which is a reducing one?
3. How much potassium permanganate is needed to release 112 cm³ of oxygen at STP conditions from an excess of hydrogen peroxide in acidic solution?

SOLUTION

1. Correct is **c**.

Explanation on the basis of electron balance:



2. Oxidising agent: MnO_4^- or Mn^{VII}

Reducing agent: H_2O_2 or $(\text{O}_2)^{-\text{II}}$

3. $V(\text{O}_2) = 112 \text{ cm}^3$

$$n(\text{O}_2) = \frac{0.112 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.005 \text{ mol}$$

$$n(\text{KMnO}_4) = 0.005 \text{ mol} \times \frac{2}{5} = 0.002 \text{ mol}$$

$$m(\text{KMnO}_4) = 0.316 \text{ g}$$

PROBLEM 3

The letters **A**, **B**, **C**, **D**, and **E** represent isomeric cyclobutane dicarboxylic acid, one of them being a racemic form.

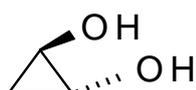
It was shown that:

- only compound **C** forms a cyclic anhydride easily,
- B** yields an cyclic anhydride only at higher temperatures,
- of all the acids under investigation, only **A** releases carbon dioxide when heated,
- D** and **E** do not change at higher temperatures,
- 2 moles of diethyl ester of malonic acid when reacted with sodium ethoxide (EtONa), are transformed to sodium salt which by reaction with methylene iodide (CH₂I₂) yields a tetraester C₁₅H₂₄O₈. This new ester gives a tetraester C₁₆H₂₄O₈ in the reaction with 2 moles of sodium ethoxide and 1 mole of methylene iodide. The last mentioned tetraester is transformed by alkaline hydrolysis and subsequent acidification to a tetracarboxylic acid which when heated, gives a mixture of **B** and **E**.

Problems:

- 3.1** Give formulas corresponding to the letters **A**, **B**, **C**, **D**, and **E**. Mark the group which is above the plane of the cycle \blacktriangle , that under the plane with \cdots

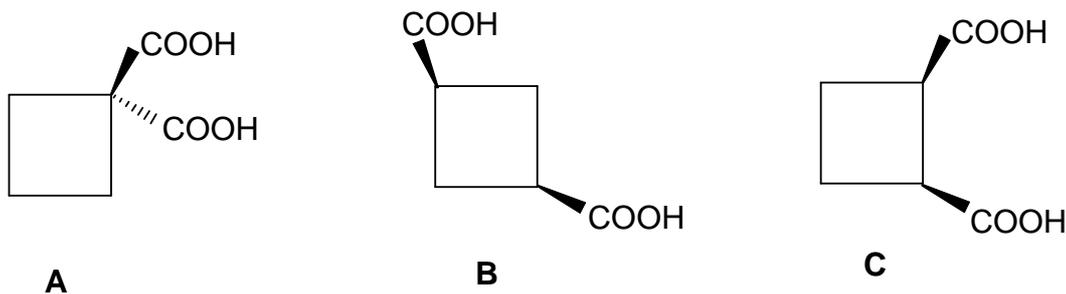
For example:

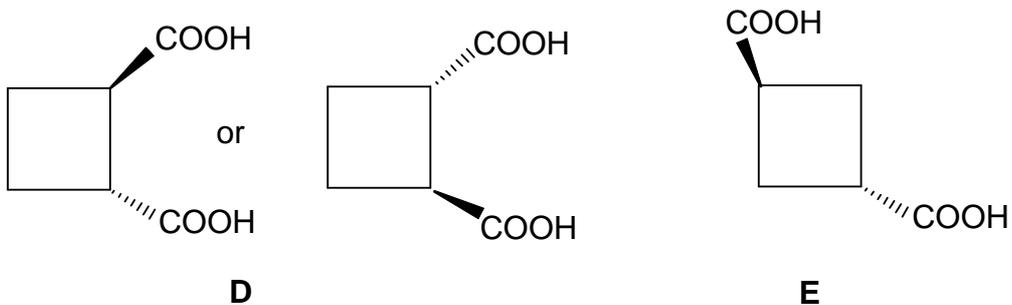


- 3.2** Express processes a), b), and c) by chemical equations.

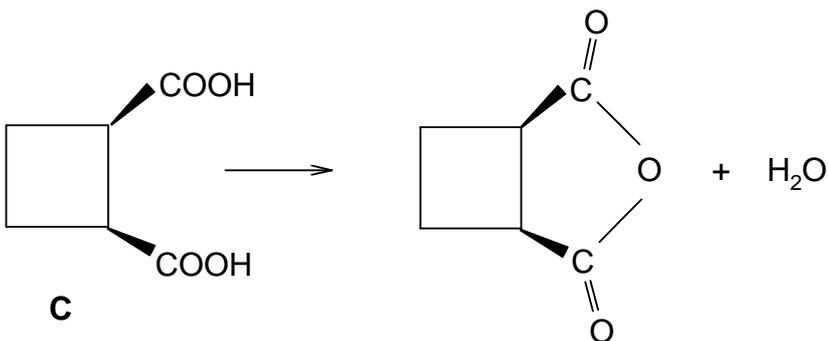
SOLUTION

3.1

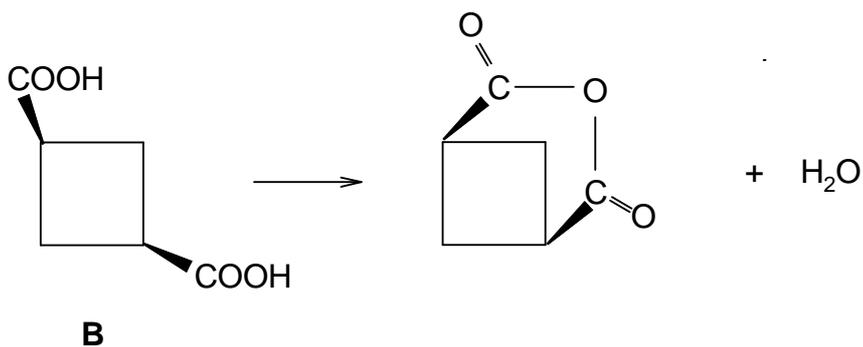




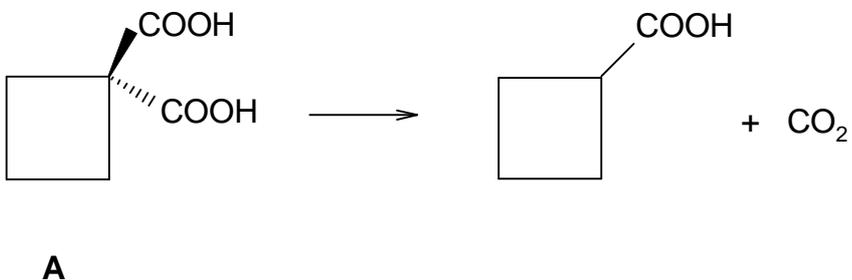
3.2 a)



b)



c)



PROBLEM 4a

Note: The International Jury did not choose Task 4a for the competition but the alternative PROBLEM 4b.

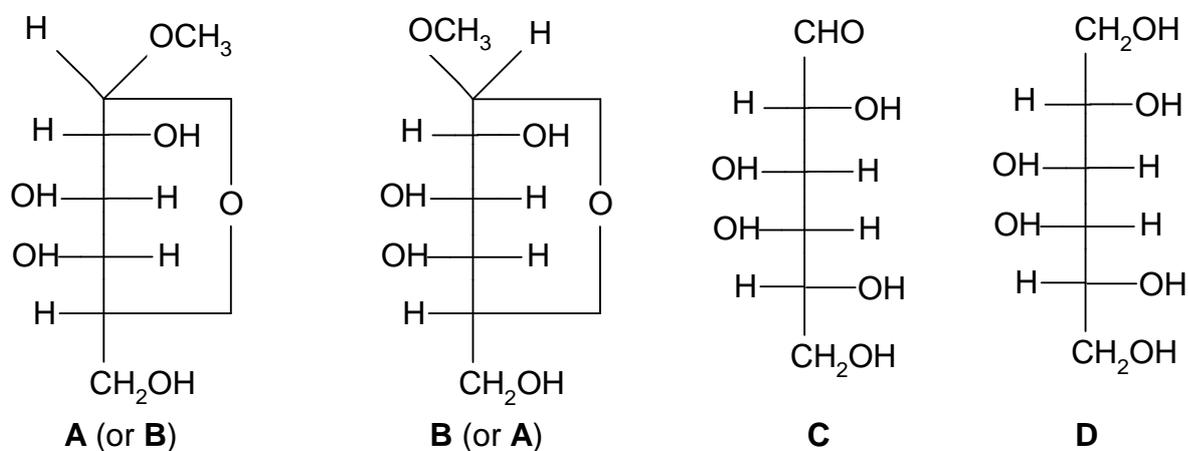
Compounds **A** and **B**, having the same summary formula $C_7H_{14}O_6$ but different physical properties (for example melting point and specific optical rotation), belong to the group of saccharides containing six-member heterocycles. When 1 % solution of sulphuric acid is added to compound **A** and **B** respectively, the same compound **C** containing 40.0 % C and 6.71 % H is obtained at boiling. After reducing compound **C** (for example catalytically with hydrogen or with hydride $Na[BH_4]$) a crystalline product **D** was isolated which did not reduce Fehling's reagent and showed no optical activity. Compound **C** was oxidised with a mild oxidising agent (e. g. with a cold sodium hypobromite solution) yielding a salt of polyhydroxy monocarboxylic acid of D-configuration.

Problems:

- Suggest the structure of the compounds **A**, **B**, **C**, and **D**.
- If you do not find the task to be unambiguous, explain why.

SOLUTION

1.



- There is another similar solution in the D-allose series.

PROBLEM 4b

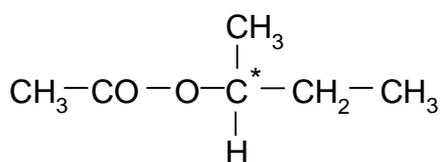
An optically active ester (11.6 g) having the summary formula $C_6H_{12}O_2$, was hydrolysed by heating with an excess of aqueous sodium hydroxide solution. After terminating the hydrolysis the alkaline reaction mixture was several times extracted with ether. The aqueous solution was not optically active. The united ether extracts were dried with anhydrous magnesium sulphate. The ether solution was filtrated, ether was distilled off from it and the residue was redistilled. 7.4 g (100 %) of a liquid boiling at 100 °C was obtained.

Problems:

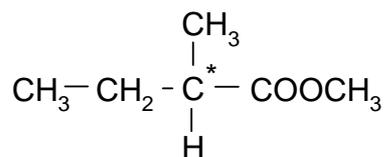
1. Write the structural formula of the ester.
2. What would be the structure of an ester with identical summary formula, i. e. $C_6H_{12}O_2$, if the aqueous solution after the alkaline hydrolysis obtained in the above mentioned way, were optically active?
3. Write down equations for the alkaline hydrolysis of both esters with sodium hydroxide solution.

SOLUTION

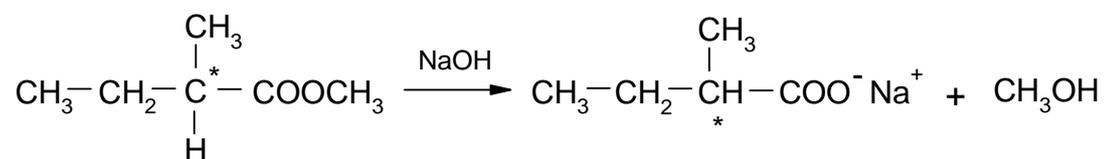
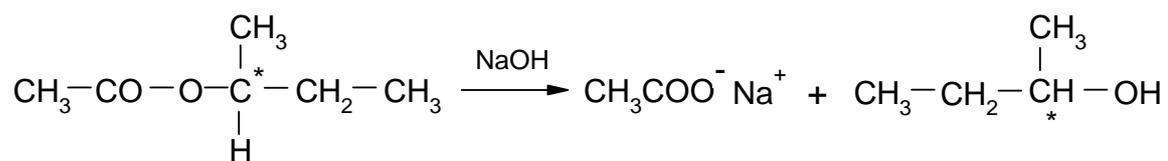
1.



2.



3.



PROBLEM 5

Two copper(I) salts of the organic acids HA and HB, slightly soluble in water, form a saturated solution in buffer of a given pH.

Problems:

- 5.1 What will be the concentration of Cu^+ cations in the solution if the solubility products of the two salts are $K_s(\text{CuA})$ and $K_s(\text{CuB})$ and the ionisation constants of the acids are $K_a(\text{HA})$ and $K_a(\text{HB})$?

SOLUTION

- 5.1 Equations for the total amounts of substances of the particles A, B, and Cu are as follows:

$$a = n(\text{A}^-) + n(\text{HA}) + n(\text{CuA})$$

$$b = n(\text{B}^-) + n(\text{HB}) + n(\text{CuB})$$

$$m = n(\text{Cu}^+) + n(\text{CuA}) + n(\text{CuB})$$

The amounts of precipitates are eliminated from the equations:

$$a + b - m = n(\text{A}^-) + n(\text{HA}) + n(\text{B}^-) + n(\text{HB}) - n(\text{Cu}^+) = 0$$

because, when forming a system of both solid salts, the total number of particles A and B ($a + b$) must be equal to the total number of cations Cu^+ , i. e. to the value of m .

When the amounts of substances are divided by the volume of the solution, we get concentrations, and thus:

$$[\text{A}^-] + [\text{HA}] + [\text{B}^-] + [\text{HB}] = [\text{Cu}^+] \quad (1)$$

$$K_s(\text{CuA}) = [\text{Cu}^+][\text{A}^-] \Rightarrow [\text{A}^-] = \frac{K_s(\text{CuA})}{[\text{Cu}^+]} \quad (2)$$

$$K_s(\text{CuB}) = [\text{Cu}^+][\text{B}^-] \Rightarrow [\text{B}^-] = \frac{K_s(\text{CuB})}{[\text{Cu}^+]} \quad (3)$$

$$K_a(\text{HA}) = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{HA}] = \frac{[\text{H}^+][\text{A}^-]}{K_a(\text{HA})} \quad (4)$$

$$K_a(\text{HB}) = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \Rightarrow [\text{HB}] = \frac{[\text{H}^+][\text{B}^-]}{K_a(\text{HB})} \quad (5)$$

By substituting (4) and (5) into (1):

$$[\text{Cu}^+] = [\text{A}^-] \left(1 + \frac{[\text{H}^+]}{K_a(\text{HA})} \right) + [\text{B}^-] \left(1 + \frac{[\text{H}^+]}{K_a(\text{HB})} \right) \quad (6)$$

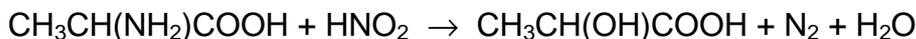
By substituting (2) and (3) into (6):

$$[\text{Cu}^+] = \frac{K_s(\text{CuA})}{[\text{Cu}^+]} \left(1 + \frac{[\text{H}^+]}{K_a(\text{HA})} \right) + \frac{K_s(\text{CuB})}{[\text{Cu}^+]} \left(1 + \frac{[\text{H}^+]}{K_a(\text{HB})} \right) \quad (7)$$

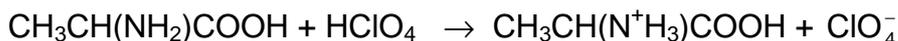
$$[\text{Cu}^+] = \sqrt{K_s(\text{CuA}) \left(1 + \frac{[\text{H}^+]}{K_a(\text{HA})} \right) + K_s(\text{CuB}) \left(1 + \frac{[\text{H}^+]}{K_a(\text{HB})} \right)}$$

PROBLEM 6

Amino acids can be determined by measuring the volume of nitrogen released in their reaction with nitrous acid (Van Slyke's method), for example:



Another method consists of the reaction of amino acids with a volumetric solution of perchloric acid, for example:



The excess of the perchloric acid is determined then by titration with a volumetric solution of sodium acetate (carried out in a non-aqueous solution).

50.0 cm³ of a 0.100-normal solution of perchloric acid were added to a sample of glycine in glacial acetic acid. The excess of the perchloric acid was determined after the reaction by titration with 0.150-normal volumetric solution of sodium acetate. The consumption was 16.0 cm³.

Problem:

- 6.1** What would be the volume of the nitrogen released at a pressure of 102 658 Pa and a temperature of 20 °C when assumed that the same quantity of sample were analysed by the Van Slyke's method?

SOLUTION

$$\mathbf{6.1} \quad n(\text{HClO}_4) = Vc = 0.0500 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = 0.00500 \text{ mol}$$

$$n(\text{NaAc}) = 0.0160 \text{ dm}^3 \times 0.150 \text{ mol dm}^{-3} = 0.00240 \text{ mol}$$

Consumed in the reaction:

$$n(\text{HClO}_4) = (0.00500 - 0.00240) \text{ mol} = 0.00260 \text{ mol}$$

$$V(\text{HClO}_4) = 0.0260 \text{ dm}^3$$

Since:

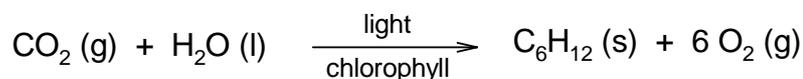
$$n(\text{HClO}_4) = n(\text{glycine}) = n(\text{N}_2) = 0.0260 \text{ mol}$$

then:

$$V(\text{N}_2) = \frac{nRT}{p} = \frac{0.0260 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.1 \text{ K}}{102.658 \text{ kPa}} = 0.617 \text{ dm}^3$$

PROBLEM 7

Photosynthesis can be summarised by the overall equation:



for which values of ΔH and ΔS at 25 °C are as follows:

$$\Delta H = 2.816 \times 10^6 \text{ J}, \quad \Delta S = -182 \text{ J K}^{-1} \text{ or}$$

$\Delta H = 2.816 \times 10^6 \text{ J mol}^{-1}$, $\Delta S = -182 \text{ J K}^{-1} \text{ mol}^{-1}$ if ΔH and ΔS values are related to one mole of reaction changes.

Imagine that there have been devised electrodes that would allow selective reduction of oxygen to water and oxidation of glucose to carbon dioxide in a galvanic cell, i. e. a reverse process when compared with that of the photosynthetic reaction.

Problems:

7.1 What will be the electromotive force of the cell in which light energy would be transformed to electric energy by means of the photosynthetic reaction?

Note: In the envelope you can find the relation between the electromotive force and the change of free enthalpy of the reaction. (Attention: If you open the envelope you lose some points.)

7.2 In case we would want to quantify the symbol "light" in the equation of photosynthesis, we would ask: how many moles of photons with wavelength for example 500 nm take part in the above reaction? Calculate.

7.3 Calculate, what would be the electric power of a square swimming pool with a side of 10 m containing green algae capable of the photosynthetic reaction if under average illumination a current of 1 mA can be expected from the area of 1 cm².

SOLUTION

7.1 Two alternative solutions:

a) By means of quantities related to one mole of reaction changes.

For the reaction taking place in the cell it would correspond:

$$\Delta G = -2.87 \times 10^6 \text{ J mol}^{-1}$$

b) By means of quantities related to the given reaction.

For the reaction taking place in the cell it would correspond:

$$\Delta G = -2.87 \times 10^6 \text{ J}$$

Relation between the electromotive force and the change of free enthalpy of the reaction taking place in a cell:

$$-\Delta G = n F E$$

where n is so-called charge number

where n is the number of moles of charges which passed through the electrode during the reaction.

In our case, n has the value equal to 24 since one molecule of oxygen is reduced according to the equation:



$$F (\text{Faraday's constant}) = 96\,487 \text{ C mol}^{-1}$$

Since one voltcoulomb is one joule, then:

$$E = \frac{-(-2.87 \times 10^6) \text{ V C mol}^{-1}}{24 \times 96\,487 \text{ C mol}^{-1}} = 1.24 \text{ V}$$

$$E = \frac{-(-2.87 \times 10^6) \text{ V C}}{24 \text{ mol} \times 96\,487 \text{ C mol}^{-1}} = 1.24 \text{ V}$$

7.2 Energy of absorbed photons is the only source of energy which enables the course of photosynthesis, and therefore, the number of absorbed photons x multiplied by their energy must be equal to the increase of energy in the system, i. e. to the value of $2.87 \times 10^6 \text{ J}$. Thus:

$$x h \nu N_A = x h \frac{c}{\lambda} N_A = 2.87 \times 10^6 \text{ J}$$

$$x = \frac{2.87 \times 10^6 \text{ J} \times \lambda}{h c N_A} =$$

$$= \frac{2.87 \times 10^6 \text{ J} \times 500.10^{-9} \text{ m}}{6.6256 \cdot 10^{-34} \text{ Js} \times 2.9979 \cdot 10^8 \text{ ms}^{-1} \times 6.022 \cdot 10^{23} \text{ mol}^{-1}} =$$

$$= 11.99 \approx 12 \text{ mol of photons}$$

7.3 The area of the swimming pool is 100 m^2 . Current density at a voltage of 1.24 V is equal to $1 \cdot 10^4 \text{ mA m}^{-2} = 10 \text{ A m}^{-2}$.

The total electric power :

$$1.24 \text{ V} \times 10 \text{ A m}^{-2} \times 100 \text{ m}^2 = 1.24 \text{ kW}$$

PROBLEM 8a

Note: The International Jury did not choose Task 8a for the 9th IChO but the alternative Task 8b.

Due to the lack of other methods in the middle of the 19th century a chemist determining the molar mass of a new element **X** chose the following procedure:

He succeeded in preparing four compounds **A**, **B**, **C**, and **D** containing the element **X** and determined its content (in mass %) in each of the compounds. At 250 °C all four compounds were in gaseous state. They were individually transferred into previously evacuated flasks until the pressure reached the value of $1.013 \cdot 10^5$ Pa and then the flasks were weighed. After subtracting the weight of the empty flask, the mass of the gas inside was determined. This procedure was repeated with nitrogen. Thus the following Table of data was obtained:

Gas	Total mass of gas	Content of element X in gas (mass %)
N ₂	0.652 g	0
A	0.849 g	97.3
B	2.398 g	68.9
C	4.851 g	85.1
D	3.583 g	92.2

Problem:

8.1 Determine the probable molar mass of element **X**.

SOLUTION

$$8.1 \quad n(\text{N}_2) = \frac{m(\text{N}_2)}{M(\text{N}_2)} = \frac{0.652 \text{ g}}{28 \text{ g mol}^{-1}} = 0.0233 \text{ mol}$$

At a temperature of 250 °C all the substances **A**, **B**, **C**, and **D** are considered to behave as ideal gases and according to Avogadro's law:

$$n(\text{N}_2) = n(\mathbf{A}) = n(\mathbf{B}) = n(\mathbf{C}) = n(\mathbf{D})$$

$$M(\mathbf{A}) = \frac{m(\mathbf{A})}{n(\mathbf{A})}$$

$$M(\mathbf{B}) = \frac{m(\mathbf{B})}{n(\mathbf{B})}$$

$$M(\mathbf{C}) = \frac{m(\mathbf{C})}{n(\mathbf{C})}$$

$$M(\mathbf{D}) = \frac{m(\mathbf{D})}{n(\mathbf{D})}$$

The mass of element **X** in one mole of **A**, **B**, **C** or **D**:

A: $M(\mathbf{A}) \times 0.973 = 35.45 \text{ g mol}^{-1}$

B: $M(\mathbf{B}) \times 0.689 = 70.91 \text{ g mol}^{-1}$

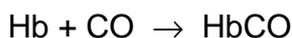
C: $M(\mathbf{C}) \times 0.851 = 177.17 \text{ g mol}^{-1}$

D: $M(\mathbf{D}) \times 0.922 = 141.78 \text{ g mol}^{-1}$

Because in one molecule of a compound there must be at least one atom **X** or its integer multiple, we must calculate the highest common measure of the molar masses obtained. It is in our case equal to 35.45 g mol^{-1} in average which can be considered as the probable molar mass of element **X**. It is only the most probable value because its integer fraction cannot be excluded.

PROBLEM 8b

Among other factors, deterioration of the environment is manifested also by air pollution with carbon monoxide. Its most powerful source are combustion engines. The toxicity of carbon monoxide is caused by the fact that it forms with the blood dye - haemoglobin (Hb), the compound carbonyl haemoglobin (HbCO):



The chemical bond in carbonyl haemoglobin is about 200 times stronger than that in oxyhaemoglobin (HbO₂) originating under common conditions. Consequently, haemoglobin cannot be used in oxygen transfer. The lack of oxygen starts to be felt from 50 ppm carbon monoxide in the air, i. e. 10 % carbonyl haemoglobin in blood.

Air oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at $1.6 \times 10^{-6} \text{ mol dm}^{-3}$ by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to $8 \times 10^{-6} \text{ mol dm}^{-3}$

Problems:

- 8.1** Calculate the rate of oxyhaemoglobin formation if the rate constant is $k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (at 37 °C – normal body temperature).
- 8.2** In some cases (carbon monoxide poisoning) an increase of the rate of oxyhaemoglobin formation up to $1.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ is needed.
- Calculate the required concentration of oxygen assuming that the concentration of haemoglobin in blood is constant.
 - Suggest of practical solution on the assumption that the concentration of oxygen in blood is proportional to the pressure of oxygen entering the lungs.

SOLUTION

$$8.1 \quad v = k[\text{Hb}][\text{O}_2]$$

$$k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[\text{Hb}] = 8 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[\text{O}_2] = 1.6 \times 10^{-6} \text{ mol dm}^{-3}$$

$$v = \underline{2.688 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$$

Because 1 mole of oxygen (O₂) is needed to form 1 mole of oxyhaemoglobin, the rate of oxygen consumption is the same as the of oxyhaemoglobin formation.

$$8.2 \quad [\text{O}_2] = \frac{v}{k [\text{Hb}]}$$

$$v = 1.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[\text{Hb}] = 8 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\underline{[\text{O}_2] = 6.5 \times 10^{-6} \text{ mol dm}^{-3}}$$

The oxygen concentration must increase up to $6.5 \times 10^{-6} \text{ mol dm}^{-3}$. Oxygen concentration can be affected by elevation of air pressure only partially. The fourfold increase of oxygen concentration would demand an increase of the air pressure four times in comparison with the normal value. This pressure would be harmful for living organisms and therefore, air enriched with oxygen is breathed.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

You will follow the concentration change of one of the reactants by the method of comparative visual colorimetry. From data obtained experimentally plot graphically the change of the reactant concentration in dependence on time.

Procedure:

1. *Making of the comparative colorimetric scale of bromine solution*

Measure with a syringe into 10 identical test-tubes the following quantities of bromine water (0.01-molar): into the first one – 10.0 cm³; 2nd – 9.0 cm³; 3rd – 8.0 cm³, 9th – 2.0 cm³; into the tenth one – 1.0 cm³. Then add to all the test-tubes (except the first one) distilled water to reach a total volume of 10.0 cm³ in each. Seal the test-tubes with stoppers and mix the solutions. Put the test-tubes in a stand with a white background. Finally calculate the concentration (in mol dm⁻³) of bromine in the solutions in all test-tubes.

2. *Reaction of bromine solution with formic acid*

Carry out the reaction by mixing 100.0 cm³ of bromine solution with 1.0 cm³ of 1.00-molar solution of formic acid. Immediately after mixing transfer 10.0 cm³ of the resulting solution to the test-tube identical with that used for colorimetric scale. By comparing the colour shade of the reaction mixture (in one-minute intervals) with that of the solutions in the scale, investigate changes of bromine concentration in dependence on time.

Put the data in a table containing time (t) and concentration of Br₂.

Task:

Plot the bromine concentration in dependence on time and read the half-time of the reaction from the diagram.

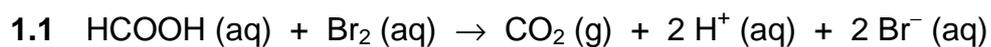
Questions:

- 1.1 Write the equation for the reaction of bromine with formic acid assuming that the reactants are in stoichiometric amounts.

1.2 In analytical chemistry a volumetric solution of bromine can be prepared by dissolving a mixture of bromate and bromide in acid medium. Explain this mode of preparation by means of a chemical equation in ionic form.

SOLUTION

Questions:



PROBLEM 2 (practical)

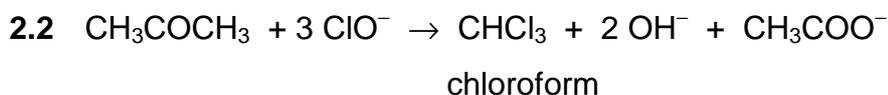
By thermometric titration of a hypochlorite solution with a solution of propanone you will find the equivalent amounts of the reactants and consequently, the reaction products.

Procedure:

For the reaction of a hypochlorite solution with a propanone use solutions tempered at laboratory temperature (check). Put 100,0 cm³ of a hypochlorite solution into a thermobeker, insert a thermometer and keep adding a 4-molar solution of propanone in 1,0 cm³ portions from burette, stirring the reaction mixture continuously by means of the thermometer (carefully, do not break!). Stir the reaction mixture thoroughly after each addition and read the highest temperature reached. Keep on adding the propanone solution as long as the temperature rises. Then add three more portions and finish the experiment. Keep the reaction mixture for possible later use.

Problems:

- 2.1 Draw a titration curve from the data of the temperature changes and consumption of propanone solution. Read the end point of the titration from the curve. Express the equivalent amounts of the reactants in moles.
- 2.2 Write equation for the chemical reaction and name the product that is formed.
- 2.3 Suggest a calculation for the approximate value of the reaction heat from the data obtained.
- 2.4 Consider the procedure of isolation of the product from the reaction mixture and give the method of its identification.
- 2.5 The exact concentration of a hypochlorite solution can also be determined by measuring the volume of oxygen released after catalytic decomposition of hypochlorite. Illustrate the principle of this method by means of a chemical equation and show schematically the procedure for the calculation.

SOLUTION

2.3 Calculation of heat evolved in the course of the reaction:

$$Q = m c \Delta t$$

Q – reaction heat,

m – mass of the solution,

c – specific heat capacity of the solutions taking part in the reaction,

Δt – temperature difference (elevation of temperature)

On the basis of the data obtained in the task, it is possible to calculate Q value per one mole of reactant.

2.4 The mixture contains:

reactants – (excess of about 3 cm³ of the 4-molar propanone solution),

products – CHCl₃, OH⁻, CH₃COO⁻.

Acetone and chloroform are separated from other substances in the aqueous solution by means of a separatory funnel and a subsequent distillation.

Identification of chloroform: smell, density.

2.5 $2 \text{ ClO}^- \rightarrow \text{O}_2$

$$2 \text{ mol} \rightarrow 1 \text{ mol} = 22.4 \text{ dm}^3$$

PROBLEM 3 (practical)

If a known excess of hydroxide solution with a known concentration is added to a weighed sample of ammonium salt and the liberated ammonia is removed by boiling, it is possible to determine the unreacted quantity of hydroxide by titration with a volumetric solution of an acid.

Procedure:

Three samples of an ammonium salt, weighed with accuracy of 0.001 g, are at your disposal. Introduce each of them into a 250 cm³ Erlenmeyer flask. Add 50.0 cm³ of a 0.2-normal sodium hydroxide solution to each sample. Put several boiling stones into each mixture and heat the flasks slowly on a small flame till there is no more ammonia in the liberating vapours. After expelling ammonia, cool the solution to the laboratory temperature, add 2 or 3 drops of indicator solution (Bromothymol blue) and titrate with a 0,2-normal volumetric solution of oxalic acid to the first lasting yellow colour of the solution.

Problems:

- 3.1 Calculate the molar mass of ammonium salt from the experimental data.
 - 3.2 The sample is a salt of a monobasic inorganic acid. Consider which one.
 - 3.3 Calculate the absolute and relative error of your determination.
 - 3.4 Give reactions by means of which ions of the salt can be proved in the solution.
-
-

10th



**5 theoretical problems
2 practical problems**

THE TENTH INTERNATIONAL CHEMISTRY OLYMPIAD 3–13 JULY 1978, TORUN, POLAND

THEORETICAL PROBLEMS

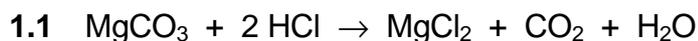
PROBLEM 1

- a) A chromium ore which does not contain water, consists of: $\text{Fe}(\text{CrO}_2)_2$, $\text{Mg}(\text{CrO}_2)_2$, MgCO_3 , and CaSiO_3 .
- b) It was found by analysis the ore contains 45.6 % of Cr_2O_3 , 7.98 % of Fe_2O_3 , and 16.12 % of MgO .
- c) When the ore was treated with a concentrated hydrochloric acid, chromium compounds being present in the ore did not react with the acid.
- d) When the reaction was finished, the ore was thoroughly washed with water (till the reaction with Cl^- was negative) and the solid residue was dried to a constant mass.

Problems:

- 1.1 Write stoichiometric and ionic equations for the reactions taking place when the ore is treated with the hydrochloric acid as given in c).
- 1.2 Calculate:
- the content of the compounds (in mass %) present in the ore,
 - amounts of substances of the compounds present in the ore.
- 1.3 Calculate the content of Cr_2O_3 (in mass %) in the dried residue obtained according to d).
- 1.4 A glass tube was filled with a sufficient amount of granulated CaO , the total mass of the filled tube having been 412.02 g. A gas formed by the reaction as given in c), was dried and then transmitted through the glass tube. Calculate the mass of the glass tube with its filling after the reaction was finished.

Relative atomic masses: $A_r(\text{Cr}) = 52.01$; $A_r(\text{Fe}) = 55.85$; $A_r(\text{Mg}) = 24.32$; $A_r(\text{Ca}) = 40.08$;
 $A_r(\text{Si}) = 28.09$; $A_r(\text{C}) = 12.01$; $A_r(\text{O}) = 16.00$.

SOLUTION

1.2 The total amount of iron is in the form of $\text{Fe}(\text{CrO}_2)_2$:

Since:



$$M_r(\text{Fe}_2\text{O}_3) = 159.70$$

$$M_r(\text{Fe}(\text{CrO}_2)_2) = 223.87 \quad \% \text{Fe}_2\text{O}_3 = 7.98$$

$$\% \text{Fe}(\text{CrO}_2)_2 = \frac{2 \times 223.87}{159.70} \times 7.98 = \mathbf{22.37}$$

The difference between the total amount of Cr_2O_3 and that being contained in $\text{Fe}(\text{CrO}_2)_2$ corresponds to the amount of Cr_2O_3 , having been in the form of $\text{Mg}(\text{CrO}_2)_2$.

% Cr_2O_3 in $\text{Fe}(\text{CrO}_2)_2$:

$$M_r: \quad \begin{array}{ccc} \text{Fe}(\text{CrO}_2)_2 & \hat{=} & \text{Cr}_2\text{O}_3 \\ 223.87 & & 152.02 \end{array}$$

$$\% \text{Cr}_2\text{O}_3 = \frac{152.02}{223.87} \times 22.37 = \mathbf{15.19}$$

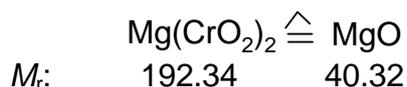
$$\% \text{Cr}_2\text{O}_3 \text{ in } \text{Mg}(\text{CrO}_2)_2 : 45.5 - 15.19 = 30.41$$

Content of $\text{Mg}(\text{CrO}_2)_2$:

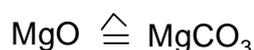
$$M_r: \quad \begin{array}{ccc} \text{Cr}_2\text{O}_3 & \hat{=} & \text{Mg}(\text{CrO}_2)_2 \\ 152.02 & & 192.34 \end{array}$$

$$\% \text{Mg}(\text{CrO}_2)_2 = \frac{192.34}{152.02} \times 30.41 = \mathbf{38.47}$$

The difference between the total amount of MgO in the ore and that corresponding to $\text{Mg}(\text{CrO}_2)_2$, is contained in MgCO_3 . % MgO and % MgCO_3 can be calculated analogously as it is given above.



$$\% \text{MgO} = \frac{40.32}{192.34} \times 38.47 = \mathbf{8.06}$$



$$\% \text{MgCO}_3 = \frac{84.32}{40.32} \times 8.06 = \mathbf{16.86}$$

Content of CaSiO_3 is obtained as complementary value to 100 %.

$$\% \text{CaSiO}_3 = 100 - (22.37 + 38.47 + 16.86) = \mathbf{22.30}$$

One kilogram of the ore contains:

$$223.7 \text{ g of } \text{Fe}(\text{CrO}_2)_2 \hat{=} 1 \text{ mol}$$

$$384.7 \text{ g of } \text{Mg}(\text{CrO}_2)_2 \hat{=} 2 \text{ mol}$$

$$168.6 \text{ g of } \text{MgCO}_3 \hat{=} 2 \text{ mol}$$

$$223.0 \text{ g of } \text{CaSiO}_3 \hat{=} 2 \text{ mol}$$

- 1.3** In order to simplify the problem we can assume that the hydrochloric acid reacts with 1 kg of the ore, i. e. with 168.6 g of MgCO_3 and with that CaO which is contained in 223.0 g CaSiO_3 , i. e. with 107.65 of CaO .

Thus, 276.25 g of the ore (168.6 g + 107.65 g) reacted while 723.75 g remain unreacted.

One kilogram of the ore contains 456 g of Cr_2O_3 (45.6 %) and the same amount remains in the unreacted part that represents:

$$\% \text{Cr}_2\text{O}_3 = \frac{456}{723.75} \times 100 = \mathbf{63.0}$$

- 1.4** The mass of the filling in the tube is increased by the mass of CO_2 formed by decomposition of MgCO_3 with hydrochloric acid. From 168.6 g of MgCO_3 87.98 g of CO_2 are formed and thus, the mass of the tube after reaction is 500 g.

PROBLEM 2

A sample of water under investigation had 10° of temporary hardness and 10° of permanent hardness. Hardness of the water was caused by cations Fe²⁺ and Ca²⁺ only.

A volume of 10.00 dm³ of the water was at disposal. From this volume 100.00 cm³ were taken for further procedure. The water was oxidised with a H₂O₂ solution and then precipitated with an aqueous ammonia solution. A brown precipitate was dried and after an appropriate heating 0.01432 g of an anhydrous product was obtained.

Problems:

- 2.1** Calculate the molar ratio of Fe²⁺ : Ca²⁺ in the water under investigation.
- 2.2** In another experiment, 10.00 dm³ of the water was used again. The temporary hardness caused by cations Ca²⁺ was removed first and the permanent hardness caused by cations Fe²⁺ was removed by addition of Na₃PO₄. Calculate the mass of the precipitate (in its anhydrous form) on the assumption that only one half of cations Fe²⁺ was oxidised to Fe³⁺ in 10.00 dm³ of the water analysed. Calculation should be made with an accuracy of one hundredth. Give the molar ratio in integers.

1° of hardness = 10 mg CaO in 1 dm³ of water.

Relative atomic masses:

$A_r(\text{Ca}) = 40.08$; $A_r(\text{Fe}) = 55.85$; $A_r(\text{C}) = 12.01$;

$A_r(\text{H}) = 1.01$; $A_r(\text{P}) = 31.00$; $A_r(\text{O}) = 16.00$.

SOLUTION

2.1 Anhydrous product: Fe₂O₃

$m(\text{Fe}_2\text{O}_3) = 0.01432 \text{ g}$ from 100 cm³ of water, i. e. 1.432 g from 10 dm³

1 mol Fe₂O₃ ⇔ 2 mol FeO

$$n(\text{Fe}_2\text{O}_3) = \frac{1.432 \text{ g}}{159.7 \text{ g mol}^{-1}} \approx 0.009 \text{ mol}$$

$$m(\text{FeO}) = n M = 2 \times 0.009 \text{ mol} \times 71.85 \text{ g mol}^{-1} \approx 1.293 \text{ g}$$

1° of hardness = 10 mg CaO / dm³ of water

$$1^\circ \text{ of hardness} = \frac{M(\text{FeO})}{M(\text{CaO})} \times 10 \text{ mg} = 12.81 \text{ mg FeO/dm}^3 \text{ of water}$$

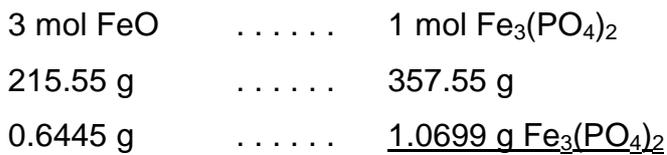
$$\frac{1.293 \text{ g FeO}}{0.1281 \text{ g FeO}} \approx 10^\circ \text{ of hardness}$$

Since the water has totally 20° of hardness, and 10° of hardness fall on FeO, the other 10° of hardness are attributed to CaO which corresponds to 1 g of CaO in 10 dm³ of the water.

Molar ratio:

$$n(\text{FeO}) : n(\text{CaO}) = \frac{m(\text{FeO})}{M(\text{FeO})} : \frac{m(\text{CaO})}{M(\text{CaO})} = \frac{1.289 \text{ g}}{71.85 \text{ g mol}^{-1}} : \frac{1 \text{ g}}{56.08 \text{ g mol}^{-1}} = 1 : 1$$

2.2 A volume of 10.00 dm³ of the water contains so much iron that corresponds to 1.293 g of FeO. 50 % of iron (0.6445 g of FeO) were oxidised to Fe(III), and therefore Fe₃(PO₄)₂ as well as FePO₄ are formed at the same time.



Mass of the precipitate: 1.0699 g + 1.3542 g = 2.4241 g

PROBLEM 3

Chromium plating is usually made by electrolysis in a solution of chromic acid. The chromium plated objects form the cathode. The anode is an alloy that is inert under given conditions, i. e. it does not react either chemically or electrochemically.

An electrolytic cell was filled with 100.0 dm³ of an aqueous solution which contained 0.230 kg of chromium acid anhydride in 1 dm³ of the solution.

In electrolysis a current of 1500 A passed through the electrolyte for 10.0 hours. After electrolysis an increase of the mass of the cathode was 0.679 kg.

The ratio of gas volumes

$$\frac{V_C}{V_A} = 1.603$$

where V_C is a volume of gases evolved at the cathode, whereas that marked as V_A is the volume of gases which are evolved at the anode. Both volumes were measured at the same conditions.

Problems

- 3.1 What part of the total charge (in %) was used for a deposition of 0.679 kg of chromium?
- 3.2 Calculate:
- the volume ratio of both gases (at STP) which are evolved as by-products at the cathode and anode,
 - current efficiency for the corresponding reactions taking place separately at the cathode and anode when the gases are evolved.

If you find any disproportion between the data calculated and those given in the task, try to explain what process would take place in the electrolytic cell which has not been considered till now.

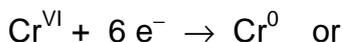
Write the corresponding summary equation for the reactions at electrodes and correct your previous calculations if possible.

SOLUTION

- 3.1 The total electric charge passed through the electrolyte:

$$Q = \frac{1500 \times 3600 \times 10}{96500} = 559.6 \text{ F}$$

Reaction at the cathode:



Deposited:

$$\frac{679 \text{ g}}{51.996 \text{ g mol}^{-1}} = 13.06 \text{ mol of chromium}$$

A charge of 78.36 F was required to deposit the above chromium.

Current efficiency:

$$\frac{78.36 \text{ F}}{559.6 \text{ F}} \times 100 = 14.0 \%$$

- 3.2** The simplest assumption: Only hydrogen is evolved at the cathode and at the same time oxygen at the anode. On this assumption the amounts of substances of the evolved oxygen and hydrogen are as follows:

$$n(\text{H}_2) = \frac{559.6 \times 0.86}{2} = 240.63 \text{ mol}$$

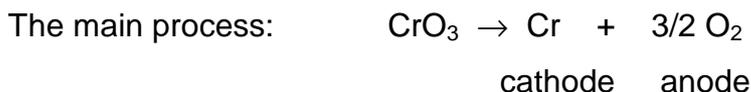
$$n(\text{O}_2) = \frac{559.6}{4} = 139.9 \text{ mol}$$

The molar ratio is:

$$\frac{n(\text{H}_2)}{n(\text{O}_2)} = \frac{V(\text{H}_2)}{V(\text{O}_2)} = \frac{240.63 \text{ mol}}{139.9 \text{ mol}} = 1.720$$

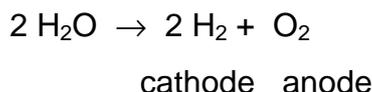
This value is different from that given in the task. Thus, beyond the mentioned reactions also other processes take place at the electrodes. The current efficiency may be calculated from the volume ratio of gases evolved, without making any investigation of what kind the processes are.

Balance of the processes:



$$\eta_1 = 14.0 \%$$

The by process: (electrolysis of water)



$$\eta_2 = ?$$

The amount of substance of the hydrogen evolved at the cathode is equal to:

$$n(\text{H}_2) = \frac{Q \cdot \eta_2}{2}$$

The amount of substance of the oxygen evolved at the anode is equal to:

$$n(\text{O}_2) = \frac{Q \cdot (\eta_1 + \eta_2)}{4}$$

According to the data given in the task:

$$\frac{V(\text{H}_2)}{V(\text{O}_2)} = \frac{n(\text{H}_2)}{n(\text{O}_2)} = \frac{\frac{Q \cdot \eta_2}{2}}{\frac{Q \cdot (\eta_1 + \eta_2)}{4}} = 1.603$$

In solving the equation for η_2 we get a value:

$$\eta_2 = 0.565 \quad (56.5 \%)$$

Volumes of the hydrogen and oxygen evolved:

$$n(\text{H}_2) = \frac{559.6 \times 0.565}{2} = 158.1 \text{ mol}$$

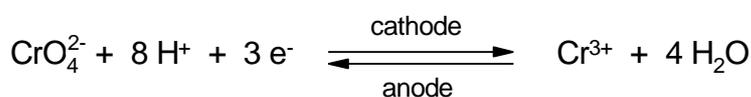
$$V(\text{H}_2) = 22.41 \text{ dm}^3 \text{ mol}^{-1} \times 158.1 \text{ mol} = 3543 \text{ dm}^3$$

$$n(\text{O}_2) = \frac{559.6 \times (0.140 + 0.565)}{4} = 98.6 \text{ mol}$$

$$V(\text{O}_2) = 22.41 \text{ dm}^3 \text{ mol}^{-1} \times 98.6 \text{ mol} = 2210 \text{ dm}^3$$

The current efficiency when the hydrogen is evolved at the cathode is equal to 56.5 %. The current efficiency when the oxygen is evolved at the anode is equal to 70.5 %.

Thus, 29.5 % of the electric charge is used without an apparent effect. Therefore some cyclic process is taking place in the electrolytic cell which causes that anion CrO_4^{2-} is reduced incompletely. One of the reactions which causes a decrease of the current efficiency value, is the following:



PROBLEM 4

A vessel of a volume of 5.0 dm³ was filled with ethane at a temperature of 300 K and normal pressure and sealed. The vessel with the gas was then heated and the pressure in it was measured at distinct temperatures. The following data were found:

T (K)	Pressure p , measured (kPa)	Pressure p' , calculated (kPa)
300	101.25	
500	169.20	
800	276.11	
1000	500.48	

Problems:

- 4.1** Calculate the pressure p' of ethane in the vessel according to the ideal gas law equation and fill in the values in a free column in the above table.
($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- 4.2** Explain the differences between theoretical value p' and those (p) obtained by measurements.
- 4.3** Write the chemical equation for the reaction which takes place probably in the vessel at higher temperatures.
- 4.4** Calculate the value for the conversion degree α of ethane and that for equilibrium constant K_p of the reaction that takes place at temperatures of 800 and 1000 K.
- 4.5** The ratio of equilibrium constant K_p at two different temperatures is according to van't Hoff's equation equal to:

$$\ln \frac{K_1}{K_2} = \frac{\overline{\Delta H}}{R} = \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$(\ln = 2.303 \log)$$

Calculate the mean value $\overline{\Delta H}$ for reaction heat in the temperature range of 800 – 1000 K.

- 4.6** What influence will have an elevation of temperature and pressure on the conversion degree of ethane?
- 4.7** Calculate the relative error of the calculation.

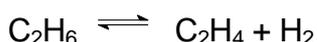
SOLUTION

4.1 The complete table contains the following data:

T (K)	Pressure p , measured (kPa)	Pressure p' , calculated (kPa)
300	101.325	101.325
500	169.820	168.706
800	276.111	269.930
1000	500.748	337.412

4.2 The p values at higher temperatures are greater than those calculated (p). Hence, the number of molecules (moles) in the system increases. Apparently, there occurs a thermal decomposition of ethane.

4.3 Alkanes are thermally decomposed to produce alkenes and hydrogen:



4.4 Clapeyron's equation for the substances undergoing thermal decomposition into two other gaseous substances, has the form:

$$p V = n(1 + \alpha) R T$$

where α is degree of decomposition.

From one mole of C_2H_6 :

α moles of C_2H_4 and α moles of H_2 are obtained, and $(1 - \alpha)$ moles of C_2H_6 remain unreacted.

From n moles of C_2H_6 :

$n\alpha$ moles of C_2H_4 and $n\alpha$ moles of H_2 are obtained, and $n(1 - \alpha)$ moles of C_2H_6 remain unreacted.

Hence, the total amounts of substances of compounds in the gaseous mixture will be:

$$\Sigma n = 2n\alpha + n(1 - \alpha) = n(1 + \alpha)$$

In comparing the theoretical and experimental values of pressure we obtain:

$$p' V = n R T \Rightarrow p' = \frac{n}{V} R T$$

$$p V = n(1 + \alpha) R T \Rightarrow p = \frac{n(1 + \alpha)}{V} R T$$

$$\frac{p'}{p} = \frac{n}{n(1 + \alpha)} \Rightarrow \alpha = \frac{p - p'}{p'}$$

$$\alpha_{800} = \frac{276.111 - 269.930}{269.930} = 0.023$$

$$\alpha_{1000} = \frac{500.748 - 337.412}{337.412} = 0.484$$

The reaction takes place in gaseous phase and thus, the equilibrium constant K_p is calculated according to the relation:

$$K_p = \frac{p_{C_2H_4} p_{H_2}}{p_{C_2H_6}}$$

$$p_{C_2H_4} = p_{H_2} = p' \alpha$$

$$p_{C_2H_6} = p' (1 - \alpha)$$

$$K_p = \frac{\alpha^2 p'}{1 - \alpha}$$

$$T = 800 \text{ K}$$

$$K_p = \frac{0.023^2 \times 269.930}{0.977} = 0.146 \text{ kPa}$$

$$T = 1000 \text{ K}$$

$$K_p = \frac{0.484^2 \times 337.412}{0.516} = 153.18 \text{ kPa}$$

4.5 According to van't Hoff's equation:

$$\overline{\Delta H} = \frac{2.303 \log \frac{K_1}{K_2} R}{\frac{1}{T_2} - \frac{1}{T_1}}$$

After substituting the known values:

$$\overline{\Delta H} = 231.36 \text{ kJ mol}^{-1}$$

4.6 The reaction is endothermic and the number of particles has increased in the course of the reaction. Thus, the equilibrium is shifted according to Le Chatelier-Brown's principle in the sense of forward reaction when the temperature rises and on the contrary, the equilibrium is shifted in the sense of reverse reaction when the pressure is elevated.

4.7 If the correct value is ΔH_1 and ΔH_2 is a calculated one then the relative error is calculated according to the relation:

$$\frac{\Delta H_1 - \Delta H_2}{\Delta H_1} \times 100 \text{ (\%)}$$

PROBLEM 5

A certain liquid organic compound **X** (being present in coal tar) with a mass of 1.06 g was burned to produce 0.90 g of water and 3.52 g of carbon dioxide. Its vapours were 3.79 times as dense as nitrogen.

The compound **X** was oxidised by a hot mixture of $\text{CrO}_3 + \text{H}_2\text{SO}_4$. A colourless crystalline substance **A** was isolated from the reaction mixture. It was soluble in an aqueous solution of NaOH or NaHCO_3 .

Compound **A** when heated loses water and converts to compound **B**. Condensation of compound **B** with phenol in the presence of H_2SO_4 or ZnCl_2 yields a substance **Y** which is very often used as an acid-base indicator.

Both compound **A** and compound **B** when heated with an excess of 1-butanol (some drops of a concentrated H_2SO_4 solution are added) gives the same liquid compound **C**.

If accepted that a carbon atom shows a tendency to form four bonds in organic compounds, it is possible to write formally two different formulas for the compound **X**. The formulas written in this way do not correspond, however, to the chemical structure of the molecule **X** because up to date nobody has succeeded in the preparation of the two hypothetical isomers.

Haayman and Witbaut carried out in 1941 an ozonisation of the compound **X** in a CH_3Cl solution. After hydrolysis of ozonides, it was found that the water layer contains three different organic compounds in a molar ratio of $\text{D} : \text{E} : \text{F} = 3 : 2 : 1$. Only two of them formed new compounds **G** and **H** by a mild oxidation, the third one remains unchanged under these conditions but the effect of stronger oxidising agents as H_2O_2 for example, results in forming a well known liquid compound **I** with a characteristic sharp smell.

A sample of a pure anhydrous compound **G** was dissolved in an aqueous 1-molar solution of H_2SO_4 and the resulting solution was titrated with a volumetric 0.05-molar KMnO_4 solution. An amount of 0.288 g of substance **G** required 25.6 cm^3 of the KMnO_4 solution.

Problems:

- 5.1 Write the summary formula for the compound **X**.
- 5.2 Based on the information and data in the task, write chemical equations for the reactions by which products **A**, **B**, and **C** are formed.
- 5.3 Give the name for compound **Y** and write the equation of its synthesis. Write its structural formula and colour in both acidic and basic solutions.

- 5.4 Write two formal structural formulas for the compound **X** as well as a more correct structural formula according to the latest findings.
- 5.5 Write the chemical equation for the ozonolysis of compound **X** by which the fact can be explained why compounds **D**, **E**, and **F** are after hydrolysis of ozonides present in water layer in a molar ration of 3 : 2 : 1.
- 5.6 Write chemical equations for the reactions of formation of compounds **G**, **H**, and **I**.
- 5.7 Write both formal structural formulas used before, and the more correct modern structural formula of another liquid organic compound if you know that the compound is also present in coal tar and it is a derivative of compound **X**. What name of a known chemist is connected in the history with the formula of this basic compound? What are the products obtained by its ozonolysis?
- 5.8 Write the names of the substances **X**, **Y**, **A – I** under the corresponding compounds in the equations.

Note:

Use in your calculation:

$$M(\text{C}) = 12 \text{ g mol}^{-1}; \quad M(\text{O}) = 16 \text{ g mol}^{-1}; \quad M(\text{H}) = 1 \text{ g mol}^{-1}; \quad M(\text{KMnO}_4) = 158 \text{ g mol}^{-1}.$$

SOLUTION

- 5.1 The empirical formula of the compound **X** can be calculated from the composition of combustion products of this compounds:

$$n(\text{H}_2\text{O}) = \frac{0.9 \text{ g}}{18 \text{ g mol}^{-1}} = 0.05 \text{ mol} \Rightarrow n(\text{H}) = 0.1 \text{ mol}$$

$$\% \text{H} = \frac{0.1 \text{ g}}{1.06 \text{ g}} \cdot 100 = 9.4$$

$$n(\text{CO}_2) = \frac{3.52 \text{ g}}{44 \text{ g mol}^{-1}} = 0.08 \text{ mol} \Rightarrow n(\text{C}) = 0.8 \text{ mol i. e. } 0.96 \text{ g}$$

$$\% \text{C} = \frac{0.96 \text{ g}}{1.06 \text{ g}} \times 100 = 90.6$$

$$\text{X: } \text{C}_x\text{H}_y \quad x : y = \frac{90.6}{12} : \frac{9.4}{1} = 4 : 5$$

Empirical formula: C_4H_5

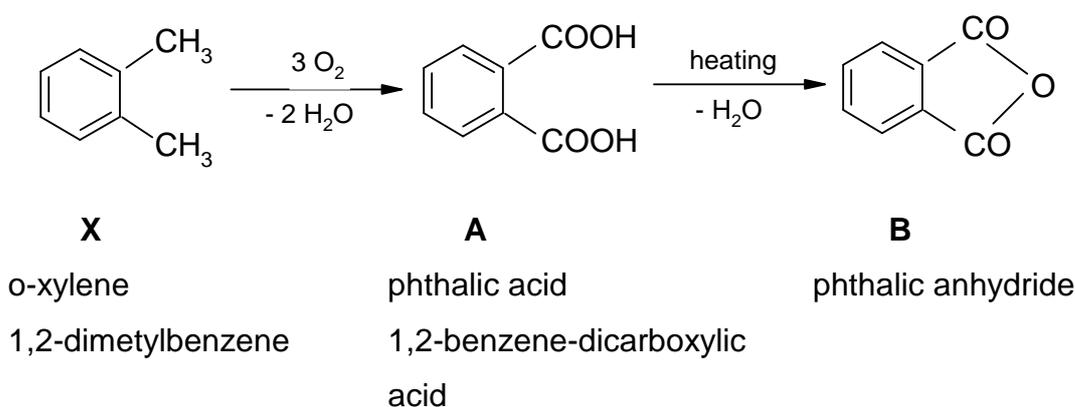
Molecular formula: $(C_4H_5)_n$

Molar mass of **X** is calculated in the following way:

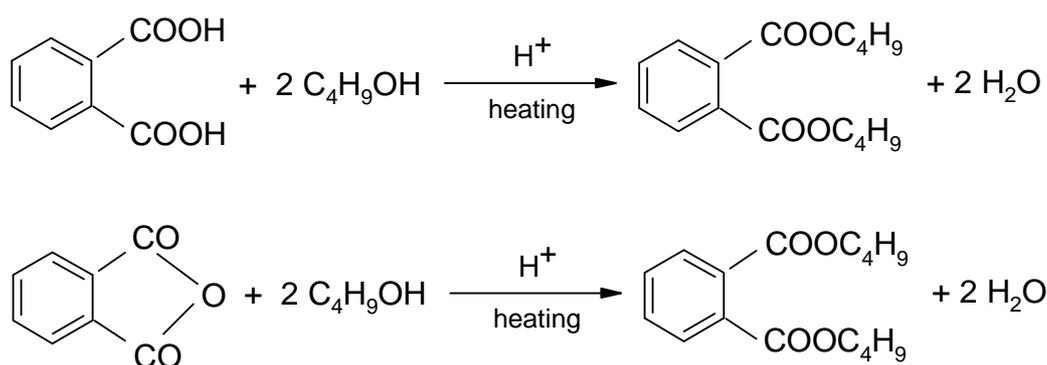
$$M(\mathbf{X}) = M(N_2) \frac{\rho(\mathbf{X})}{\rho(N_2)} = 28 \text{ g mol}^{-1} \times 3.79 = 106 \text{ g mol}^{-1}$$

Molecular formula of the compound **X** is C_8H_{10} .

5.2 The information given in the task and concerning compound **X** supports the assumption that compound **X** is o-xylene.

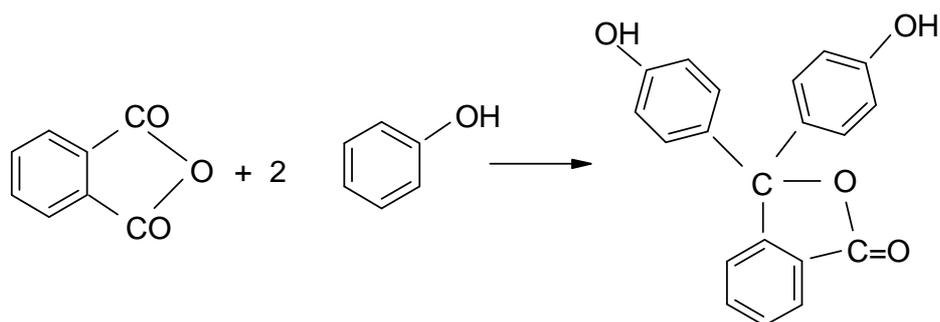


Phthalic acid (**A**) or its anhydride (**B**) when heated with an excess of 1-butanol with addition of a certain amount of mineral acid as a catalyst, yield dibutyl ester of phthalic acid – **C**:



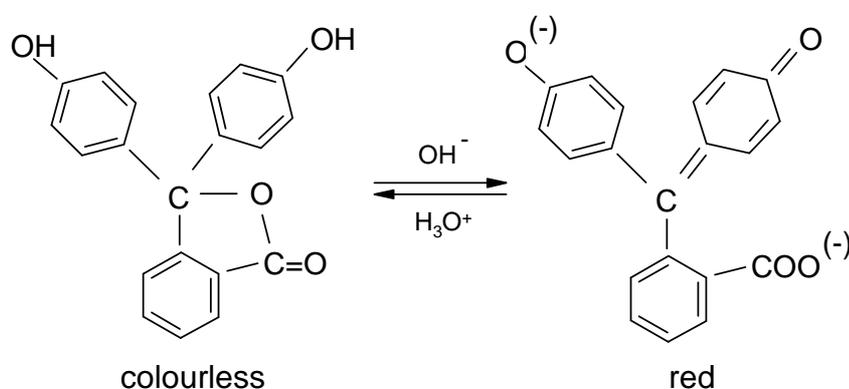
C : dibutyl phthalate

5.3 Condensation of the anhydride of phthalic acid with phenol in the presence of H_2SO_4 or anhydrous ZnCl_2 :

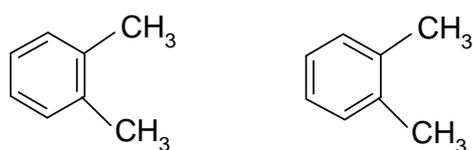


Y : phenolphthalein

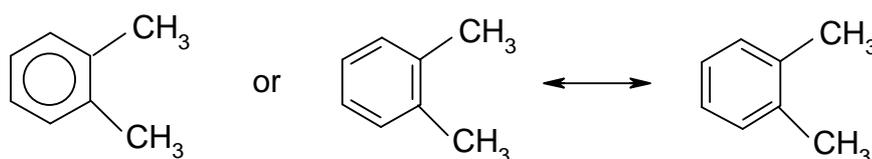
Phenolphthalein is used as acid-base indicator which is colourless in an acidic solution but purple red in an alkaline solution.



5.4 Kekule's formulas for o-xylene:



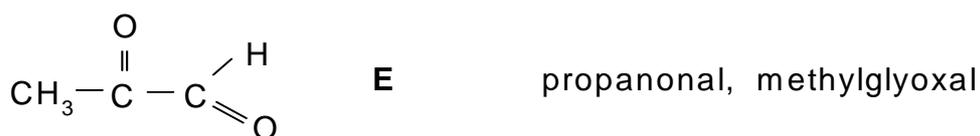
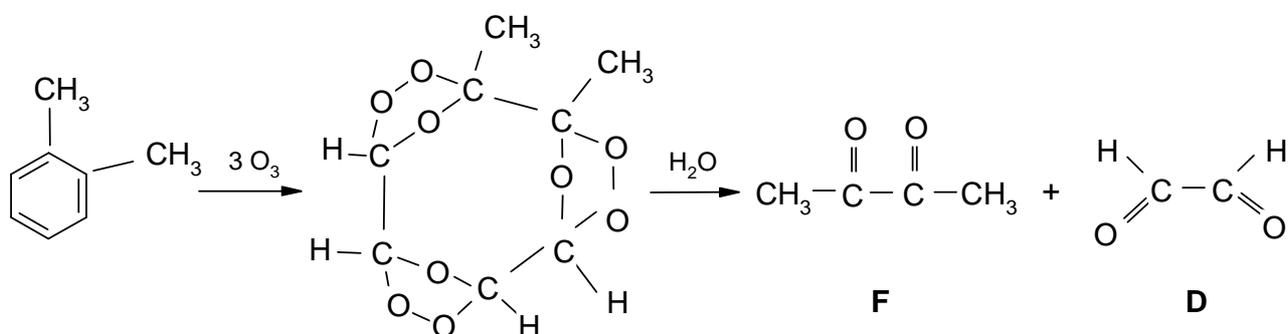
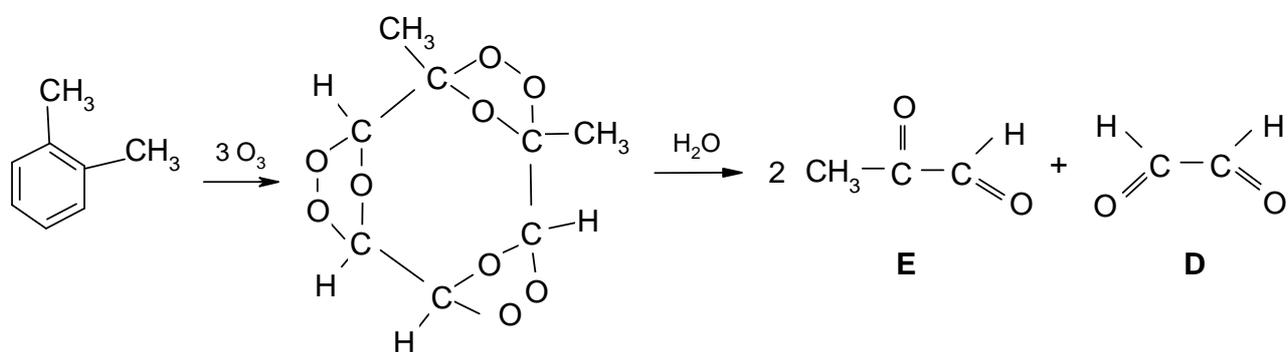
would allow to suggest that this compound does exist in two isomeric forms. Nobody, however, has succeeded in obtaining the two isomers of o-disubstituted benzene. At present it is already known that all bonds C-C as well as C-H in benzene and its derivatives are equivalent. Therefore, the formula for o-xylene can be written in the following way:



This kind of writing of the formulas expresses that the π -bonds are equally divided on the whole benzene ring. Of course, such formulas no longer support the existence of two isomeric forms of o-xylene.

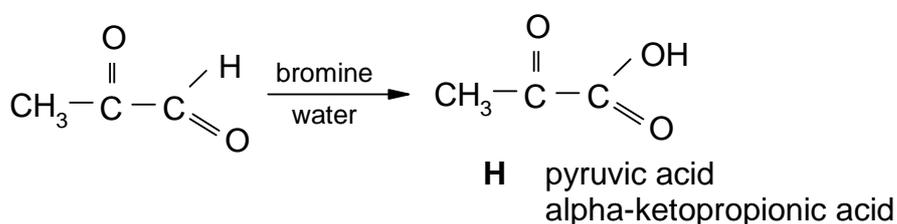
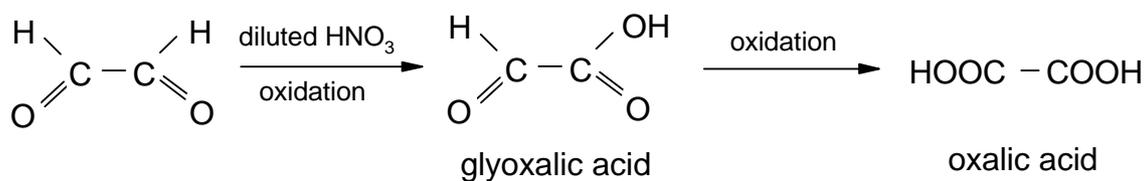
In 1941 Haayman and Witbaut provided further chemical evidence for the equivalence of the six C-C bonds in the benzene ring. They allowed to react o-xylene with ozone and obtained two different triozonides in a molar ratio of 1 : 1. Products of ozonolysis were decomposed by water to form three different substances:

5.5

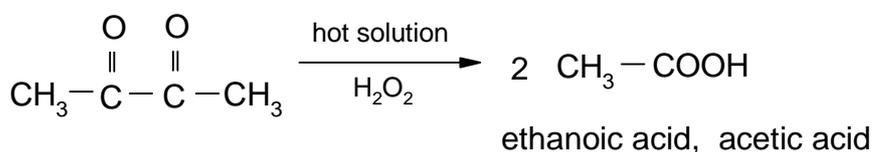


Products in the resulting mixture after hydrolysis of ozonides are in a molar ratio 3 : 2 : 1 and it proves the equivalence of C-C bonds in the benzene ring.

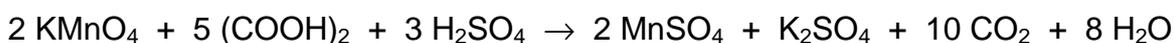
5.6 From the three above obtained compounds **D**, **E**, and **F** only the first two are easily oxidized to the corresponding acids:



Compound **F** requires a stronger oxidising agents, such as aqueous solutions of H_2O_2 , HIO_4 , etc.



Oxalic acid is used as a standard substance in preparation of volumetric KMnO_4 solutions:



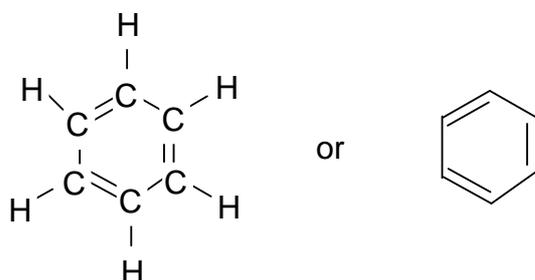
Experimental data on determination of compound **G** by titration with a 0.05-molar KMnO_4 solution show that compound **G** is oxalic acid, and thus they do confirm the correctness of the solution.

$$n(\text{KMnO}_4) = c V = 0.05 \text{ mol dm}^{-3} \times 0.0256 \text{ dm}^3 = 0.00128 \text{ mol}$$

$$n((\text{COOH})_2) = 5/2 \times 0.00128 \text{ mol} = 0.0032 \text{ mol}$$

It corresponds to 0.288 g of substance **G** what is in agreement with the result given in the task.

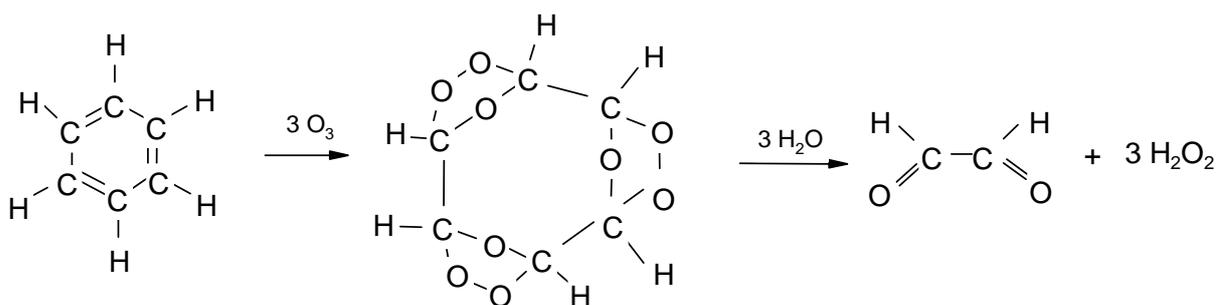
5.7 In 1865 Kekulé suggested a cyclic formula for benzene:



It was, however, proved by experiments that all atoms of carbon and hydrogen are in the benzene molecule equivalent. For the same reason as given under 4, the formula of benzene is at present written in the form:



Ozonolysis of benzene yields a triozone which after hydrolysis gives glyoxal:



PRACTICAL PROBLEMS**PROBLEM 1 (practical)**

Four aqueous solutions are available on the laboratory desk. These are solutions of HCl, NaOH, NH₃, and CH₃COOH whose concentrations are approximately 1 mol dm⁻³. The concentration of HCl solution is the only one that is exactly determined and known.

Using the volumetric solution of HCl, determine the exact concentrations of the other solutions. A burette, pipette, titration flasks and indicators methyl orange and phenolphthalein are at your disposal. Perform twice each titration and calculate the mean value for concentration. The third determination is needed to be carried out only in such a case when the results of the previous two titrations differ more than by 2 %.

Now you will perform the following thermochemical measurements of neutralisation heat evolved in the reactions of the above given solutions of acids and bases:

- a) Measure quantitatively exactly 50.0 cm³ of the hydrochloric acid solution into a beaker. Measure into another equal beaker a volume of NaOH solution that contains such a number of moles of NaOH as that of HCl being present in the first beaker. Then measure the temperatures of both solutions with a precision of 0.2 K. Pour quickly the content of the first beaker into the other using the thermometers as a glass stick and stir the resulting solution with the thermometer. Determine the final highest temperature of the mixture.
- b) Perform analogous measurement with the following pairs of acids and bases:
HCl – NH₃, CH₃COOH – NaOH, CH₃COOH – NH₃.

Problems:

- 1.1** What indicators have been used for the individual determinations? Give approximately pH regions in which the mentioned indicators show colour transitions. Give reasons for the use of the individual indicators using only ionic equations for the reactions which are characteristic of specific properties of salts being formed in the individual neutralisation reactions. Calculate the concentrations of all solutions under investigations.

- 1.2 Write the calorimetric equation in its general form by means of which the neutralisation heat can be calculated. Calculate the thermal effect for each neutralisation reaction under investigation and give the value in relation to one mole of the water formed.

Densities of the solutions are as follows:

$$\rho(\text{HCl}) = 1.02 \text{ g cm}^{-3}$$

$$\rho(\text{NaOH}) = 1.04 \text{ g cm}^{-3}$$

$$\rho(\text{NH}_3) = 0.99 \text{ g cm}^{-3}$$

$$\rho(\text{CH}_3\text{COOH}) = 1.01 \text{ g cm}^{-3}$$

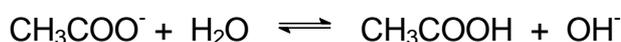
In the calculations consider the specific heat capacity value for the solutions equal to $4.19 \text{ J g}^{-1} \text{ K}^{-1}$ whereas the heat capacity of glass and thermometer may be neglected.

- 1.3. Have you obtained equal results in all four cases? If not, order the particular reaction systems according to the decreasing value of reaction heat. What reactions cause the above mentioned differences? Express the reactions by means of chemical equations.
- 1.4 The exact methods showed that neutralisation heat in the reaction of the strong acid with a strong base (i. e. the reaction heat when 1 mole of water is formed from H^+ and OH^- ions) is equal to $57.57 \text{ kJ mol}^{-1}$. Calculate the relative error of your determination.

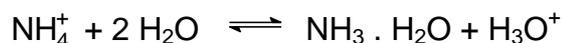
SOLUTION

- 1.1. In titrating a strong acid with a strong base, both phenolphthalein and methyl orange can be used as acid-base indicators. The drop on the titration curve covers the colour changes of both indicators (pH values from 4 – 10).

Only phenolphthalein can be used in the case when a weak acid is titrated with a strong base because the neutralisation occurs at higher pH values (the colour transition of phenolphthalein is in the region of $\text{pH} = 8 - 10$). A salt formed undergoes hydrolysis (more precisely its anion) and the solution exhibits a basic reaction:



In titrating a strong acid with a weak base or vice versa, methyl orange is used (pH = 3 – 4.5) and due to hydrolysis the resulting solution shows an acidic reaction:



The exact concentrations of the aqueous solutions of sodium hydroxide and ammonia are determined by titrations with the volumetric solution of hydrochloric acid. The exact concentration of the acetic acid solution is then determined by a titration with the sodium hydroxide solution.

- 1.2** When the specific heat capacities of glass and thermometer are neglected the neutralisation heat can be then calculated according to a simple relation:

$$\Delta H_{\text{neutr.}} = (m_1 + m_2) c (T_2 - T_1)$$

m_1 – mass of the first solution,

m_2 – mass of the second solution,

c – specific heat capacity of the solutions,

T_1 – temperatures of the solutions before mixing,

T_2 – temperatures of the solutions after mixing.

If the temperatures of the solutions before mixing are not equal then T_1 will be the mean temperature of both. Finally, the neutralisation heat value should be related to 1 mole of water formed.

- 1.3** The results obtained for the neutralisation of a strong base with a weak acid and vice versa, as well as for the reaction of a weak acid with a weak base, are lower than those obtained for the neutralisation of a strong acid with a strong base. A part of the heat is consumed for ionisation of a weak electrolyte:



A similar equation can be written for $\text{NH}_3 \cdot \text{H}_2\text{O}$.

PROBLEM 2 (practical)

The values of standard reduction potentials are given for the following redox systems:

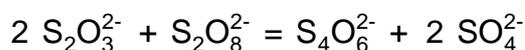
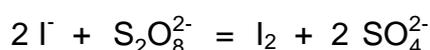
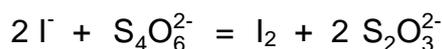


Problems:

2.1 Set in order the oxidation forms of the above given redox systems from the weakest to the strongest oxidising agent (write into Table 1)

In a similar way order the reduction forms from the weakest to the strongest reducing agent.

2.2 In the bellow given equations mark by arrows the expected possible course (direction) of the chemical reaction (Table 1).



2.3 On the assumption that solutions of the same concentration are used, is it possible to tell without making any experiment which of the given reactions would run at a higher rate and which ones at a lower rate?

In order to confirm your hypothesis given under 3, perform the following three qualitative experiments:

Experiment 1

Pour 20.0 cm³ of a 0.10-molar solution of Na₂S₂O₃ into an Erlenmeyer flask and quickly add under intense stirring 1.0 cm³ of a 0.10-molar iodine solution.

Experiment 2

Measure 20.0 cm³ of a 0.10-molar solution of (NH₄)₂S₂O₈ into an Erlenmeyer flask and quickly add under intense stirring 4.0 cm³ of a 0.10-molar potassium iodide solution.

Experiment 3

Put 20.0 cm³ of a 0.10-molar solution of (NH₄)₂S₂O₈ into an Erlenmeyer flask and then quickly add under intense stirring 2.0 cm³ of a 0.10-molar sodium thiosulphate solution.

Since both the reactants and reactant products are colourless, the course of the reaction can be followed indirectly. For that purpose, add to the solution after 1 – 2 minutes two or three drops of a 0.10-molar iodine solution. If the result of your experiment is surprising, perform experiment No 3 again but allow solutions of $\text{Na}_2\text{S}_2\text{O}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to react for 10 minutes.

Order the reactions from experiments No 1 – 3 (into Table 3) according to their increasing reaction rate and then answer the question whether it is possible on the basis of known values of the standard reduction potentials to guess, at least qualitatively, the reaction rate for the reaction mixture containing two pairs of redox systems.

Conclusions made on the above experiments make it possible to investigate the influence of concentration of each of the starting substances on the rate of the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ ions.

Perform experiment No 4 according to the following instructions:

Experiment 4

- Measure successively into a 250 cm³ Erlenmeyer flask: 25.0 cm³ of a 0.20-molar potassium iodide solution, 10.0 cm³ of a 0.01-molar sodium thiosulphate solution, 5.0 cm³ of a starch paste, and stir the content of the flask.
- Measure 25.0 cm³ of a 0.20-molar $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution into a 100 cm³ beaker. Pour the content of the beaker quickly into the flask, press a stop-watch and stir the content of the flask. Measure the time till the moment when the solution becomes blue.

Perform analogously experiment No 4 three times over, using the bellow given volumes of the 0.20-molar potassium iodide solution, while the volumes of $\text{Na}_2\text{S}_2\text{O}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solutions as well as that of the starch paste remain unchanged. Moreover, add to the solution the bellow given volumes of a 0.20-molar potassium nitrate solution so that the volume of the resulting solution is always the same. Explain the use of potassium nitrate in this case.

4 (ii): 15.0 cm³ 0.20-molar KI + 10.0 cm³ 0.20-molar KNO_3

4 (iii): 10.0 cm³ 0.20-molar KI + 15.0 cm³ 0.20-molar KNO_3

4 (iv): 5.0 cm³ 0.20-molar KI + 20.0 cm³ 0.20-molar KNO_3

2.4 List the results of experiments No 1-4 briefly and clearly in the attached Tables.

Write formulas of the corresponding substances above the arrows in Table 1 (as required under 2.1) and mark the expected course of the mentioned chemical reactions by arrows in the equations.

For a qualitative evaluation of reaction rate (Table 2) use terms such as: very rapid, rapid, slow, very slow.

Fill in Table 3 exactly according to the titles of the columns.

2.5 Calculate the reaction rate according to the formula:

$$v = \frac{\Delta c(\text{S}_2\text{O}_8^{2-})}{\Delta \tau} \quad (\text{mol dm}^{-3} \text{ s}^{-1})$$

$\Delta c(\text{S}_2\text{O}_8^{2-})$ - concentration change of $\text{S}_2\text{O}_8^{2-}$ in a time interval.

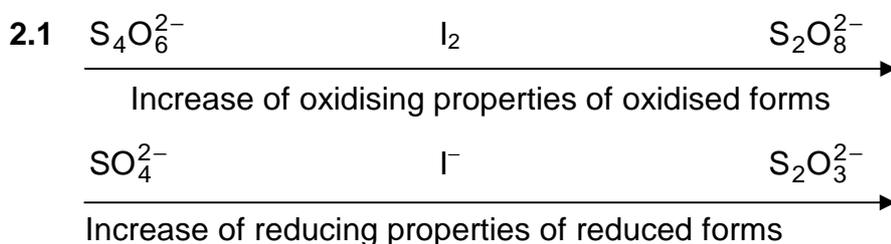
Plot (on the attached mm-paper) the dependence of reaction rate on the concentration of I^- anions at a constant concentration of $\text{S}_2\text{O}_8^{2-}$ anions in the solution.

2.6 Making use of the knowledge gained from the preceding experiment and the solutions which are at your disposal, suggest another experiment which would make it possible to investigate the reaction rate dependence on concentration of $\text{S}_2\text{O}_8^{2-}$ anions at a constant concentration of I^- anions in the solution.

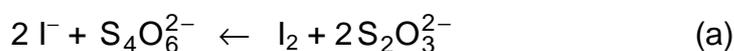
Considering Table 3, fill in Table 4. Mark the columns in the Table, suggest a plan of the experiment and list experimental results as well as the calculated values. Similarly as before, plot the dependence under investigation on a mm-paper.

2.7 Write a general relation for the reaction rate dependence on the concentration of reactants and then using the diagrams attached, calculate the values for the reaction rate constant for both cases and determine their mean value.

SOLUTION



2.2 The expected course of the chemical reactions:





2.3 The formulation of any hypothesis either supporting or neglecting the possibility of predicting the reaction rate, should be accepted as correct.

Results of experiments Nos 1-3:

- 1 - reaction (a) is very rapid;
- 2 - reaction (b) is slow;
- 3 - reaction (c) is very slow, its course can hardly be observed.

Conclusion: The known differences between the values of standard reduction potentials of two pairs of redox systems do not allow to guess even qualitatively the proper relations between the rates of the corresponding reactions.

2.4 You are required to fill in the following data into Table 3:

- volumes of individual solutions,
- the total volume of the solution (65 cm^3),
- calculated values for I^- and $\text{S}_2\text{O}_8^{2-}$ concentrations,
- reaction time,
- calculated values for the reaction rate.

The addition of 0.20-molar KNO_3 solution is needed to keep the constant ionic strength of the resulting solution.

In plotting the reaction rate in dependence on the values of $[\text{I}^-]^2$ (at the constant concentration of $\text{S}_2\text{O}_8^{2-}$ anions) we get a straight line crossing the beginning of the coordinate system.

Table 4 should be filled in analogously as Table 3 where, moreover, the individual columns should be specified.

Solutions for the experiment are prepared in the same way but the solution of KI (25 cm^3) will form a constant addition, whereas those of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{SO}_4$ will form a changeable addition in the resulting solution and the other conditions are equal. Ammonium sulphate plays the same role in the solution as potassium nitrate in the preceding experiment.

In this case the reaction rate versus the concentration of $\text{S}_2\text{O}_8^{2-}$ anions is plotted (at a constant concentration of I^- anions) to give also a straight line crossing the beginning of the coordinate system.

2.5 The rate of the reaction:

$$v = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]^2$$

a) $[\text{I}^-] = \text{const} \Rightarrow v = k'[\text{S}_2\text{O}_8^{2-}]$

$$k = \frac{k'}{[\text{I}^-]^2}$$

k' is the slope of the straight line.

b) $[\text{S}_2\text{O}_8^{2-}] = \text{const} \quad v = k''[\text{I}^-]^2$

$$k'' = k[\text{S}_2\text{O}_8^{2-}]$$

$$k = \frac{k''}{[\text{S}_2\text{O}_8^{2-}]}$$

k'' is the slope of the straight line.

The values of the rate constants obtained from the procedures a) and b) should be theoretically equal. If they partly differ, calculate the mean value of the rate constant.

11th



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE ELEVENTH INTERNATIONAL CHEMISTRY OLYMPIAD 2-11 JULY 1979, LENINGRAD, SOVIET UNION

THEORETICAL PROBLEMS

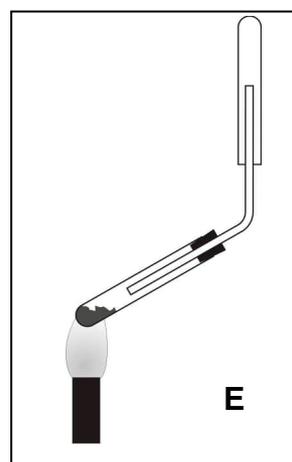
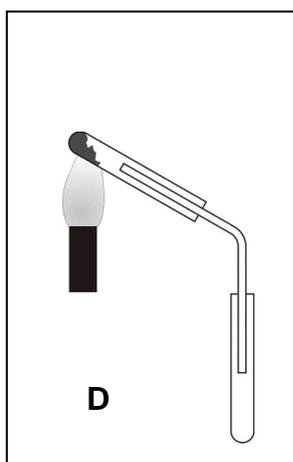
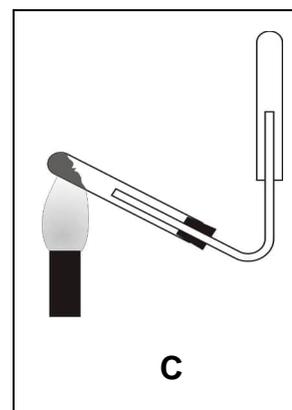
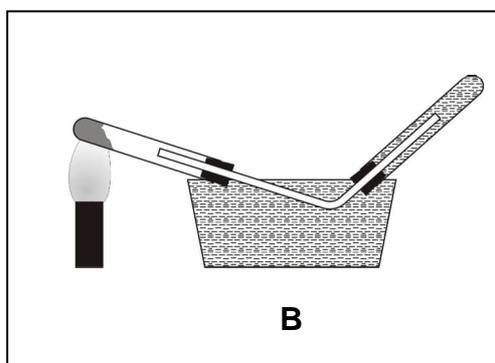
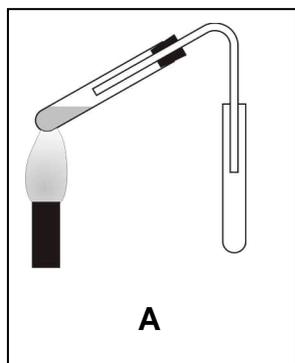
PROBLEM 1

When carrying out this programmed assignment, encircle those letters which in your opinion correspond to the correct answers to each of the 20 questions.

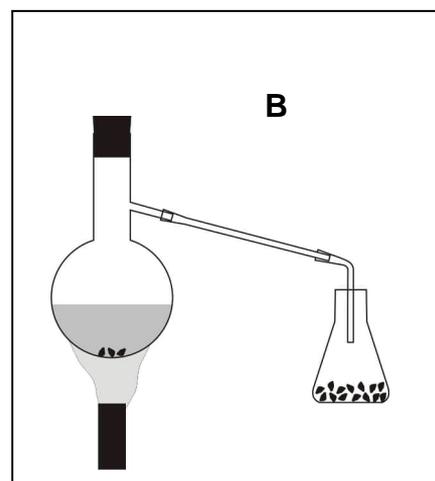
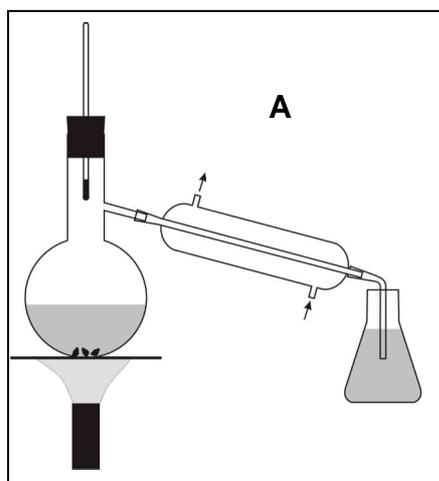
1. Which element is oxidized in the reaction between ethylene and an aqueous solution of potassium permanganate?
A) carbon, B) hydrogen, C) potassium, D) manganese, E) oxygen.
2. How many litres of CO₂ will approximately be evolved in the reaction of 18 g of potassium hydrogen carbonate with 65 g of 10 % sulphuric acid?
A) 1, B) 2, C) 3, D) 4, E) 5.
3. Which of the following hydrocarbons gives the maximum heat yield on complete combustion of 1 litre of the gas:
A) propane, B) methane, C) acetylene, D) ethylene, E) all give the same yield.
4. How many isomers can have a compound if its formula is C₃H₅Br?
A) 1, B) 2, C) 3, D) 4, E) 5.
5. Which of the following hydrocarbons will be the best engine fuel?
A) cyclooctane, B) 2,2-dimethylhexane, C) normal octane, D) 3-ethylhexane, E) 2,2,4-trimethylpentane.
6. With which of the following compounds will an aqueous solution of a higher oxide of element No 33 react?
A) CO₂, B) K₂SO₄, C) HCl, D) NaOH, E) magnesium.
7. What must be the minimum concentration (% by mass) of 1 kg of a potassium hydroxide solution for a complete neutralisation of 3.57 moles of nitric acid?
A) 5 %, B) 10 %, C) 15 %, D) 20 %, E) 25 %.

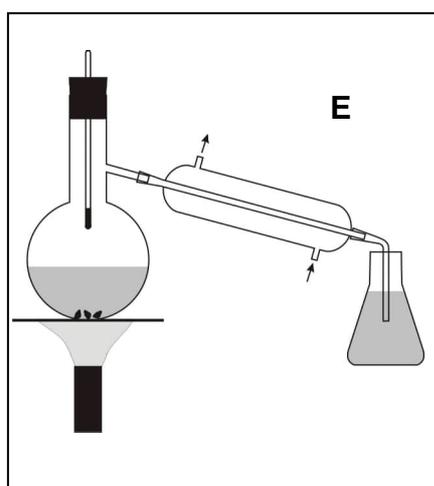
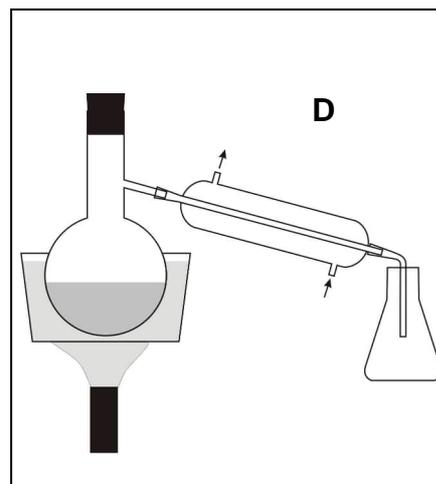
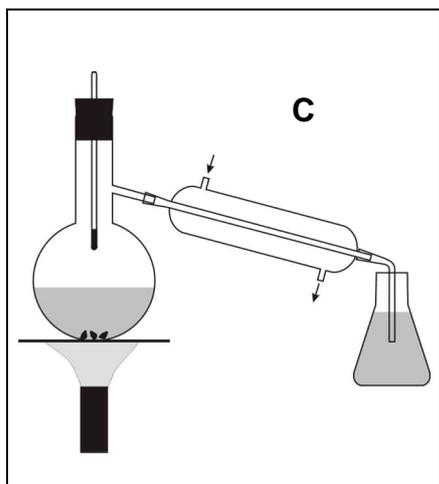
8. How many compounds with the formula C_3H_9N can exist?
A) 1, B) 2, C) 3, D) 4, E) 5.
9. In which of the following compounds has the nitrogen content (in mass %) a maximum value?
A) potassium nitrate, B) barium nitrate, C) aluminium nitrate, D) lithium nitrate, E) sodium nitrate.
10. To which carbon atom (indicate the serial number) will chlorine mainly add in the reaction of HCl with penten-2-oiс acid?
A) 1, B) 2, C) 3, D) 4, E) 5.
11. How many moles of water are there per mole of calcium nitrate in a crystallohydrate if the water content is 30.5 % by mass?
A) 1, B) 2, C) 3, D) 4, E) 5.
12. Which of these organic acids is the strongest?
A) benzoic, B) 2-chlorobenzoic, C) 4-methylbenzoic, D) 2-aminobenzoic, E) 4-bromobenzoic.
13. Which of these acids has the highest degree of dissociation?
A) HClO, B) HClO₂, C) HClO₃, D) HClO₄, E) all have the same degree.
14. Which of the salts given below do not undergo hydrolysis?
A) potassium bromide, B) aluminium sulphate, C) sodium carbonate, D) iron(III) nitrate, E) barium sulphate.
15. How many litres of air are approximately required for complete combustion of 1 litre of ammonia?
A) 1, B) 2, C) 3, D) 4, E) 5.
16. Which element is oxidised in the thermal decomposition of sodium hydrogen carbonate?
A) sodium, B) hydrogen, C) oxygen, D) carbon, E) none.
17. Which of the following changes have no effect on the chemical equilibrium in the thermal decomposition of CaCO₃?
A) temperature elevation, B) pressure decrease, C) addition of catalyst, D) a change in the CO₂ concentration, E) an increase in the amount of the initial substance.
18. Which of the substances given below will be formed at the Pt-anode in the electrolysis of an aqueous solution of aluminium chloride?
A) aluminium, B) oxygen, C) hydrogen, D) aluminium hydroxide, E) chlorine.

19. The apparatus shown in the figures is intended for preparing ammonia under laboratory conditions. The test tube being heated contains a mixture of NH_4Cl and $\text{Ca}(\text{OH})_2$. Which of the figures is correct?



20. Which of the apparatuses shown in the figures is the best one for the synthesis of bromethane from potassium bromide, concentrated sulphuric acid and ethanol?





SOLUTION

- | | | | |
|-------|-------------|--------------|--------------|
| 1 – A | 6 – D and E | 11 – D | 16 – E |
| 2 – C | 7 – D | 12 – B | 17 – C and E |
| 3 – A | 8 – D | 13 – D | 18 – B and E |
| 4 – E | 9 – D | 14 – A and E | 19 – C |
| 5 – E | 10 – C | 15 – D | 20 – A |

PROBLEM 2

An alloy comprises the following metals: cadmium, tin, bismuth, and lead. A sample of this alloy weighing 1.2860 g, was treated with a solution of concentrated nitric acid. The individual compound of metal **A** obtained as a precipitate, was separated, thoroughly washed, dried and calcinated. The mass of the precipitate after the calcination to constant mass, was 0.3265 g.

An aqueous ammonia solution was added in excess to the solution obtained after separation of the precipitate. A compound of metal **B** remained in the solution while all the other metals precipitated in the form of sparingly soluble compounds. The solution was first quantitatively separated from the precipitate, and then hydrogen sulphide was passed through the separated solution to saturation. The resulting precipitate containing metal **B** was separated, washed and dried. The mass of the precipitate was 0.6613 g.

The precipitate containing the compounds of metals **C** and **D** was treated with an excess of a NaOH solution. The solution and the precipitate were then quantitatively separated. A solution of HNO₃ was added to the alkaline solution to reach pH 5 – 6, and an excess of K₂CrO₄ solution was added to the resulting transparent solution. The yellow precipitate was separated, washed and quantitatively transferred to a beaker. Finally a dilute H₂SO₄ solution and crystalline KI were added. Iodine produced as a result of the reaction was titrated with sodium thiosulphate solution in the presence of starch as an indicator. 18.46 cm³ of 0.1512 normal Na₂S₂O₃ solution were required.

The last metal contained in the precipitate as a sparingly soluble compound was transformed to an even less soluble phosphate and its mass was found to be 0.4675 g.

2.1 Write all equations of the chemical reactions on which the quantitative analysis of the alloy sample is based. Name metals **A**, **B**, **C**, and **D**. Calculate the mass percentage of the metals in the alloy.

SOLUTION

2.1 The action of nitric acid on the alloy:





Weight form of tin determination:



Calculation of tin content in the alloy:

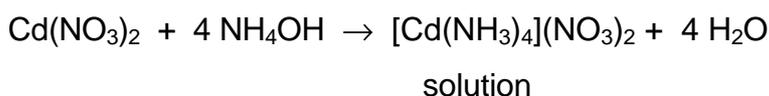
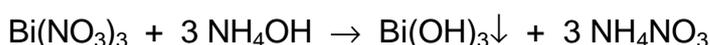
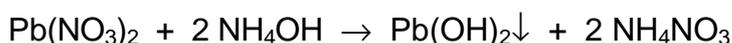
$$M(\text{Sn}) = 118.7 \text{ g mol}^{-1}; \quad M(\text{SnO}_2) = 150.7 \text{ g mol}^{-1}$$

$$\frac{m(\text{Sn})}{m(\text{SnO}_2)} = \frac{M(\text{Sn})}{M(\text{SnO}_2)}; \quad m(\text{Sn}) = \frac{118.7 \text{ g mol}^{-1} \times 0.3265 \text{ g}}{150.7 \text{ g mol}^{-1}} = 0.2571 \text{ g}$$

Mass percentage of tin (metal A) in the alloy:

$$w(\text{Sn}) = \frac{0.2571 \text{ g}}{1.2860 \text{ g}} = 0.1999 = 19.99 \%$$

The reactions taking place in the excess of aqueous ammonia solution:



Saturating of the solution with hydrogen sulphide:



Calculation of the cadmium content in the alloy:

$$M(\text{Cd}) = 112.4 \text{ g mol}^{-1}; \quad M(\text{CdS}) = 144.5 \text{ g mol}^{-1}$$

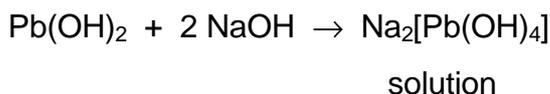
$$m(\text{Cd}) = \frac{112.4 \text{ g mol}^{-1} \times 0.6613 \text{ g}}{144.5 \text{ g mol}^{-1}} = 0.5143 \text{ g}$$

Mass percentage of cadmium (metal B) in the alloy:

$$w(\text{Cd}) = \frac{0.5143 \text{ g}}{1.2860 \text{ g}} = 0.3999 = 39.99 \%$$

The reactions taking place in the excess of sodium hydroxide solution:

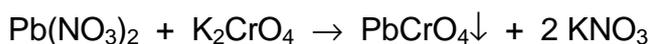
The action of excess sodium hydroxide on lead(II) and bismuth(III) hydroxides:



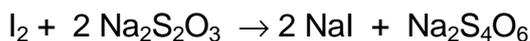
Acidification of the solution with nitric acid (pH = 5 – 6):



The reaction with K_2CrO_4 :



The reactions on which the quantitative determination of lead in $PbCrO_4$ precipitate is based:



Percentage of lead (metal C) in the alloy:

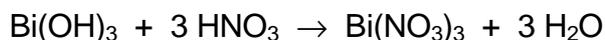
$$w(Pb) = \frac{c(Na_2S_2O_3) \times V(Na_2S_2O_3) \times M(Pb)}{m(\text{alloy}) \times 3}$$

(One Pb^{2+} ion corresponds to one CrO_4^{2-} ion which accepts 3 electrons in the redox reaction considered.)

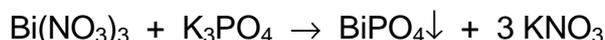
$$w(Pb) = \frac{0.1512 \text{ mol dm}^{-3} \times 0.01846 \text{ dm}^3 \times 207.2 \text{ g mol}^{-1}}{1.286 \text{ g} \times 3} = 0.1499 = 14.99 \%$$

In order to convert bismuth(III) hydroxide to phosphate it is necessary:

a) to dissolve the bismuth(III) hydroxide in an acid:



b) to precipitate Bi^{3+} ions with phosphate ions:



Calculation of the bismuth content in the alloy:

$$M(Bi) = 209 \text{ g mol}^{-1}; \quad M(BiPO_4) = 304 \text{ g mol}^{-1}$$

$$m(Bi) = \frac{209 \text{ g mol}^{-1} \times 0.4676 \text{ g}}{304 \text{ g mol}^{-1}} = 0.3215 \text{ g}$$

Percentage of bismuth (metal D) in the alloy:

$$w(Bi) = \frac{0.3215 \text{ g}}{1.2860 \text{ g}} = 0.2500 = 25.00 \%$$

Composition of the alloy: % Cd = 40, % Sn = 20, % Pb = 15, % Bi = 25

PROBLEM 3

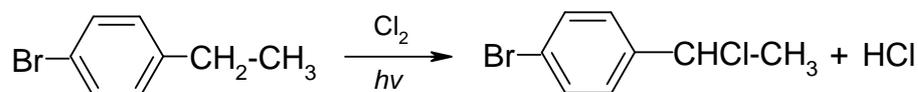
Which chemical processes can take place in the interaction of:

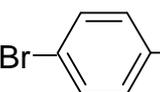
- aluminium ammonium sulphate with baryta water,
- potassium chromate, ferrous chloride and sulphuric acid,
- calcinated soda and sodium hydrogen sulphate,
- 4-bromoethyl benzene and chlorine,
- n-propyl alcohol, phenol and concentrated sulphuric acid?

Write ionic equations for the reactions that proceed in aqueous solutions. For the other chemical reactions write complete equations and indicate the type of the reaction. Indicate the differences in the reaction conditions for those reactions that may lead to the formation of various substances.

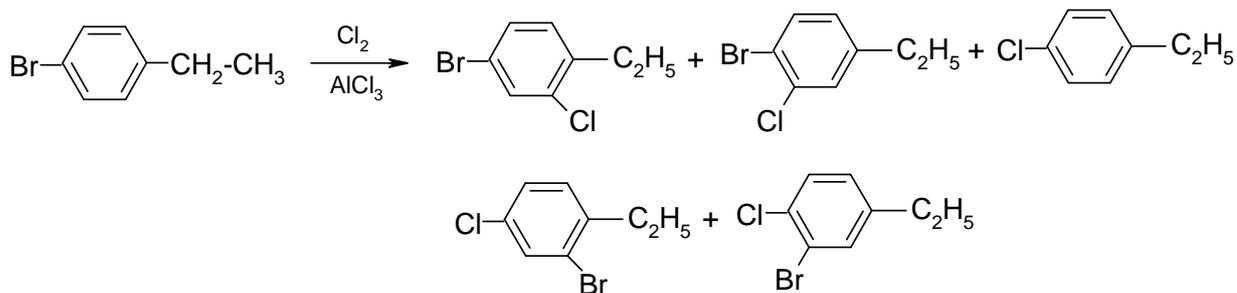
SOLUTION

- (a) a-1 $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \downarrow$
- a-2 $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O}$
- a-3 $\text{Al}^{3+} + 3 \text{OH}^- \rightarrow \text{Al}(\text{OH})_3 \downarrow$
- a-4 $\text{Al}(\text{OH})_3 + \text{OH}^- \rightarrow [\text{Al}(\text{OH})_4]^-$
- a-5 possibly: $\text{Ba}^{2+} + 2 [\text{Al}(\text{OH})_4]^- \rightarrow \text{Ba}[\text{Al}(\text{OH})_4]_2 \downarrow$
- (b) b-1 $2 \text{CrO}_4^{2-} + 2 \text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$
- b-2 $6 \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 6 \text{Fe}^{3+} + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$
- b-3 with high concentrations of Cl^- and H_2SO_4 :
 $\text{Cr}_2\text{O}_7^{2-} + 4 \text{Cl}^- + 6 \text{H}^+ \rightarrow \text{CrO}_2\text{Cl}_2 + 3 \text{H}_2\text{O}$
- (c) c-1 with excess of H^+ : $\text{CO}_3^{2-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{O} \cdot \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \uparrow$
- c-2 with excwss of CO_3^{2-} : $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$
- (d) d-1 free radical substitution (upon exposure to light or on heating)



small quantity of  and polychlorination

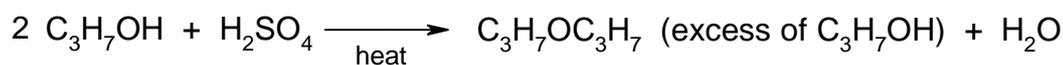
d-2 in the presence of electrophilic substitution catalysts:
and as side reaction products:



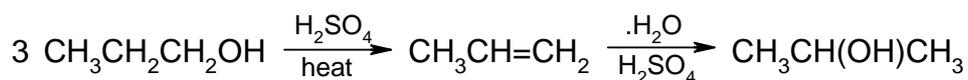
(e) e-1



e-2

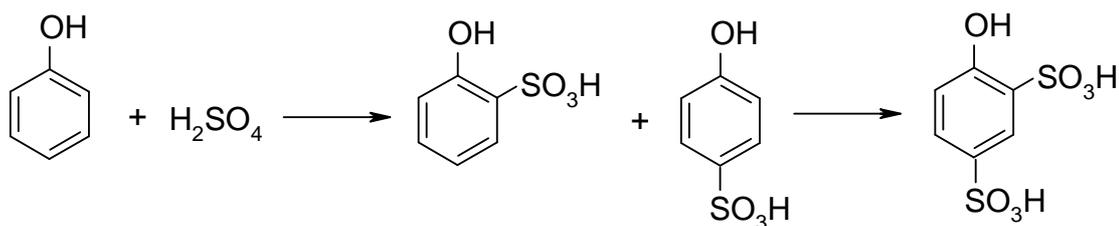


e-3

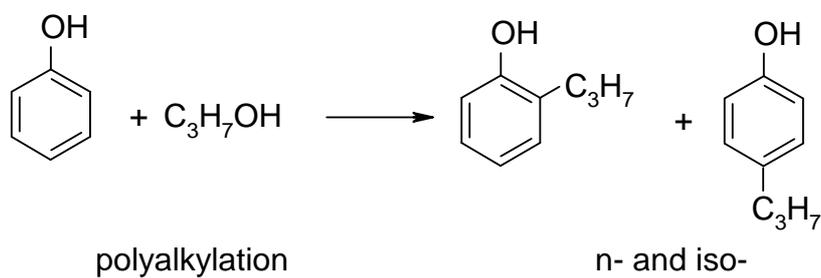


(in e-1 and e-2)

e-4



e-5



e-6 partial oxidation of C_3H_7OH and C_6H_5OH with subsequent condensation or esterification

PROBLEM 4

Compound **X** contains nitrogen and hydrogen. Strong heating of 3.2 g of **X** leads to its decomposition without the formation of a solid residue. The resulting mixture of gases is partially absorbed by sulphuric acid (the volume of the gaseous mixture decreased by a factor of 2.8). The non-absorbed gas, that is a mixture of hydrogen and nitrogen, occupies under normal conditions a volume of 1.4 dm³ and has a density of 0.786 g dm⁻³.

Determine the formula of compound **X**.

SOLUTION

If the density of the mixture of N₂ and H₂ is known, its composition can be determined as

$$0.786 \times 22.4 \times (n + 1) = 28n + 2$$

Hence $n = 1.5$. The mass of the mixture is $0.786 \text{ g dm}^{-3} \times 1.4 \approx 1.1 \text{ g}$. Consequently, the mixture of gases absorbed by sulphuric acid (these gases could be NH₃ and N₂H₄) had an average molar mass of

$$\frac{3.2 \text{ g} - 1.1 \text{ g}}{1.4 \text{ dm}^3 \times (2.8 - 1)} \times 22.4 \text{ dm}^3 \text{ mol}^{-1} \approx 18.67 \text{ g mol}^{-1}$$

while NH₃ corresponds to 17 g mol⁻¹.

This means that the absorbed gaseous products consist of a mixture of NH₃ and N₂H₄.

The composition of the absorbed fraction is

$$\frac{32 + 17n}{n + 1} = 18.67$$

$$n = 8, \text{ i. e. } 8 \text{ NH}_3 + \text{N}_2\text{H}_4.$$

As a result, the overall ratio of the components of the mixture is as follows:

8 NH₃ + N₂H₄ + 3 N₂ + 2 H₂ which corresponds to a composition of the initial substance **X**: N : H = (2 + 8 + 6) : (4 + 24 + 4) = 1 : 2.

The initial substance **X** is hydrazine N₂H₄.

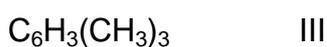
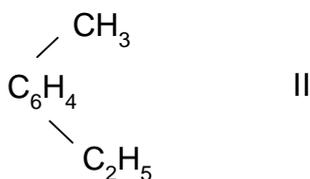
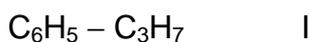
PROBLEM 5

Benzene derivative **X** has the empirical formula C_9H_{12} . Its bromination in the light leads to the formation of two monobromo derivatives in approximately identical yield. Bromination in the dark in the presence of iron also gives two monobromo derivatives. If the reaction is carried out to a higher degree, the formation of four dibromo derivatives may occur.

Suggest the structure for compound **X** and for the bromination products. Write schemes for the reactions.

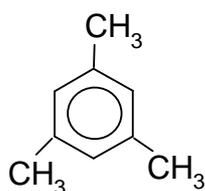
SOLUTION

The compound with the empirical formula C_9H_{12} can be:

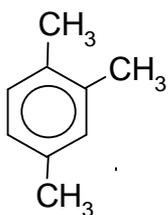


Under the action of bromine in the light without catalysts, bromination of the aliphatic portion will occur, predominantly on the carbon atoms bonded to the aromatic nucleus. When the reaction is conducted in the dark in presence of iron, the latter is converted to $FeBr_3$ and catalyzes the bromination of the aromatic ring.

Compound **X** cannot be **I** (as then only one monobromo derivative would be formed in the light); it cannot be one of the isomers IIIa, IIIb either.

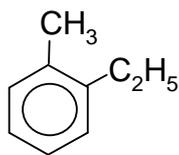


IIIa - Only one monobromo derivative is possible in the bromination of the CH_3 groups.

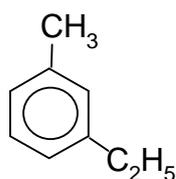


IIIb - Three different monobromo derivatives are possible under the same conditions.

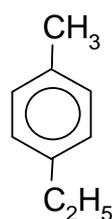
Thus, selection must be made from the following four structures:



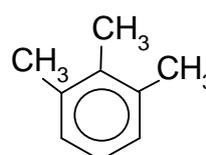
IIa



IIb



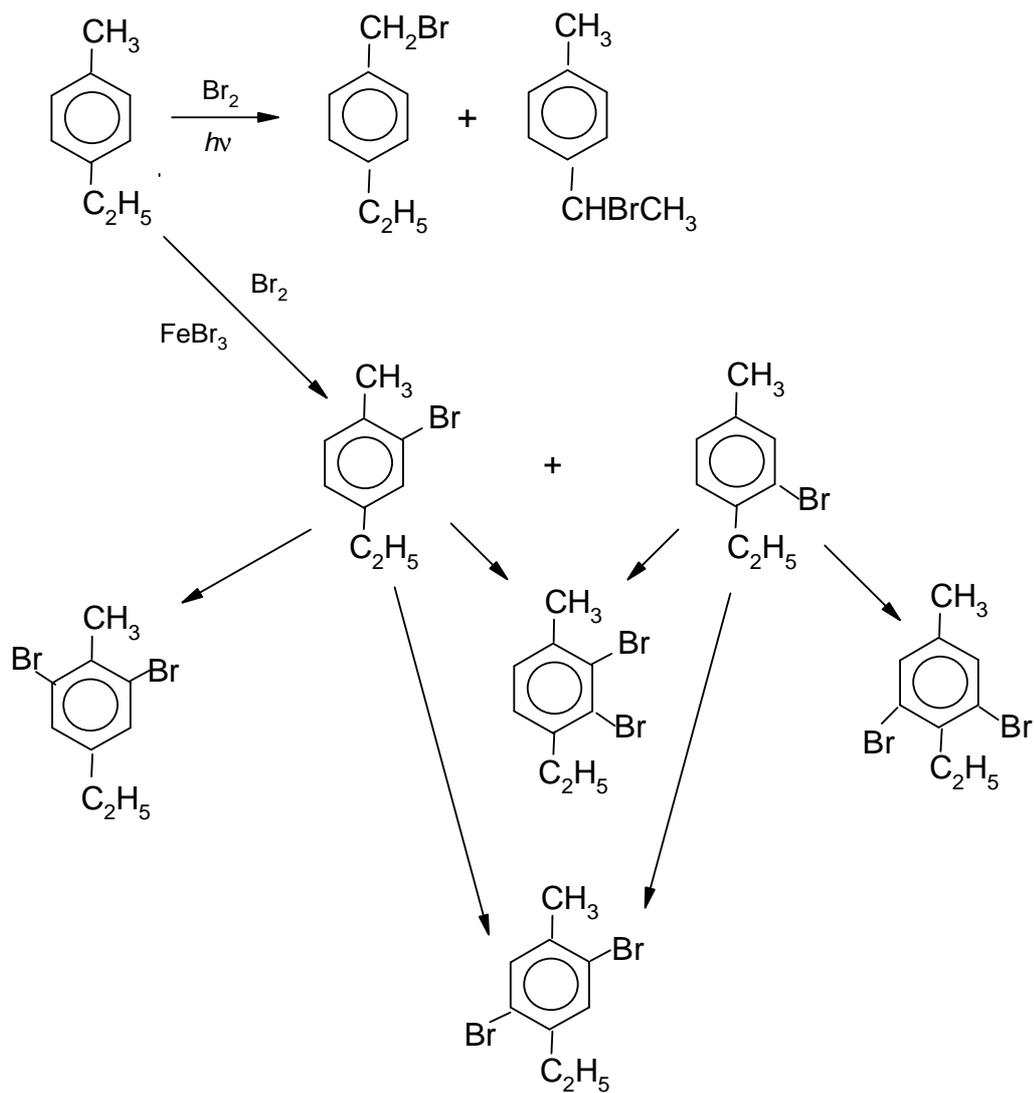
IIc



IIIc

The condition that two monobromo derivatives can be formed in the dark, rules out structures IIa and IIb. The condition of the possibility of four dibromo derivatives rules out structure IIIc. Hence, the only possible structure of compound **X** is IIc.

The scheme of the bromination reaction (next page):



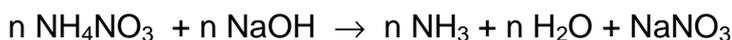
PROBLEM 6

130 g of an unknown metal M were treated with excess of a dilute nitric acid. Excess hot alkaline solution was added to the resulting solution and 1.12 dm³ of a gas evolved (normal conditions).

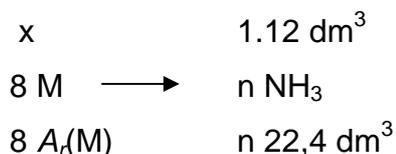
What metal M was dissolved in the nitric solution?

SOLUTION

The gas that evolved during the reaction with the alkaline solution was ammonia. Therefore, one of the products resulting from dissolution of the metal M in the acid is ammonium nitrate. Thus, the reaction equations will have the form:



Hence, the scheme:



where n is the valency of the metal (oxidation number of M^{n+}) and $A_r(M)$ is the relative atomic mass of the metal.

$$8 A_r(M) \Rightarrow 22.4 \times n$$

$$13 \text{ g} \Rightarrow 1.12 \text{ dm}^3$$

$$A_r(M) = \frac{13 \text{ g} \times 22.4 \text{ dm}^3 \times n}{8 \text{ g} \times 1.12 \text{ dm}^3} = 32.5 n$$

If	$n = 1$	then	$A_r(M) = 32.5$	no metal
	$n = 2$		$A_r(M) = 65$	zinc
	$n = 3$		$A_r(M) = 97,5$	none
	$n = 4$		$A_r(M) = 130$	none

Answer: The unknown metal is zinc.

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

10 numbered test tubes, 20 cm³ each, contain 0.1 M solutions of the following substances: barium chloride, sodium sulphate, potassium chloride, magnesium nitrate, sodium orthophosphate, barium hydroxide, lead nitrate, potassium hydroxide, aluminium sulphate, sodium carbonate. Using only these solutions as reagents, determine in which of the numbered test tubes each of the above given substances, is found.

Draw up a plan of the analysis and write equations of the reactions to be carried out. Do not forget to leave at least 2 cm³ of the solutions in each test tube for checking. If in the course of the analysis an additional quantity of a solution is needed, you may ask the teacher to give it to you but in such case you will lose some points.

SOLUTION

Table:

	BaCl ₂	Na ₂ SO ₄	KCl	Mg(NO ₃) ₂	Na ₃ PO ₄	Ba(OH) ₂	Pb(NO ₃) ₂	KOH	Al ₂ (SO ₄) ₃	Na ₂ CO ₃
BaCl ₂		↓	—	—	↓	—	↓	—	↓	↓
Na ₂ SO ₄	↓		—	—	—	↓	↓	—	—	—
KCl	—	—		—	—	—	↓	—	—	—
Mg(NO ₃) ₂	—	—	—		↓	↓	—	↓	—	↓
Na ₃ PO ₄	↓	—	—	↓		↓	↓	—	↓	—
Ba(OH) ₂	—	↓	—	↓	↓		↓	—	↓	↓
Pb(NO ₃) ₂	↓	↓	↓	—	↓	↓		↓	↓	↓
KOH	—	—	—	↓	—	—	↓		↓	—
Al ₂ (SO ₄) ₃	↓	—	—	—	↓	↓	↓	↓		↓
Na ₂ CO ₃	↓	—	—	↓	—	↓	↓	—	↓	

Using the table, the entire problem cannot be solved at once: all the precipitates are white and there are substances that form the same number of precipitates. From the number of precipitates only KCl (1), Mg(NO₃)₂ (4), and Pb(NO₃)₂ (8) can be determined immediately.

Furthermore, Na₂SO₄ and KOH (giving three precipitates each) can be differentiated via the reaction with Mg(NO₃)₂ (Mg(OH)₂).

Ba(OH)₂ and Al₂(SO₄)₃ (giving 6 precipitates each): through the reaction with KOH (Al(OH)₃).

BaCl₂, Na₃PO₄ and Na₂CO₃ (giving 5 precipitates each): first the reaction with Na₂SO₄ indicates BaCl₂. Then the reaction with BaCl₂: Al₂(SO₄)₃ yields AlCl₃ (BaSO₄ precipitate is filtered off). Evolution of CO₂ and formation of Al(OH)₃ in the reaction with AlCl₃ solution indicates Na₂CO₃.

PROBLEM 2 (practical)

Determine the mass of potassium permanganate in the solution you are given. You are provided with hydrochloric acid of a given concentration, a potassium hydroxide solution of an unknown concentration, an oxalic acid solution of an unknown concentration, and a sulphuric acid solution (2 N).

Equipment and reagents:

A burette for titration, indicators (methyl orange, litmus, phenolphthalein), pipettes (volumes 10, and 15 or 20 cm³), 2 volumetric flasks (250 cm³), 2 titration flasks (100 – 150 cm³).

12th



6 theoretical problems
3 practical problems

THE TWELFTH INTERNATIONAL CHEMISTRY OLYMPIAD 13–23 JULY 1980, LINZ, AUSTRIA

THEORETICAL PROBLEMS

PROBLEM 1

The dissociation of (molecular) chlorine is an endothermic process, $\Delta H = 243.6 \text{ kJ mol}^{-1}$. The dissociation can also be attained by the effect of light.

- 1.1 At what wavelength can the dissociating effect of light be expected?
- 1.2 Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?
- 1.3 What is the energy of the photon with the critical wavelength?

When light that can effect the chlorine dissociation is incident on a mixture of gaseous chlorine and hydrogen, hydrogen chloride is formed. The mixture is irradiated with a mercury UV-lamp ($\lambda = 253.6 \text{ nm}$). The lamp has a power input of 10 W. An amount of 2 % of the energy supplied is absorbed by the gas mixture (in a 10 litre vessel). Within 2.5 seconds of irradiation 65 millimoles of HCl are formed.

- 1.4 How large is the quantum yield (= the number of product molecules per absorbed photons)?
- 1.5 How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

SOLUTION

- 1.1 $\lambda_1 = \frac{c}{\nu_1}$ from $\Delta H = N_A h \nu_1$ it follows that

$$\lambda_1 = \frac{c N_A h}{\Delta H} = \frac{3 \cdot 10^8 \times 6.02 \cdot 10^{23} \times 6.6 \cdot 10^{-34}}{2.436 \cdot 10^5} = 4.91 \cdot 10^{-7} \text{ m} = 491 \text{ nm}$$

1.2 Short-wave light is effective, as its photons have a greater energy than required whereas the photons of longer-wavelength light are too poor in energy to affect the dissociation.

$$1.3 \quad E_1 = h \nu_1 = \frac{h c}{\lambda_1} = \frac{6.6 \times 10^{-34} \times 3 \cdot 10^8}{4.91 \cdot 10^{-7}} = 4.03 \cdot 10^{-19} \text{ J}$$

1.4 The quantum yield $\varnothing = \frac{\text{the number of HCl molecules formed}}{\text{the number of absorbed photons}}$

$$\varnothing = \frac{\frac{n(\text{HCl}) \times N_A}{\frac{E_{tot}}{h c}}}{\frac{0.2 \times 2.5}{\frac{6.6 \times 10^{-34} \times 3 \times 10^8}{2.536 \times 10^{-7}}}} = \frac{6.5 \times 10^{-2} \times 6.02 \times 10^{23}}{0.2 \times 2.5} = 6.1 \times 10^4$$

The energy input = $10 \times 0.02 = 0.2 \text{ W}$

1.5 The observed quantum yield is based on a chain mechanism.

The start of reaction chain: $\text{Cl}_2 + h\nu \rightarrow 2 \text{Cl}\bullet$

The propagation of the chain: $2 \text{Cl}\bullet + \text{H}_2 \rightarrow \text{HCl} + 2 \text{H}\bullet$

$\text{H}\bullet + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}\bullet$

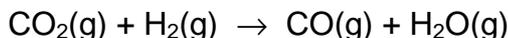
The chain termination mainly by: $2 \text{H}\bullet \rightarrow \text{H}_2$

$2 \text{Cl}\bullet \rightarrow \text{Cl}_2$

$\text{H}\bullet + \text{Cl}\bullet \rightarrow \text{HCl}$

PROBLEM 2Water gas equilibrium

The homogeneous gas reaction



is termed the water gas reaction.

Problems:

2.1 Calculate the Gibbs reaction energy, ΔG_{1000}^0 , for the water gas reaction at 1000 K from the reaction enthalpy: $\Delta H_{1000}^0 = 35040 \text{ J mol}^{-1}$ and the reaction entropy: $\Delta S_{1000}^0 = 32.11 \text{ J mol}^{-1} \text{ K}^{-1}$.

2.2 What is the value of the equilibrium constant K_p of the water gas reaction at 1000 K?

2.3 What are the values of the equilibrium constants K_x and K_c (x : mole fraction, c : concentration in mol dm^{-3} at the same temperature (1000 K)? (Note: The gas behaves ideally.)

2.4 A mixture of gases containing 35 vol. % of H_2 , 45 vol. % of CO and 20 vol. % of H_2O vapours is heated to 1000 K. What is the composition of the mixture after the establishment of the water gas equilibrium?

2.5 Calculate the reaction enthalpy value, ΔH_{1400}^0 , at 1400 K from the reaction enthalpy value, ΔH_{1000}^0 , and the values of the molar heat, c_p^0 , (valid in the temperature range 1000 K to 1400 K)

$$\Delta H_{1000}^0 = 35040 \text{ J mol}^{-1}$$

$$c_p^0(\text{CO}_2) = 42.31 + 10.09 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{H}_2) = 27.40 + 3.20 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{CO}) = 28.34 + 4.14 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{H}_2\text{O}) = 30.09 + 10.67 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\left(\text{It holds that } \int_a^b (c_1 + c_2 x) dx = c_1(b-a) + 0.5c_2(b^2 - a^2) \right)$$

2.6 What can you say on the basis of the above findings on ΔH^0 about the shift in the water gas equilibrium with increasing temperature?

SOLUTION

$$2.1 \quad \Delta H^{\circ}_{1000} = 35040 \text{ J}$$

$$\Delta S^{\circ}_{1000} = 32.11 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^{\circ}_{1000} = \Delta H^{\circ}_{1000} - T \Delta S^{\circ}_{1000} = 35040 - 1000 \times 32.11 = 2930 \text{ J}$$

$$2.2 \quad \Delta G^{\circ} = -RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G^{\circ}}{RT} = -\frac{2930}{8314} = -0.352418$$

$$K_p = 0.7030$$

2.3 As the numbers of moles do not change in the reaction, the reaction is independent on the concentration and pressure and therefore, $K_x = K_p = K_c$ (dimensionless). Volume fraction and mole fraction are identical in an ideal gas.

2.4 The original composition of the gas:

$$x_{0,\text{CO}} = 0.45; \quad x_{0,\text{H}_2} = 0.35; \quad x_{0,\text{H}_2\text{O}} = 0.20; \quad x_{0,\text{CO}_2} = 0.00;$$

If the mole fraction of the CO_2 formed at the equilibrium is denoted as x then the equilibrium concentrations can be obtained from:

$$\text{CO:} \quad x_{0,\text{CO}} - x$$

$$\text{CO}_2: \quad x$$

$$\text{H}_2\text{O:} \quad x_{0,\text{H}_2\text{O}} - x$$

$$\text{H}_2: \quad x_{0,\text{H}_2} + x$$

$$K_p = K_x = \frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} x_{\text{H}_2}} = \frac{(x_{0,\text{CO}} - x)(x_{0,\text{H}_2\text{O}} - x)}{x(x_{0,\text{H}_2} + x)} = 0.703$$

$$(x_{0,\text{CO}} - x)(x_{0,\text{H}_2\text{O}} - x) = K(x_{0,\text{H}_2} + x)x$$

$$x_{0,\text{CO}} x_{0,\text{H}_2\text{O}} - x(x_{0,\text{H}_2\text{O}} + x_{0,\text{CO}}) + x^2 = K x x_{0,\text{H}_2} + K x^2$$

where $K = K_x$

$$x^2(1 - K) - x(x_{0,\text{H}_2\text{O}} + x_{0,\text{CO}} + K x_{0,\text{H}_2}) + x_{0,\text{CO}} x_{0,\text{H}_2\text{O}} = 0$$

On substitution of the numerical values,

$$x^2(1 - 0.703) - x(0.20 + 0.45 + 0.703 \times 0.35) + 0.45 \times 0.20 = 0$$

$$0.297 x^2 - 0.89605 x + 0.09 = 0$$

$$x^2 - 3.01703 x + 0.303030 = 0$$

$$x_{1,2} = 1.508515 \pm \sqrt{2.275618 - 0.303030} = 1.508515 \pm \sqrt{1.972588}$$

$$x = 1.508515 \pm 1.404488 = 0.104027$$

(The plus sign leads to a solution that has no physical significance, $x > 1$.)

$$x = 0.104$$

$$x_{\text{CO}} = 0.346; \quad x_{\text{H}_2} = 0.454; \quad x_{\text{H}_2\text{O}} = 0.096; \quad x_{\text{CO}_2} = 0.104;$$

$$2.5 \quad \Delta C_p^0 = C_p^0(\text{CO}) + C_p^0(\text{H}_2\text{O}) - C_p^0(\text{CO}_2) - C_p^0(\text{H}_2)$$

$$= -11.28 + 1.52 \times 10^{-3} \text{ T J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta H_{1400}^0 &= \Delta H_{1000}^0 + \int_{1000}^{1400} C_p^0 dT = \Delta H_{1000}^0 + \int_{1000}^{1400} (c_1 + c_2 T) dT \\ &= \Delta H_{1000}^0 + c_1 (1400 - 1000) + 0.5 c_2 (1.96 \times 10^6 - 1 \times 10^6) = \\ &= \Delta H_{1000}^0 - 11.28 \times 400 + (1.52 \times 10^{-3} \times 4.8 \times 10^5) = \\ &= \Delta H_{1000}^0 - 4512 + 729.6 = \\ &= 35040 - 4512 + 729.6 = 31258 \text{ J} \end{aligned}$$

On the basis of the van't Hoff reaction isobar

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H}{RT^2}$$

2.6 $\ln K_p$ increases with increasing temperature for positive (endothermic) heat of reaction, i.e. the equilibrium shifts with increasing temperature in favour of the reaction products, CO and H₂O.

PROBLEM 3

(Chemistry of ions, stoichiometry, redox reactions)

A white crystalline solid compound **A** exhibits the following reactions:

- 1) The flame of a Bunsen burner is intensively yellow coloured.
- 2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an SO₂ solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
- 3) If an AgNO₃ solution is added to the discoloured solution obtained by 2) and acidified with HNO₃, a yellow precipitate is obtained that is insoluble on addition of NH₃, but can be readily dissolved by adding CN⁻ or S₂O₃²⁻.
- 4) If an aqueous solution of **A** is treated with KI and dilute H₂SO₄ a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a Na₂S₂O₃ solution.
- 5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g KI and a few cm³ of dilute H₂SO₄ are added. The deep brown solution formed is titrated with 0.1000 M Na₂S₂O₃ solution until the solution is completely discoloured. The consumption is 37.40 cm³.

Problems:

- 3.1 What elements are contained in the compound **A**?
- 3.2 What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.
- 3.3 Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.
- 3.4 Decide on the basis of 5) which compound is present.

SOLUTION

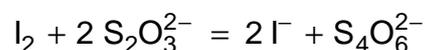
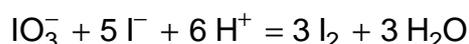
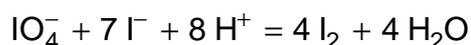
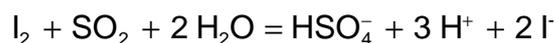
- 3.1 The solid must contain Na and I. The yellow colouration of the flame of the Bunsen burner indicates the presence of Na. A yellow silver salt that is dissolved only by strong complexing agents such as CN⁻ or S₂O₃²⁻, must be AgI.
- 3.2 Reactions 1) to 4) indicate an Na salt of an oxygen containing acid of iodine:

Both SO_2 and I^- are oxidised. While in the first case I^- is formed with an intermediate of I_2 (or I_3^- , brown solution), in the second I_2 (or I_3^-) is formed.

As the solution of **A** is neutral, NaIO_3 and NaIO_4 come into consideration.

$$M(\text{NaIO}_3) = 22.99 + 126.905 + 3 \times 16.000 = 197.895 = 197.90 \text{ g mol}^{-1}$$

$$M(\text{NaIO}_4) = 22.99 + 126.905 + 4 \times 16.000 = 213.895 = 213.90 \text{ g mol}^{-1}$$



1st hypothesis: The compound is NaIO_3 .



$$0.1000 \text{ g } \text{NaIO}_3 \text{ } \frac{0.1000 \times 6}{197.90} = 3.032 \times 10^{-3} \text{ moles } \text{S}_2\text{O}_3^{2-}$$

The hypothesis is false.

2nd hypothesis: The compound is NaIO_4 .



$$0.1000 \text{ g } \text{NaIO}_4 \text{ } \frac{0.1000 \times 8}{213.90} = 3.740 \times 10^{-3} \text{ moles } \text{S}_2\text{O}_3^{2-}$$

The compound **A** is NaIO_4 .

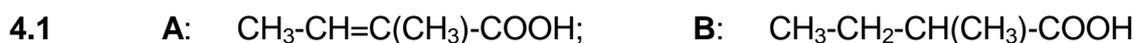
PROBLEM 4

(Organic chemistry, stereochemistry)

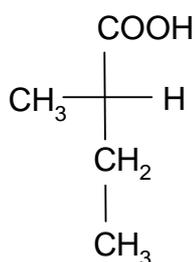
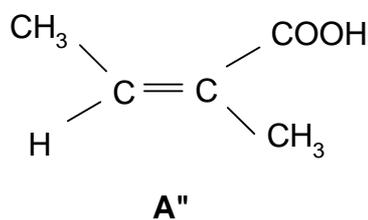
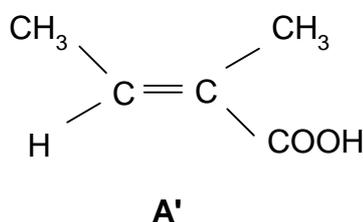
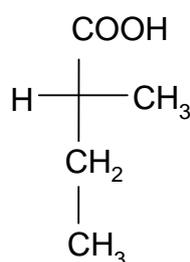
Carbonic acid **A** with an overall formula of $C_5H_8O_2$ yields two geometric isomers, cis (**A'**) and trans (**A''**). On hydrogenation with Pt/H_2 the same racemic carboxyl acid **B** is obtained from both stereoisomers that can be separated into enantiomers (+)-**B** and (-)-**B**. **A'** and **A''** rapidly react with one mole of bromine in CCl_4 in the dark at 20 °C to yield **C**.

Problems:

- 4.1 What is the constitution of **A** and **B**?
- 4.2 Write the stereo formulae for **A'** and **A''** and the Fischer projection formulae for the enantiomer **B** (not considering the signs (+) or (-)).
- 4.3 How many stereo isomers of **C** are simultaneously formed when **A'** and **A''** are treated with bromine?
- 4.4 Briefly, give reasons for your answer to c).
- 4.5 Write the Fischer projection formulae and one Newman projection formula (conformation) for all the stereoisomers of **C**. Denote those that are mutually enantiomeric and diastereoisomeric.

SOLUTION

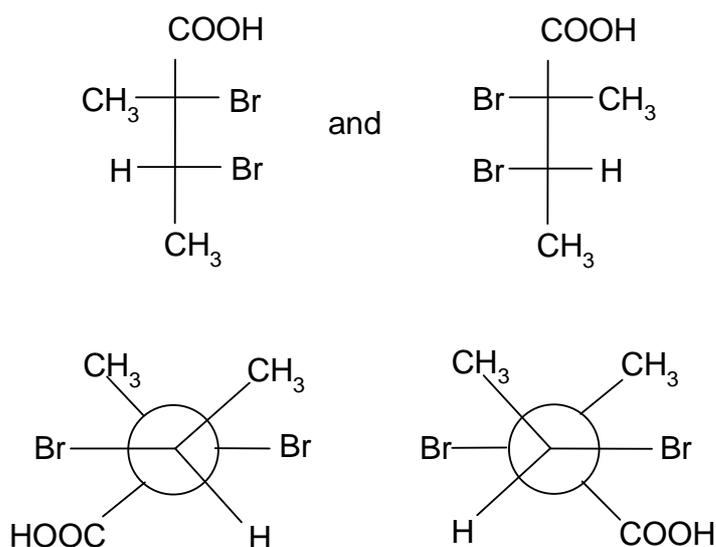
4.2

**B**

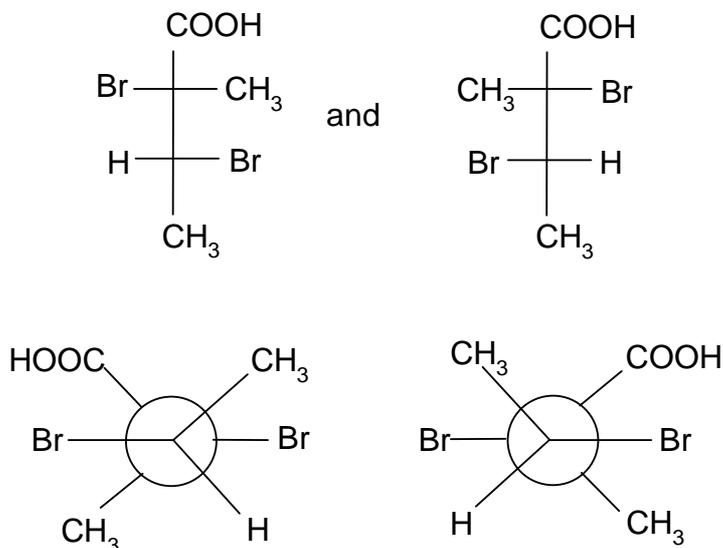
4.3 Always two (see e): 1 to 4

4.4 The addition of bromine to the alkene gives trans compound under the given conditions. On the addition, two (non-identical) asymmetrical C atoms (chirality centres) are formed yielding together $2^2 = 4$ stereo isomers of which always two are mutually enantiomeric.

4.5 from A':



from A'':



1 and 2 or 3 and 4 are enantiomeric. 1 to 3 and 4, and 2 to 3 and 4 are diastereomeric

PROBLEM 5

(Inorganic chemistry)

From 20 mg of partially methylated disilane, $\text{Si}_2\text{H}_{6-x}(\text{CH}_3)_x$, 27.8 cm³ of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

- 5.1 Why the Si-Si bond of the disilane reacts during hydrolysis?
- 5.2 Why the Si-H bonds of the disilane react during hydrolysis?
- 5.3 Calculate the degree of substitution x of the methylated disilane.
- 5.4 Write the complete reaction equation for the hydrolysis.
- 5.5 How many isomers can form the calculated compound? Give the structural formula for each isomer.

SOLUTION

- 5.1 The Si-Si bond is coordination unsaturated and thus, has a tendency to react with nucleophilic reagents with the bond breakage.
- 5.2 Similar to all compounds with negatively polarised hydrogen, this bond also reacts with protons from water with formation of elemental hydrogen.

5.3 $(\text{CH}_3)_x\text{Si}_2\text{H}_{6-x}$

$$\begin{array}{ll} \text{Molecular mass:} & 2 \text{ Si} \quad 2 \times 28.086 \\ & (6-x) \text{ H} \quad (6-x) \times 1.008 \\ & x \text{ CH}_3 \quad x \times 15.035 \\ & 56.172 + 1.008 (6 - x) + 15.035 x = 62.22 + 14.027 x \end{array}$$

$$\text{Sample mass: } 20 \text{ mg} \Rightarrow \frac{20}{62.22 + 14.027 x} \text{ mmol}$$

$$\text{Hydrogen evolved: } n = \frac{pV}{RT} \text{ mmol H}_2 \text{ (V in cm}^3\text{)}$$

$$n = \frac{0.974 \times 27.8}{0.08314 \times 294} \text{ mmol}$$

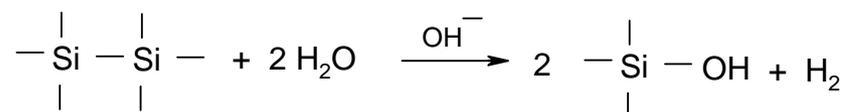
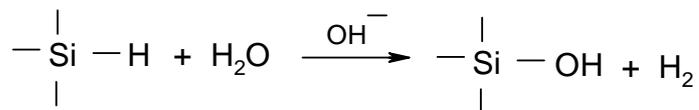
(SiH) (SiSi)

$$(6 - x + 1) \times \frac{20}{62.22 + 14.027 x} = \frac{0.974 \times 27.8}{0.08314 \times 294}$$

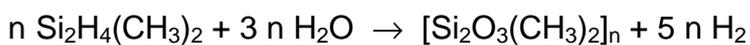
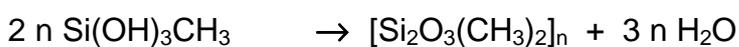
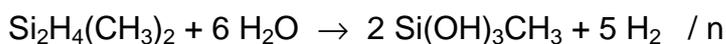
$$x = 1.9999$$

Hence, the degree of substitution = 2

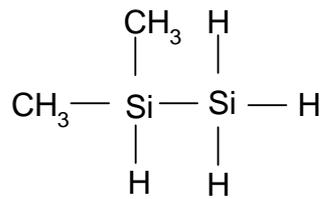
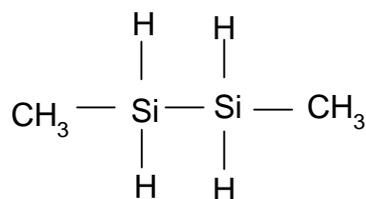
5.4



Hence (for a symmetrical isomer):



5.5 Two:



PROBLEM 6

(Organic chemistry, syntheses)

Benzaldehyde and malonic acid reacted in pyridine at 80 °C yielding (among others) CO₂ and compound **A** in a yield of ca. 80 % of the theoretical value. Catalytic hydrogenation of 1.48 g **A** on Pt at room temperature and normal pressure yielded **B** with a consumption of 0.25 litre of hydrogen. On reaction of **B** with a polyphosphoric acid (the Friedel-Crafts' conditions) compound **C** can be isolated accompanied by two acidic, isomeric side products. The side products **Da** and **Db** can be formed in a greater amount at a high concentration of **B** in the reaction medium, and can be suppressed by dilution.

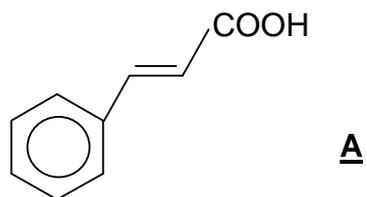
The elemental analysis of **C** yields 81.8 % of carbon and 6.1 % of hydrogen. The corresponding values for **Da** and **Db**, identical within the experimental error, are 76.6 % and 6.4 %, respectively. An amount of 2.82 g **Da**, as well as **Db** requires ca. 100 cm³ 0.1 N potassium hydroxide solution for its neutralization. **C** can be purified by distillation (b. p. 243 – 245 °C) and then exhibits a melting point of 40 °C and density of 1.09 g/cm³. The relative molecular mass can be obtained by mass spectrometry and its value is 132.

Using this information solve the following problems:

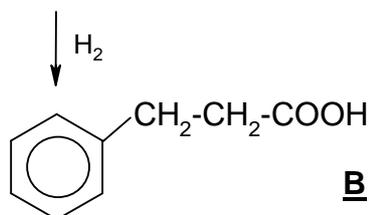
- 6.1 The structural formula of **A**.
- 6.2 The structural formula of **B**.
- 6.3 The structural formula of **C**.
- 6.4 The structural formulae of **Da** and **Db**.
- 6.5 Give an alternative pathway for the synthesis of **A** using the simplest possible starting materials and forming at least one C–C bond.
- 6.6 Give an alternative pathway for the synthesis of **B** using the simplest possible starting materials and forming at least one C–C bond.
- 6.7 Give structural formulae for the products of the following reactions:
 - a) **C** + hydroxylamine (with acid catalysis) →
 - b) **C** + phenylmagnesium bromide (C₆H₅MgBr) and subsequent treatment under acidic conditions →
 - c) **C** + benzaldehyde + C₂H₅O[−] Na⁺ →

SOLUTION

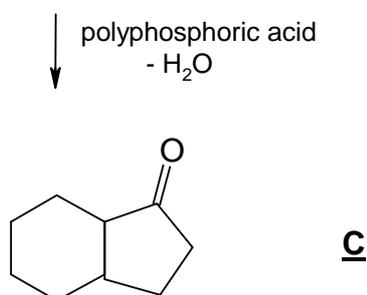
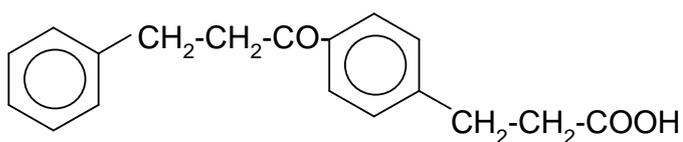
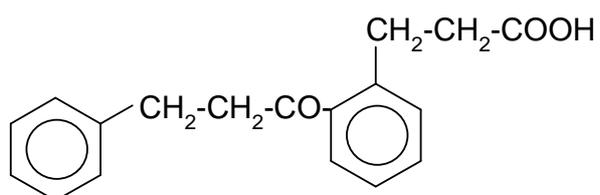
6.1 Condensation



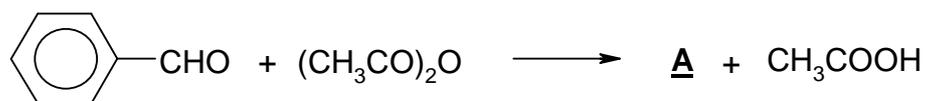
6.2 Hydrogenation



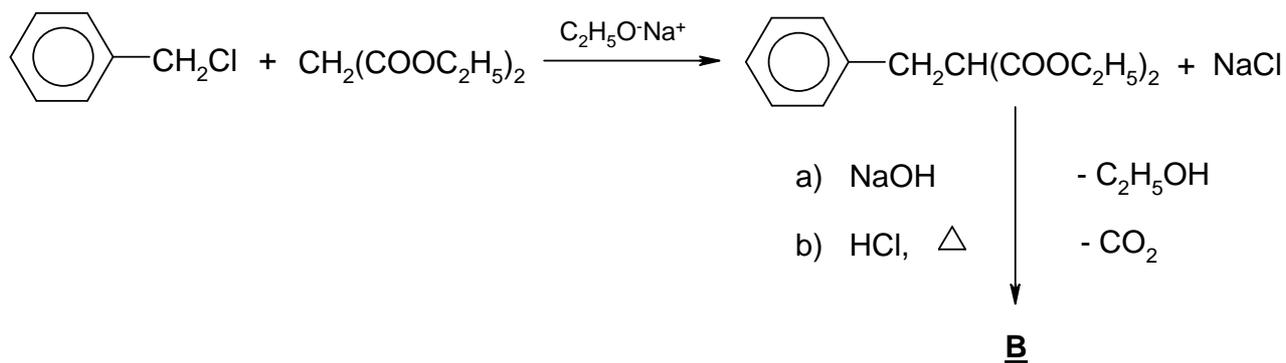
6.3 Intramolecular cyclization

6.4 In addition to **C** two positional isomers **Da** and **Db** are formed.

6.5 For example, Perkin reaction: Treatment of benzaldehyde with acetic acid anhydride:

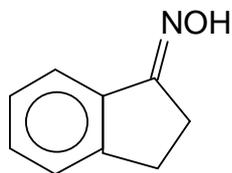


6.6 For example, by malonic ester synthesis

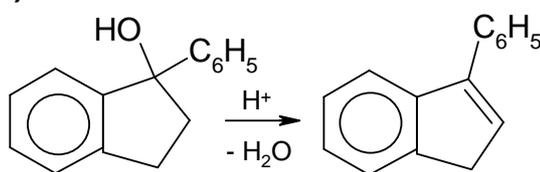


6.7 Reactions a), b), and c) are typical reactions of the carbonyl group.

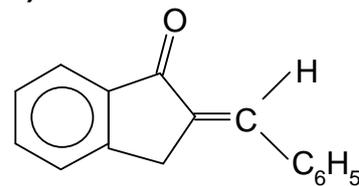
a)



b)



c)



(E)

two stereoisomers
(syn and anti)

two stereoisomers

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Qualitative organic analysis

Four different substances that all occur in the nature, are present in 4 test tubes. Find two substances that form basic components of fodders and human foodstuff. Only these two substances are to be identified. Propose the names and structural formulae for those two substances on the basis of combustion tests, solubility experiments, identification of the functional groups and the determination of the melting point.

As an aid the following can be used:

A table of melting points, the Thiele apparatus for melting point determination, a solubility scheme and the following reagents:

diethyl ether, NaHCO₃ (5 %), NaOH (2 M), HCl (2 M), H₂SO₄ conc., H₃PO₄ conc., ethanol, Tollens' reagents, (an ammoniac Ag solution), Fehling's solution I and II, phenylhydrazine hydrochloride, β-naphthol, NaNO₂ (solid) Ca(OH)₂ sat., FeCl₃ (5 %), ice, 2,4-dinitrophenylhydrazine, ninhydrine solution (1 % alk.), Seliwanoff's reagent (resorcinol/HCl), phloroglucine.

The requirements: An exact description of the experiments, reaction equations (or reaction schemes where the equation cannot be given) for the reaction required for the identification, the names and the structural formulae of the two test substances.

APPENDIX 1

Determination of the melting point by the Thiele apparatus

A finely pulverized sample is placed in a capillary that is sealed at one side, to a height of 2 – 4 mm. To fill the capillary, it is immersed in the sample. The sample is cautiously wiped off the capillary walls and the content of the capillary is brought to the bottom by cautious tapping. Then the capillary is placed in the opening so that the sample is at the height of the mercury bead of the thermometer. As the heat transmitter, suitable high-boiling silicone oil is used in this apparatus.

To determine the melting point of an unknown organic substance, an approximate melting range is sought first. Thus the heating is carried out according to the figure at about 5 °C/min. For an exact determination another sample is brought about 10 °C below the determined melting range at about 5 °C/min and then the temperature is very slowly, 1 – 2 °C/min., brought to complete melting. The temperature, at which the substance is clearly melted, is taken as the melting point.

APPENDIX 2

Tables of melting points (MP, in °C) and boiling points (BP, in °C)

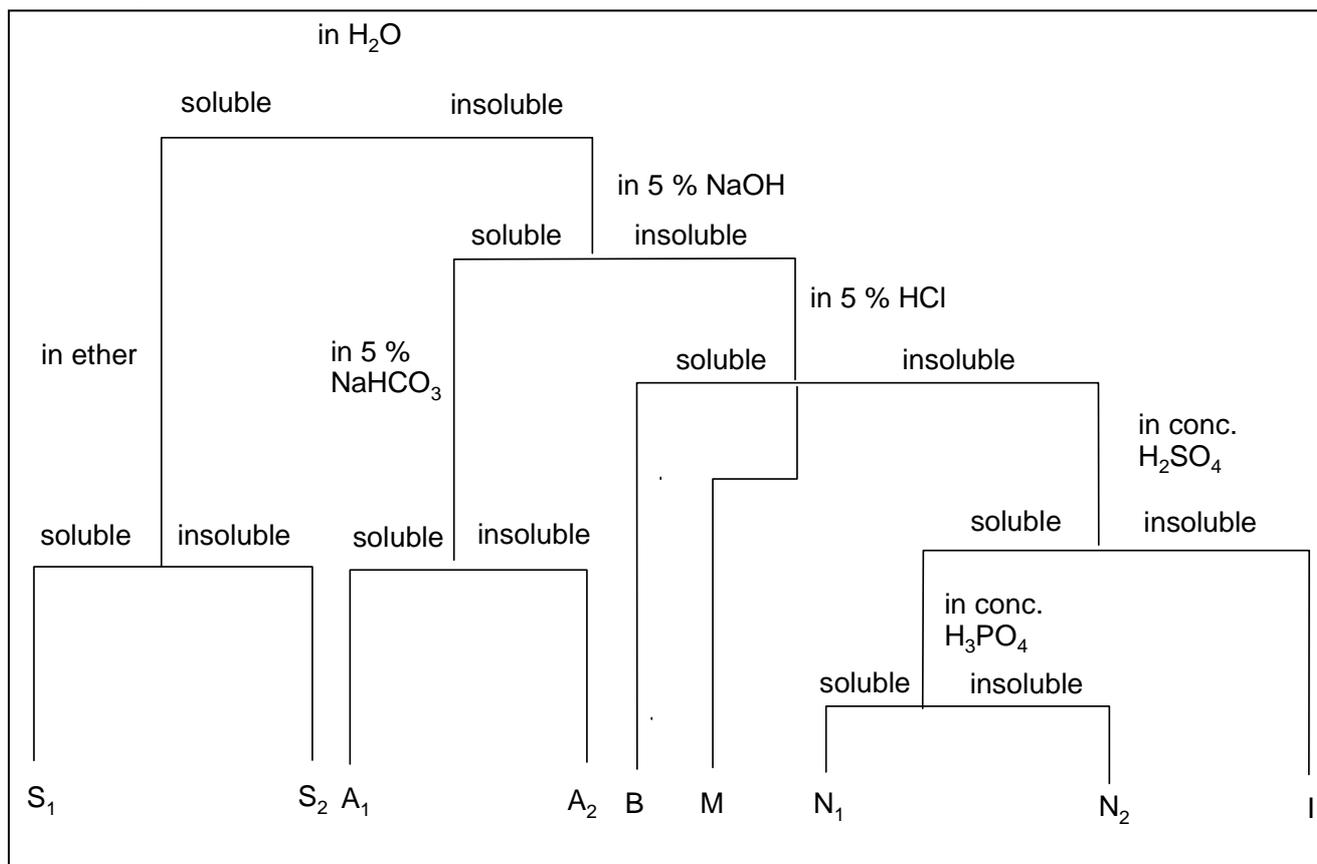
Compound	MP	BP	Compound	MP	BP
ALDEHYDES					
Pentanal	-	103	Acrolein	-	52
Benzaldehyde	-	179	Furfurol	-	161
Salicylaldehyde	-	196	o-Chlorobenzaldehyde	11	214
o-Nitrobenzaldehyde	44	-	α-Naphthaldehyde	34	-
p-Dimethylamino-benzaldehyde	74	-	Vanillin	81	-
ALCOHOLS					
tert.-Butanol	25	82	Propanol-1	-	97
n-Pentanol	-	136	Ethyleneglycol	-	197
Cyclohexylalcohol	-	160	Butanediol-1,4	-	230
Triphenylcarbinol	165	-	Glycerine	-	290
AMINES					
Diethylamide	-	56	Morpholine	-	130
Cyclohexylamine	-	134	α-Naphthylamine	50	300
Aniline	-	184	p-Bromoaniline	66	-
Diphenylamine	54	-	m-Nitraniline	114	-
o-Phenylenediamine	102	-	p-Aminophenol	186 D	-
ACIDS					
Palmitic acid	63	-	n-Valeric acid	-	186
Stearic acid	70	-	Oleic acid	14	222
Oxalic acid (. 2 H ₂ O)	101	-	Mandelic acid	118	-
Acetylsalicylic acid	135	-	Benzoic acid	122	-
Phthalic acid	203	-	Malonic acid	135	-
Anthranilic acid	146	-	S-Naphthoic acid	185	-
Glycine	232 D	-	p-Hydroxybenzoic acid	215	-

HALOGENDERIVATIVES					
n-Butyl bromide	-	100	p-Dichlorobenzene	53	-
Cyclohexyl iodide	-	179	p-Bromotoluene	28	185
Trichloroethylene	-	67	Hexachlorobenzene	230	-
KETONES					
Diethyl ketone	-	102	Methylisobutyl ketone	-	118
Cyclohexanone	-	156	Acetophenone	20	202
Benzophenone	49	-	p-Bromoacetophenone	51	-
Benzil	95	-	dl-Camphor	178	-
CARBOHYDRATES					
d-Ribose	95 D	-	β -Maltose	165	-
α -d-Glucose	146	D	β -d-Fructose		
Saccharose	180	-	α -Lactose		
HYDROCARBONS					
n-Heptane	-	99	Pentene-2	-	36
cis-Decaline	-	194	Cyclohexene	-	84
Cumol	-	216	Diphenyl	70	-
Anthracene	216	-	Styrene	-	146
MERCAPTANS – THIOPHENOLS					
n-Amylmercaptan	-	126	p-Thiocresol	-	200
Thiophenol	-	169	p-Bromothiophenol	74	-
PHENOLS					
p-Cresol	36	200	o-Nitrophenol	45	-
α -Naphthol	94	-	Resorcinol	110	-
Pyrocatechol	105	-	β -Naphthol	123	-
Picric acid	122	-	Phloroglucine	218	-
ACID DERIVATIVES					
Acetyl bromide	-	77	Acetamide	82	-
Butyric acid chloride	-	102	N-Methylacetanilide	102	-
4-Nitrobenzoylchloride	73	-	Urea	132	-
Butyric acid ethylester	-	121	Sodium formate	255	-
Malonic acid diethylester	-	199	Al-Acetate	200 – 320 D	-
Palmitic acid cetylester	54	-	Ba-Propionate	ca. 300	-

D after the number denotes decomposition.

APPENDIX 3

Solubility scheme



S₁: Substances with higher volatility;

All low molecular alcohols, aldehydes, ketones, acids, amines, nitriles and acid chlorides.

S₂: Substances with low volatility, often distillable without decomposition: polyols, salts, hydroxyaldehydes and hydroxyketones, carbohydrates, amino- and hydroxyl acids.

A₁: Substances with low volatility: higher molecular acids, nitrophenols.

A₂: Substances with high boiling points: Phenols, primary and secondary nitro compounds, sulfonamides, weak acids.

B: Substances with high boiling points, distillable with water vapour: Basic compounds, amines (with maximum of a few aryl groups), hydrazine.

M: Low volatility substances:

Neutral compounds, tertiary nitro compounds, nitroaniline, azo- and azoxy compounds, nitrito-, nitrate-, sulphuric-, and phosphoric acid esters.

N₁: Substances with small volatility:

Alcohols, aldehydes, methyl ketones and esters with less than 9 C atoms, neutral compounds, ethers, olephins.

N₂: Substances with a very low volatility:

Alcohols, aldehydes, ketones, esters and thioalcohols with more than 9 C atoms, neutral compounds, ethers, olephins.

I: Substances with low boiling point:

Inert compounds, hydrocarbons, halogenoalkanes.

APPENDIX 4

Preparation of the reagents

Tollen's reagent

Mix 0.5 cm³ 2 M NaOH + 1 cm³ 0.1 M AgNO₃ in 2 M NH₃.

Fehling's reagent

I: 1.73 g CuSO₄ · 5 H₂O in 25 cm³ of water

II: 8.5 g Seignette salt + 2.5 g NaOH in 25 cm³ H₂O

Seliwanoff's reagent

125 g resorcinol is dissolved in 250 cm³ of diluted HCl (83 cm³ conc. HCl + 167 cm³ H₂O), preparing only a necessary amount.

Phenylhydrazine solution

0.5 g of phenylhydrazine hydrochloride + 0.5 cm³ glacial acetic acid in 2 cm³ H₂O are shaken until a clear solution is obtained.

2,4-dinitrophenylhydrazine solution,

2 cm³ of conc. H₂SO₄ are added to 0.4 g of 2,4-dinitrophenylhydrazine and then, with stirring and shaking, 3 cm³ of H₂O are added. To the warm solution, 10 cm³ of 95 % ethanol are added.

SOLUTION

In the four test tubes, pure sodium chloride, D-fructose, palmitic acid (hexadecanoic acid), and vanillin were present. D-fructose, as a building block of cane sugar, and palmitic acid, as the building block of most animal and plant fats, were identified.

a) *Fructose*

Melting range: 102 – 105 °C

Combustion test: Carbonizes during combustion with caramel smell.

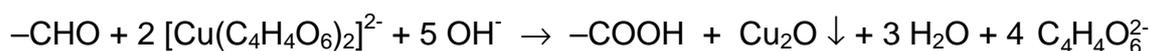
Solubility: Readily soluble in water, insoluble in diethyl ether.

Identification of the functional groups:

Aldehydic group:

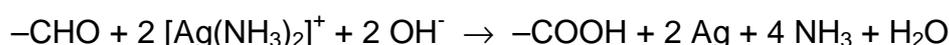
1. With Fehling's reagent

The oxidation of the carbonyl group with simultaneous reduction of Cu(II) to Cu(I).

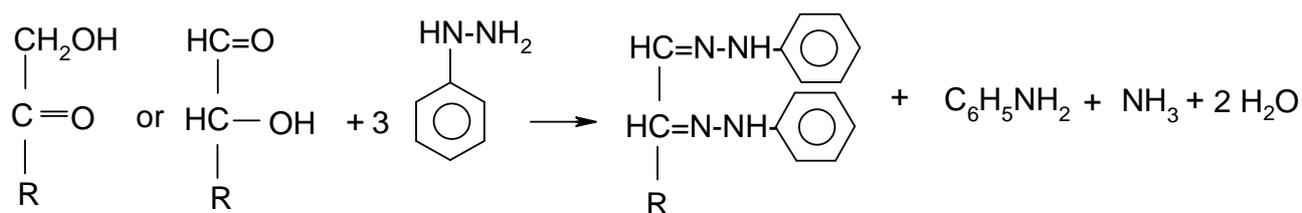


2. With Tollen's reagent

The oxidation to the carboxyl group with simultaneous reduction of Ag(I) to Ag.



Osazone formation (indication of monoses)



Ketose

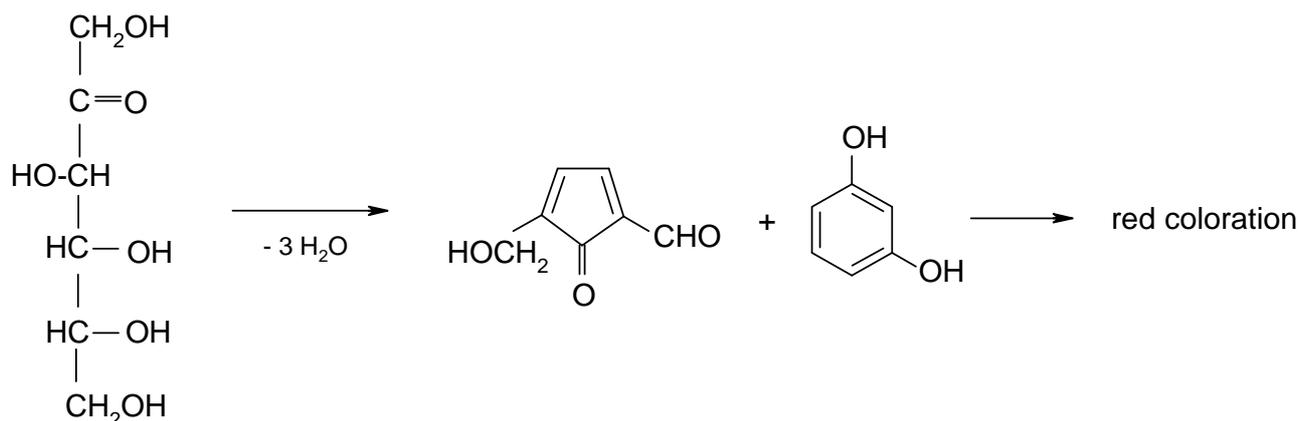
Aldose

Phenyl-
hydrazine

Osazone

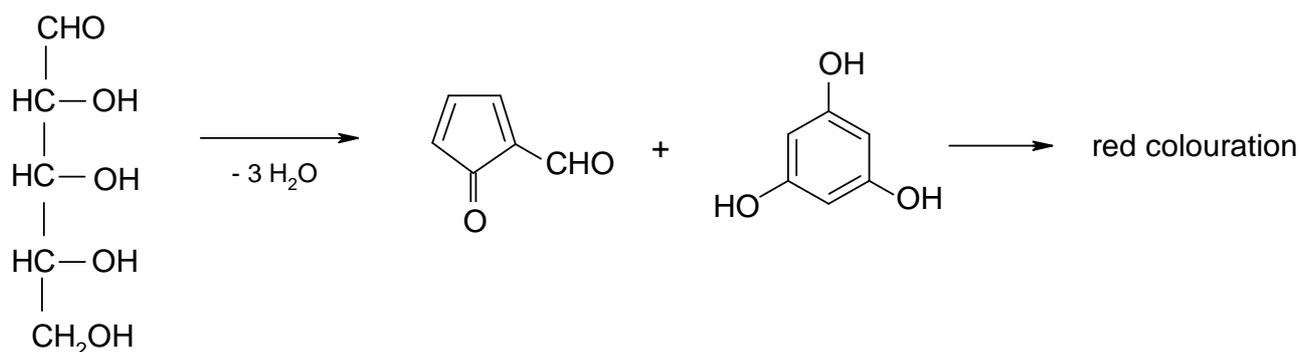
Test for ketohexoses (Saliwanoff's reaction)

Ketohexoses form, with heating in acidic solution, 5-hydroxy-methylfurfural that condenses with resorcinol to red-coloured substances.

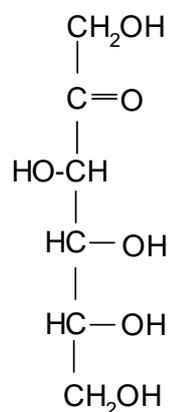


Test for pentoses (Tollens test)

Pentoses, in contrast to hexoses, form furfural in acidic solution that condenses with phloroglucine to give red coloured substances.



Name: The above reactions, the solubility behaviour and the melting range indicate that this substance is D-fructose, a building block of cane sugar.



When giving the configuration, use the Fischer projection.

b) Palmitic acid

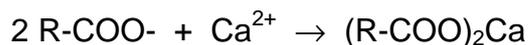
Melting range: 60 – 63 °C

Combustion test: Burns with yellowish, slightly smoking flame.

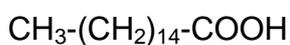
Solubility: Insoluble in water, very well soluble in 2 M NaOH, less soluble in 5 % NaHCO₃.

Identification of the functional groups:

From alkaline solution a colourless substance is precipitated by Ca²⁺:



On the basis of flammability the solubility behaviour and the precipitation of the calcium salt from alkaline solution one can conclude that the substance is an organic carboxyl acid. The melting range indicates palmitic acid = hexadecanoic acid.



PROBLEM 2 (practical)

In 10 reagent bottles are 10 different pure metal samples. By evaluating the solubility and by the following identification, only the six following elements are to be specified by their sample numbers:

calcium, iron, aluminium, zinc, magnesium, tin.

It is expected to specify:

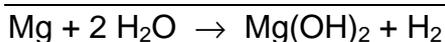
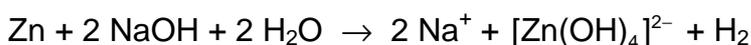
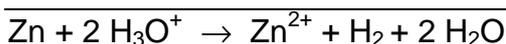
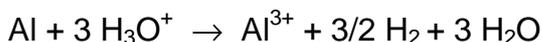
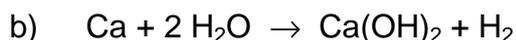
- the symbol of the identified metal and the corresponding bottle number,
- a reaction equation for dissolution of each of the six metals,
- an unambiguous verbal proof or a proof in the form of a chemical equation.

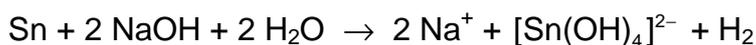
The following chemicals are at disposal:

HCl conc., HCl (2 M), H₂SO₄ (2 M), CH₃COOH (2 M), NaOH (2 M), NH₃ (2 M), NH₄SCN (0.2 M), CH₃COONa (conc.), 3 % H₂O₂, Na₂CO₃ (0.2 M), H₂S (0.1 M), Na₂HPO₄ (0.2 M), K₄Fe(CN)₆ (0.2 M), K₃Fe(CN)₆ (0.2 M), morin (in CH₃OH), quinalizarine (in C₂H₅OH), urotropine (20 %), dithizone (in CCl₄), (NH₄)₂C₂O₄ (0.2 M), distilled water.

SOLUTION

- See the list at the end.





- c) Ca^{2+} : white precipitate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$;
 Fe^{2+} : blue with $\text{K}_3[\text{Fe}(\text{CN})_6]$
or after oxidation with H_2O_2 : blue with $\text{K}_4[\text{Fe}(\text{CN})_6]$ or red with NH_4SCN , or
brown precipitate with NaOH ;
 Al^{3+} : green fluorescence with morine (in dilute acetic acid);
 Zn^{2+} : white precipitate with H_2S (in acetic acid),
with dithizone red coloration of the organic phase;
 Mg^{2+} : with quinalizarine light blue lacquer (alkali solution);
 Sn^{2+} : with H_2S deep brown precipitate (weakly acidic solution),
blue fluorescence of the outer wall of a glass bottle filled with cold water
that was immersed in an Sn^{2+} solution (acidified with HCl),
in the flame of a Bunsen burner ("light test").
-
-

PROBLEM 3 (practical)***Titrimetric determination of potassium peroxodisulfate ($K_2S_2O_8$)***A) *Principle*

To the sample ($K_2S_2O_8$) a measured amount of a Fe(II) solution is added in an excess. The excess of the Fe(II) is determined using a standard $KMnO_4$ solution.

B) *Procedures*1) Determination of the concentration of the Fe(II) solution, $[Fe(NH_4)_2(SO_4)_2]$

To a titration vessel, 25.0 cm³ Fe(II) solution, 10 cm³ H_3PO_4 (ca. 3.7 mol dm⁻³) and 10 cm³ H_2SO_4 (ca. 1 mol dm⁻³) are added and titrated with the $KMnO_4$ solution to a pink colouration. The concentration of $KMnO_4$ in the solution is exactly 0.02 mol dm⁻³. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_1) is to be given.

2) Determination of peroxodisulfate in the same solution

a) The dissolved sample is diluted with distilled water to 100 cm³ in a standard flask and mixed.

b) 25.0 cm³ of this solution are transferred to a titration vessel and mixed with 10 cm³ H_3PO_4 (ca. 3.7 mol dm⁻³), 10 cm³ H_2SO_4 (ca. 1 mol dm⁻³) and 25.0 cm³ of the Fe(II) solution. The mixture is allowed to stand for 5 minutes and titrated with the $KMnO_4$ solution (0.02 mol dm⁻³) to a pink colourization. Two titrations are carried out and the consumption of the $KMnO_4$ solution is recorded. The mean value (= V_2) is to be given.

C) *Calculation and evaluation*

I) Reaction equations: To be given:

Partial equations with electron balance

Overall equations

1) Reaction of peroxodisulfate with Fe(II):

Partial:

a) $S_2O_8^{2-}$

b) Fe^{2+}

c) Overall reaction:

2) Reaction of Fe(II) with permanganate:

Partial:



c) Overall reaction:

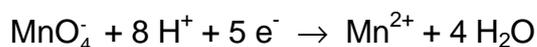
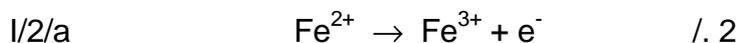
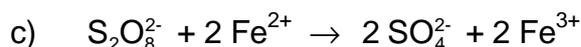
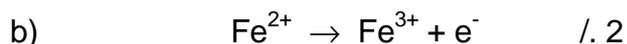
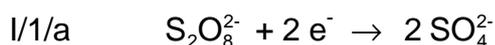
II) The concentration of the Fe(II) solution

- 1) Give the consumption of the KMnO_4 solution (cm^3) for 25.0 cm^3 of the Fe(II) solution (= V_1); See Procedure 1.
- 2) Calculate the concentration of the Fe(II) solution in mol dm^{-3} .

III) Determination of $\text{K}_2\text{S}_2\text{O}_8$

- 1) Give the consumption of the KMnO_4 solution in the back-titration of the excess Fe(II) solution in cm^3 (= V_2); See Procedure 2.
- 2) How many mg $\text{K}_2\text{S}_2\text{O}_8$:
- 3) Calculate the concentration of $\text{K}_2\text{S}_2\text{O}_8$ in the sample solution in mol dm^{-3} .

SOLUTION



II/1 $V_1 \text{ cm}^3 \text{ KMnO}_4 (0.02 \text{ mol dm}^{-3}) / 25 \text{ cm}^3 \text{ Fe(II)}$

2. $c(\text{Fe}^{2+}) = \frac{V_1 \times 0.02 \times 5}{25} = \dots\dots\dots \text{ mol/l}$

III/1 $V_2 \text{ cm}^3 \text{ KMnO}_4$ solution (0.02 mol dm^{-3}) for the back titration

2.

$$\alpha) \frac{(V_1 - V_2) \times 0.02 \times 5}{1000} \times \frac{270.33}{2} = \dots\dots\dots \text{mg K}_2\text{S}_2\text{O}_8$$

$$\beta) \frac{25 \times c(\text{Fe}^{2+}) - V_2 \times 0.02 \times 5}{1000} \times \frac{270.33}{2} = \dots\dots\dots \text{mg K}_2\text{S}_2\text{O}_8$$

3.

$$\alpha) \frac{(V_1 - V_2) \times 0.02 \times 5}{1000} \times \frac{40}{2} = \dots\dots\dots \text{mol K}_2\text{S}_2\text{O}_8 / \text{dm}^3$$

$$\beta) \frac{25 \times c(\text{Fe}^{2+}) - V_2 \times 0.02 \times 5}{1000} \times \frac{40}{2} = \dots\dots\dots \text{mol} / \text{dm}^3$$

13th



International Chemistry Olympiad

**6 theoretical problems
3 practical problems**

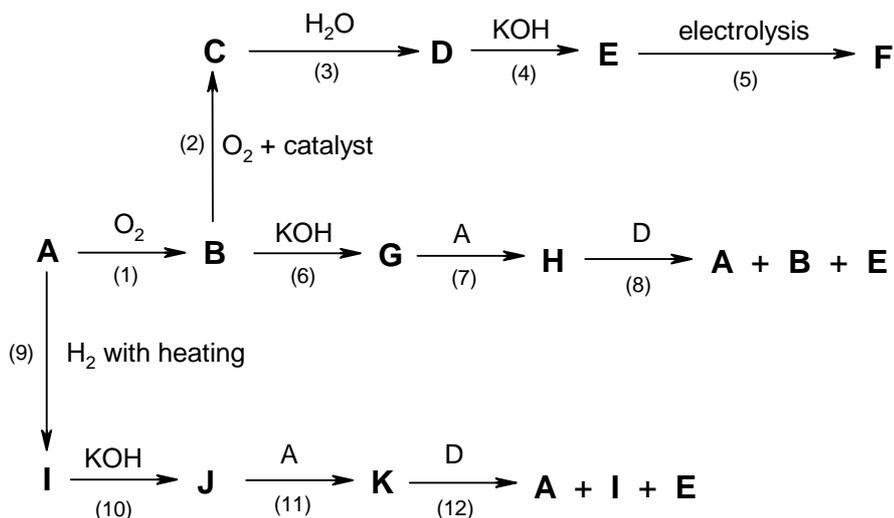
THE THIRTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 13–23 JULY 1981, BURGAS, BULGARIA

THEORETICAL PROBLEMS

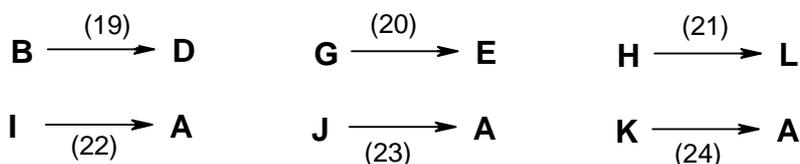
PROBLEM 1

The sample **A** participates in the transformations in scheme 1. Only the products containing **A** are shown in the scheme 1.

Scheme 1



- Substance **A** is a solid and is insoluble in water.
- Substances **B** and **I** are gases soluble in water.
- Substances **E**, **F**, **J** and **K** are solid and soluble in water.
- Aqueous solutions of **B**, **G**, **H**, **I**, **J** and **K** react with **F**, the products in all cases being **E** and **D**.
- The following transformations occur during the interaction with an aqueous solution of iodine:



Write the chemical equations for the above interactions and balance them.

SOLUTION

Schéma:

- (1) $S + O_2 \rightarrow SO_2$
- (2) $2 SO_2 + O_2 \rightarrow 2 SO_3$
- (3) $SO_3 + H_2O \rightarrow H_2SO_4$
- (4) $2 KOH + H_2SO_4 \rightarrow K_2SO_4 + 2 H_2O$
- (5) $2 SO_4^{2-} - 2 e^- \rightarrow S_2O_8^{2-}$
- (6) $SO_2 + 2 KOH \rightarrow K_2SO_3 + H_2O$
- (7) $K_2SO_3 + S \rightarrow K_2S_2O_3$
- (8) $K_2S_2O_3 + H_2SO_4 \rightarrow K_2SO_4 + S + SO_2 + H_2O$
- (9) $H_2 + S \rightarrow H_2S$
- (10) $H_2S + 2 KOH \rightarrow K_2S + 2 H_2O$
- (11) $K_2S + x S \rightarrow K_2S_{(x+1)}$
- (12) $K_2S_{(x+1)} + H_2SO_4 \rightarrow K_2SO_4 + x S + H_2S$

d)

- (13) $SO_2 + 2 H_2O + K_2S_2O_8 \rightarrow K_2SO_4 + 2 H_2SO_4$
- (14) $K_2SO_3 + H_2O + K_2S_2O_8 \rightarrow 2 K_2SO_4 + H_2SO_4$
- (15) $K_2S_2O_3 + 5 H_2O + 4 K_2S_2O_8 \rightarrow 5 H_2SO_4 + 5 K_2SO_4$
- (16) $H_2S + 4 H_2O + 4 K_2S_2O_8 \rightarrow 5 H_2SO_4 + 4 K_2SO_4$
- (17) $K_2S + 4 H_2O + 4 K_2S_2O_8 \rightarrow 4 H_2SO_4 + 5 K_2SO_4$
- (18) $K_2S_{(x+1)} + (4x + 1) H_2O + 4 x K_2S_2O_8 \rightarrow 5 x H_2SO_4 + (4x + 1) K_2SO_4 \quad (+S)$

e)

- (19) $SO_2 + 2 H_2O + I_2 \rightarrow H_2SO_4 + 2 HI$
- (20) $K_2SO_3 + H_2O + I_2 \rightarrow K_2SO_4 + 2 HI$
- (21) $2 K_2S_2O_3 + I_2 \rightarrow 2 KI + K_2S_4O_6$
- (22) $H_2S + I_2 \rightarrow 2 HI + S$
- (23) $K_2S + I_2 \rightarrow 2 KI + S$
- (24) $K_2S_x + I_2 \rightarrow 2 KI + x S$

A: S **B:** SO₂ **C:** SO₃ **D:** H₂SO₄
E: K₂SO₄ **F:** K₂S₂O₈ **G:** K₂SO₃ **H:** K₂S₂O₃
I: H₂S **J:** K₂S **K:** K₂S_x **L:** K₂S₄O₆

PROBLEM 2

Maleic acid (H_2A) is a weak dibasic acid. The correlation between the relative quantities of H_2A , HA^- , A^{2-} :

$$\alpha_0 = \frac{c(\text{H}_2\text{A})}{c} \quad \alpha_1 = \frac{c(\text{HA}^-)}{c} \quad \alpha_2 = \frac{c(\text{A}^{2-})}{c}$$

and pH values of the solution show that:

- a) $\alpha_0 = \alpha_1$ for pH = 1.92
 b) $\alpha_1 = \alpha_2$ for pH = 6.22

Find:

- 2.1** The values of the dissociation constants of maleic acid for the first (K_1) and the second (K_2) degree of dissociation.
- 2.2** The values of α_0 , α_1 , and α_2 for pH = 1.92 and pH = 6.22.
- 2.3** What is the value of pH when α_1 attains a maximum value? Find the maximum value of α .
- 2.4** Which of the acid-base indicators in the table are suitable for titration of a 0.1 M solution of maleic acid (as a monobasic and as a dibasic acid) with 0.1 M NaOH?

Fill in the table 1 with the correct answers.

All the activity coefficients should be considered equal to 1.

Indicator	pH interval
Methyl green	0.1 – 2.0
Tropeolin 00	1.4 – 3.2
β -Dinitrophenol	2.4 – 4.0
Bromphenol blue	3.0 – 4.6
Congo red	3.0 – 5.2
Methyl red	4.4 – 6.2
Bromphenol red	5.0 – 6.8
Bromthymol blue	6.0 – 7.6
Phenol red	6.8 – 8.0
Cresol red	7.2 – 8.8

Thymol blue	8.0 – 9.6
Phenolphthalein	8.2 – 10.0
Alizarine yellow	10.1 – 12.1
Tropeolin 0	11.0 – 13.0
1,3,5-Trinitrobenzene	12.2 – 14.0

Table 1

2.1		$K_1 =$
		$K_2 =$
2.2	pH = 1.92	$\alpha_0 =$
		$\alpha_1 =$
		$\alpha_2 =$
	pH = 6.22	$\alpha_0 =$
		$\alpha_1 =$
		$\alpha_2 =$
2.3		pH =
		$\alpha_1 =$
2.4	First indicator equivalence point	pH =
		1.
		2.
		3.
		4.
	Second indicator equivalence point	pH =
1.		
2.		
3.		
4.		

SOLUTION

$$2.1 \quad \alpha_0 = \alpha_1$$

$$K_1 = c_{\text{H}^+} = 10^{-\text{pH}} = 10^{-1.92} = 1.20 \times 10^{-2}$$

$$\alpha_1 = \alpha_2$$

$$K_2 = c_{\text{H}^+} = 10^{-\text{pH}} = 10^{-6.22} = 6.02 \times 10^{-7}$$

$$2.2 \quad F = c_{\text{H}^+}^2 + K_1 c_{\text{H}^+} + K_1 K_2$$

$$\text{pH} = 1.92; \quad c_{\text{H}^+} = 10^{-1.92} = 1.20 \times 10^{-2}; \quad F = 2.88 \times 10^{-4}$$

$$\alpha_0 = \alpha_1 = \frac{c_{\text{H}^+}^2}{F} = \frac{(1.20 \cdot 10^{-2})^2}{2.88 \cdot 10^{-4}} = 0.500$$

$$\alpha_2 = \frac{K_1 K_2}{F} = \frac{1.20 \cdot 10^{-2} \times 6.02 \cdot 10^{-7}}{2.88 \cdot 10^{-4}} = 2.51 \times 10^{-5}$$

$$\text{pH} = 6.22; \quad c_{\text{H}^+} = 10^{-6.22} = 6.02 \times 10^{-7}; \quad F = 1.445 \times 10^{-8}$$

$$\alpha_0 = \frac{c_{\text{H}^+}^2}{F} = \frac{(6.02 \times 10^{-7})^2}{1.445 \times 10^{-8}} = 2.51 \times 10^{-5}$$

$$\alpha_1 = \alpha_2 = \frac{K_1 K_2}{F} = \frac{1.20 \times 10^{-2} \times 6.02 \times 10^{-7}}{1.445 \times 10^{-8}} = 0.500$$

$$2.3 \quad (\alpha)_{c_{\text{H}^+}}' = \frac{[K_1 F - K_1 c_{\text{H}^+} (2c_{\text{H}^+} + K_1)]}{F^2} = 0$$

$$c_{\text{H}^+}^2 = K_1 K_2$$

$$c_{\text{H}^+} = \sqrt{(1.20 \times 10^{-2} \times 6.02 \times 10^{-7})} = 8.50 \times 10^{-5} \text{ mol dm}^{-3}$$

$$F = 1.034 \times 10^{-6} \quad \text{pH} = 4.07$$

$$\alpha_1 = \frac{K_1 c_{\text{H}^+}}{F} = \frac{1.20 \times 10^{-2} \times 8.50 \times 10^{-5}}{1.034 \times 10^{-6}} = 0.986$$

The pH and the maximum value of α_1 can be estimated either by calculating α_1 for a set of values of c_{H^+} in the interval $1 \times 10^{-5} - 1 \times 10^{-3} \text{ mol dm}^{-3}$ or from the condition that α_1 can reach a maximum value only when $\alpha_0 = \alpha_2$

2.4 The first equivalence point is found in the region of the α_1 maximum at pH = 4.07

$$\text{where } c_{\text{HA}^-} = c_{\text{NaHA}} = \frac{0.1}{2} = 0.05 \text{ mol dm}^{-3}.$$

The second equivalence point is found in the alkaline region, where:

$$c_{\text{OH}^-} = c_{\text{HA}^-} \quad c_{\text{A}^{2-}} = \frac{0.1}{3} - c_{\text{OH}^-} = 0.0333$$

$$c_{\text{H}^+}^2 = \frac{K_2 c_{\text{HA}^-}}{c_{\text{A}^{2-}}} = \frac{K_2 c_{\text{OH}^-}}{c_{\text{A}^{2-}}} = \frac{K_2 K_w}{c_{\text{H}^+} c_{\text{A}^{2-}}}$$

$$c_{\text{H}^+} = \sqrt{\frac{K_2 K_w}{c_{\text{A}^{2-}}}} = \sqrt{\frac{6.02 \times 10^{-7} \times 1 \times 10^{-14}}{0.0333}} = 4.25 \times 10^{-10} \text{ mol dm}^{-3}$$

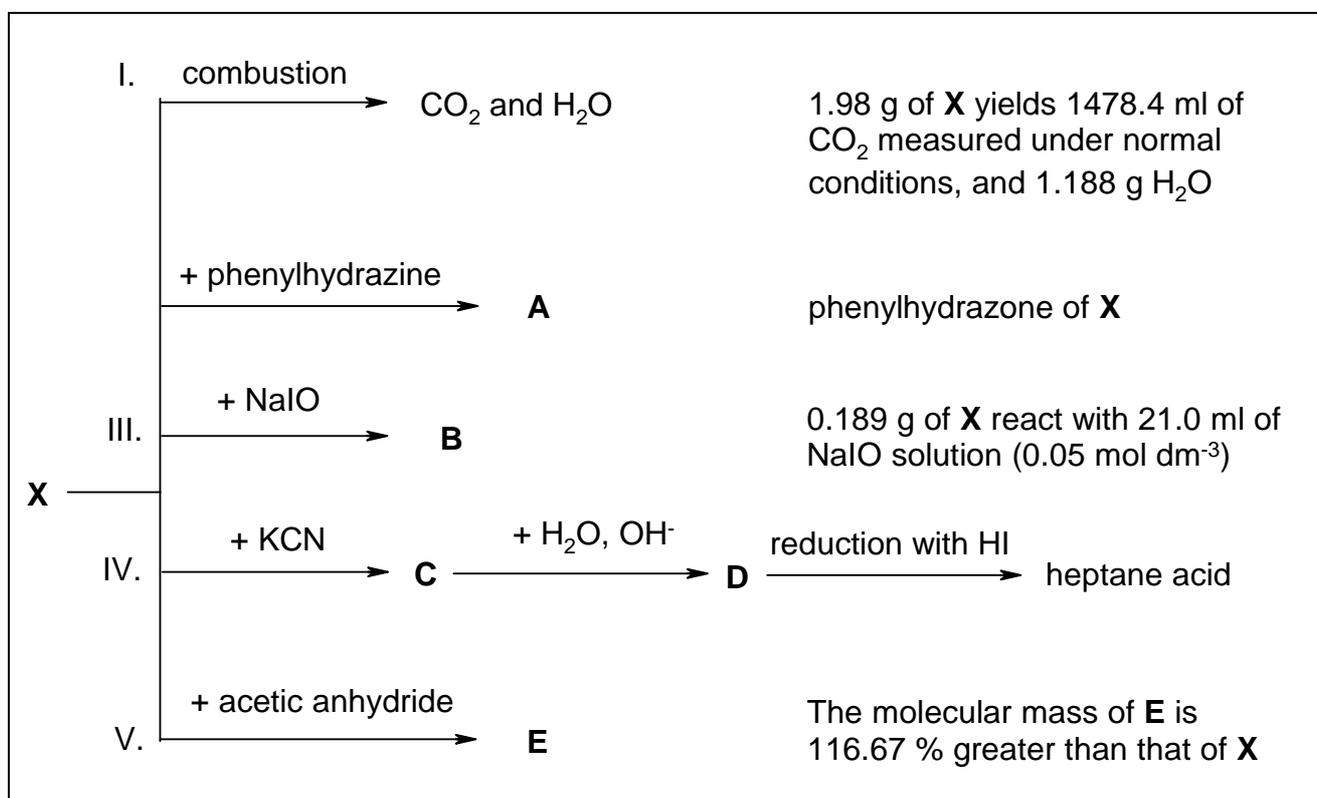
$$\text{pH} = 9.37$$

Indicators:

Bromphenol blue, Congo red, thymol blue, phenolphthalein.

PROBLEM 3

Compound **X** has been isolated from a neutral product. Different reagents have been used to establish the structure of **X**. The following results were obtained:



3.1 What conclusions can be drawn on the composition and the structure of **X** on the basis of the data obtained from each of the above interactions. The conclusions should be formulated in the most concise and clear way. Fill in the table without describing how you reached your conclusions.

- I.
- II.
- III.
- IV.
- V.

3.2 Write the formula of substance **X** on the basis of the data about the composition and structure obtained in point 1.

3.3 Write the formulae of substances **A**, **B**, **C**, **D**, and **E** and the formula for heptane acid.

3.4 To what natural substances could this structure correspond? Write the name of the substance and draw the structural formula which best describes its structure properties.

3.5 Give three properties of this compound that do not correspond to the structure found in point 2.

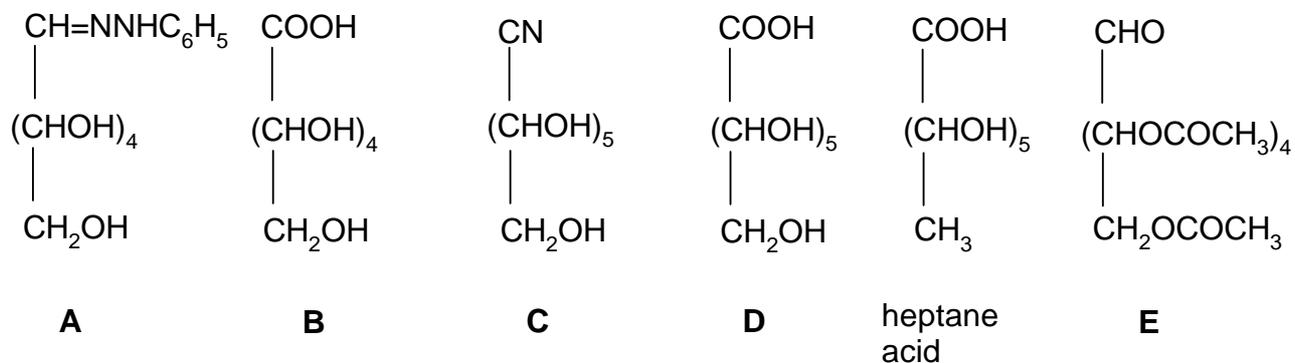
SOLUTION

3.1

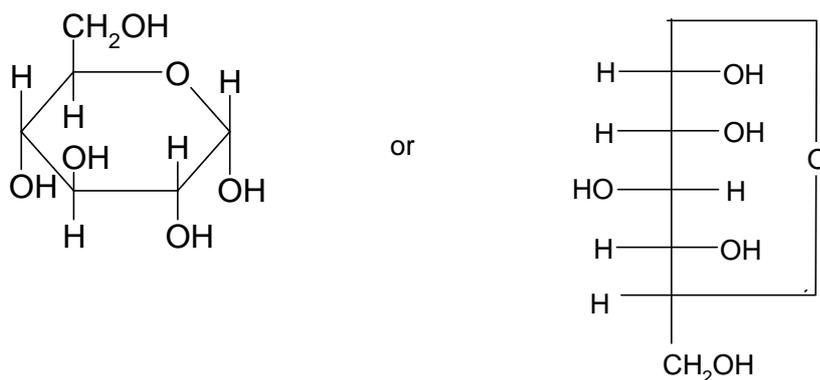
Reaction	Yielding
I	The simplest empirical formula, CH ₂ O
II	Presence of a C=O group
III	Presence of a –CHO group <i>M</i> , calculated for a single CHO- 180/ <i>n</i> (<i>n</i> – number of CHO groups)
IV	Continuous chain of 6 C atoms 1 CHO, C ₆ H ₁₂ O ₆ (<i>M</i> = 180)
V	5 OH groups

3.2 HOCH₂(CHOH)₄CHO

3.3



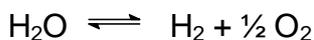
3.4 D – (+) – glucose



- 3.5** – does not participate in some reactions typical for aldehydes (e. g. with NaHSO₃ or Schiff's reagent),
- the mutarotation phenomenon,
 - a stronger reactivity of one of the five OH groups (displayed for example in the interaction with CH₃OH and HCl leading to the methylation of only one OH group).
-
-

PROBLEM 4

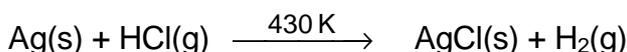
The thermal decomposition of water



can be traced ($\alpha = 10^{-3}$) at temperature above 1700 K. This process can be realized at temperatures 800 – 900 K as well as through subsequent stages carried out in a cycle. Suggest such a process on the basis of the reactions:



and



satisfying the following requirements:

- Only water should be consumed during the process.
- Oxygen and hydrogen alone should be the end products of the process.
- In addition to the above substances, a 25 % ammonia solution is needed for the cycle.
- The temperature for each step in the cycle should not exceed 840 K.

SOLUTION

- $2 \text{ CuO} + 2 \text{ MgCl}_2 + \text{H}_2\text{O} \xrightarrow{840 \text{ K}} 2 \text{ CuCl} + 2 \text{ MgO} + 2 \text{ HCl} + 0.5 \text{ O}_2$
- $\text{Ag} + 2 \text{ HCl} \xrightarrow{430 \text{ K}} 2 \text{ AgCl} + \text{H}_2$
- $2 \text{ CuCl} + 4 \text{ NH}_3 \longrightarrow 2 [\text{Cu}(\text{NH}_3)_2]^+ + 2 \text{ Cl}^-$
- $2 \text{ AgCl} + 4 \text{ NH}_3 \longrightarrow 2 [\text{Ag}(\text{NH}_3)_2]^+ + 2 \text{ Cl}^-$
- $2 [\text{Cu}(\text{NH}_3)_2]^+ + 2 [\text{Ag}(\text{NH}_3)_2]^+ \longrightarrow 2 \text{ Ag} \downarrow + 2 [\text{Cu}(\text{NH}_3)_4]^{2+}$
- $2 [\text{Cu}(\text{NH}_3)_4]^{2+} + 2 \text{ MgO} \xrightarrow{\text{boiling}} 2 \text{ CuO} \downarrow + 2 \text{ Mg}^{2+} + 8 \text{ NH}_3 \uparrow$
- $2 \text{ Mg}^{2+} + 4 \text{ Cl}^- \xrightarrow{\text{evaporation}} 2 \text{ MgCl}_2$
- $\text{H}_2\text{O} \longrightarrow \text{H}_2 + 0.5 \text{ O}_2$

PROBLEM 5

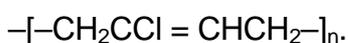
Compounds **B** and **C** are structural isomers. They can be obtained when hydrocarbon **A** interacts with chlorine. Hydrocarbon **A** is a basic product of an industrial organic synthesis. It can react with ozone, yielding an ozonide.

Isomer **B** can be used for the technical production of compounds **D** and **E** that are the initial compounds in the production of the fibre nylon:



Compound **D** is soluble in bases, **E** in acids.

The reaction between isomer **C** and an alcohol solution of an alkaline base yields monomer **F** which is used for the production of chloroprene (neoprene) rubber

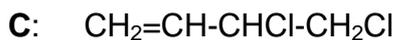


This method has a technical application.

- 5.1 Write down the structural formulae of **A**, **B**, **C**, **D**, **E**, **F** and their names in the IUPAC nomenclature.
- 5.2 Write down the mechanism of the reaction between hydrocarbon **A** and chlorine. What type of reaction is it in terms of its mechanism? Which of the two isomers is obtained in larger quantities under ordinary conditions?
- 5.3 Write down the equations for:
 - the production of **D** and **E** from isomer **B**,
 - the production of monomer **F** from isomer **C**,
 - the ozonolysis of hydrocarbon **A** and hydrolysis of the ozonide.
- 5.4 Write down the chemical scheme for an industrial production of hydrocarbon **A** from the hydrocarbon which is main component of natural gas.
- 5.5 For chloroprene rubber, write down the formulae of the possible steric forms of the elementary unit.

SOLUTION

- 5.1 **A:** $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
1,3-butadiene
- B:** $\text{ClCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$
1,4-dichloro-2-butene



3,4-dichloro-1-butene



hexanedioic acid

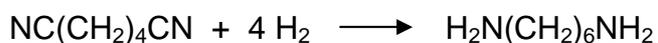
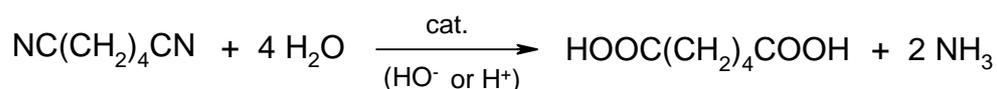
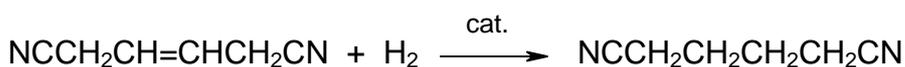
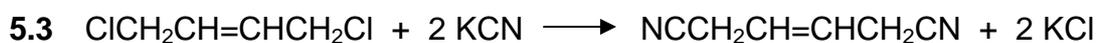
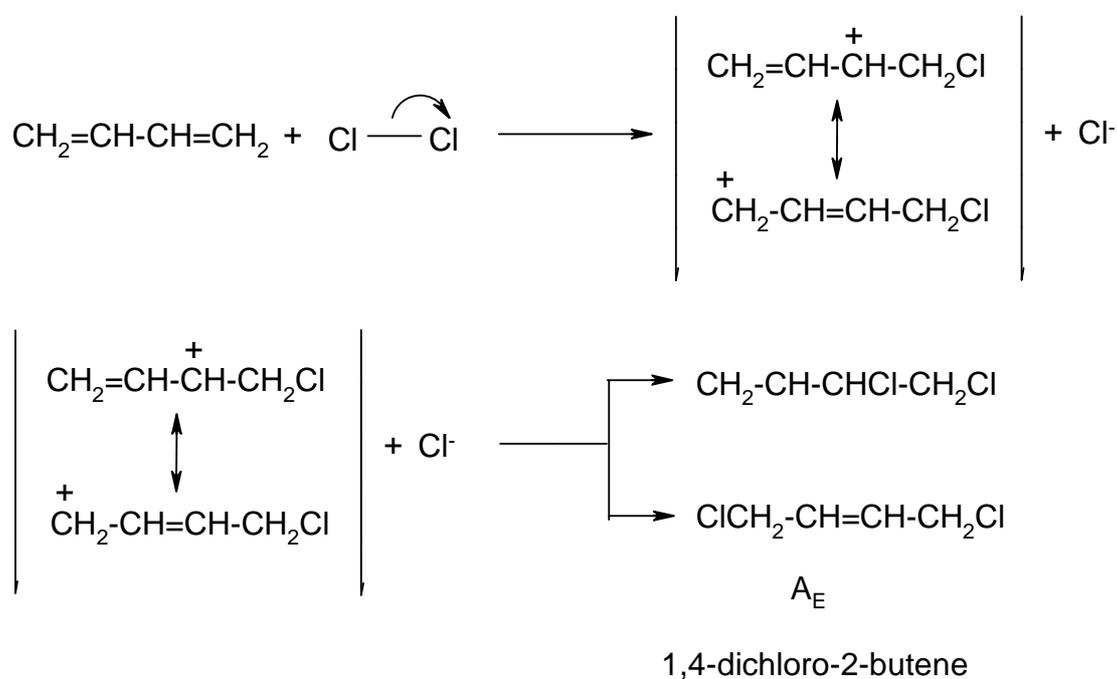


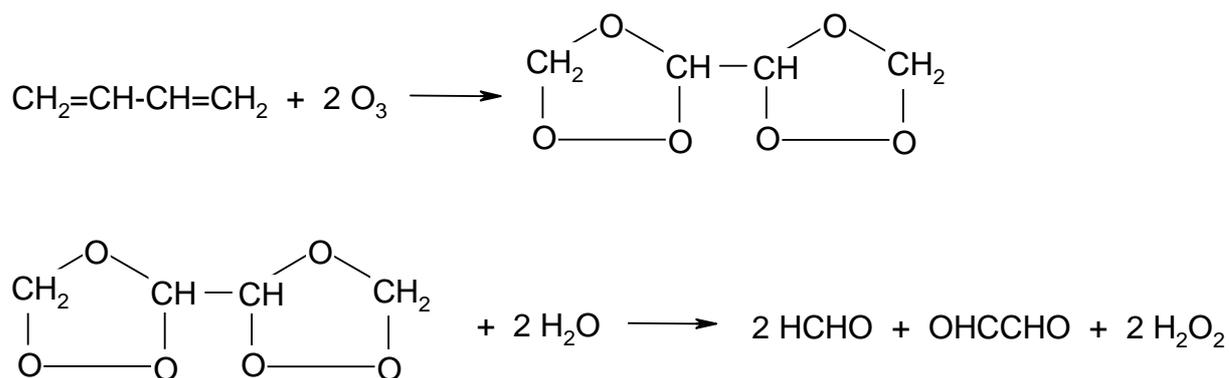
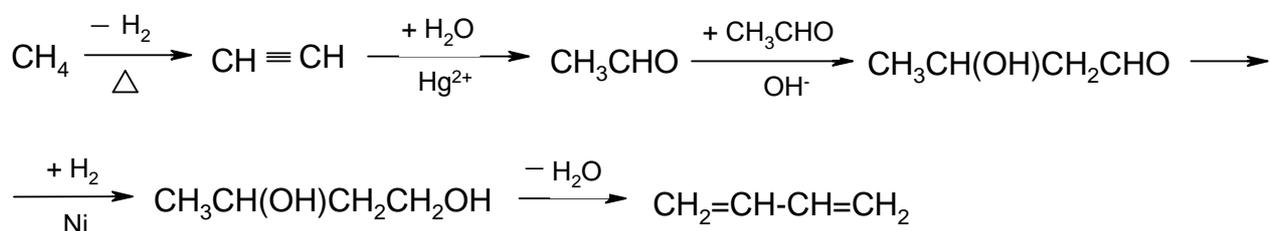
1,6-hexandiamine



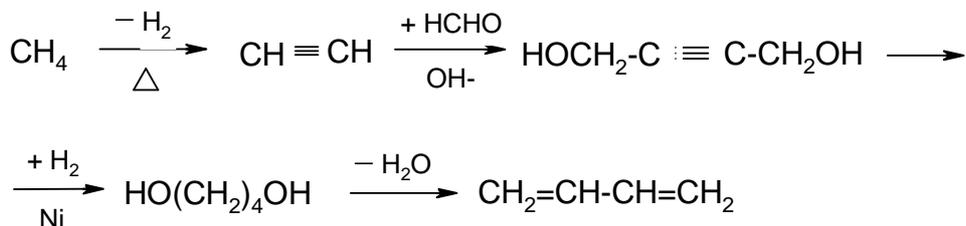
2-chloro-1,3-butadiene

5.2

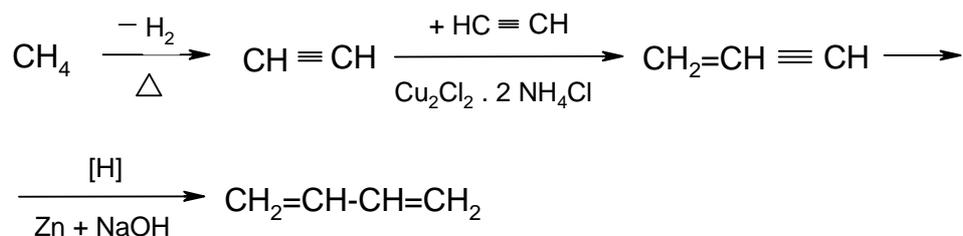



5.4


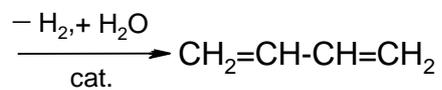
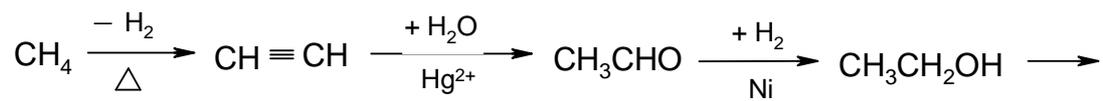
or



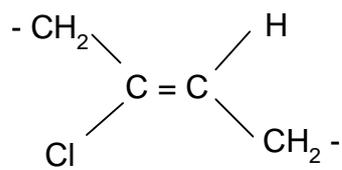
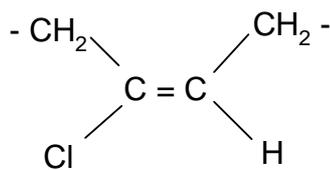
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or

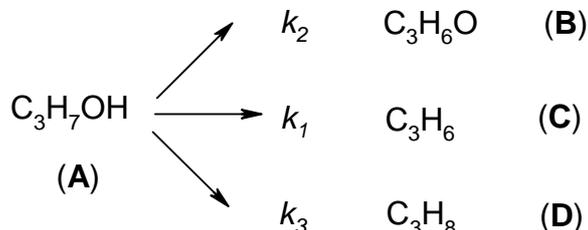


5.5



PROBLEM 6

The catalytic decomposition of isopropanol on the surface of a V_2O_5 catalyst, leading to the products in the scheme, satisfies a first order kinetic equation.



Five seconds after initiation of the reaction at 590 K, the concentrations of the components in the reaction mixture are:

$$c_A = 28.2 \text{ mmol dm}^{-3}$$

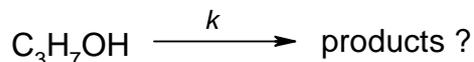
$$c_B = 7.8 \text{ mmol dm}^{-3}$$

$$c_C = 8.3 \text{ mmol dm}^{-3}$$

$$c_D = 1.8 \text{ mmol dm}^{-3}$$

6.1 What is the initial concentration c_0 of C_3H_7OH in the system?

6.2 What is the value of the rate constant k for the process:



6.3 What is the interval of time ($\tau_{1/2}$) in which the concentration of C_3H_7OH will reach the value $c = c_0/2$?

6.4 What are the values of rate constants k_1 , k_2 , and k_3 ?

6.5 What are the values of concentrations c_B , c_C , c_D at $t = \tau_{1/2}$?

The equation describing the concentration changes of **A** with time t for the first order reaction has the form:

$$c_A = c_0 \exp(-k t)$$

or

$$\log (c_0 / c_A) = 0.4343 k t$$

or

$$\ln (c_0 / c_A) = k t$$

Fill in the table with the answers obtained.

1	$c_0 =$
2	$k =$
3	$\tau_{1/2}$
4	$k_1 =$
	$k_2 =$
	$k_3 =$
5	$c_B =$
	$c_C =$
	$c_D =$

SOLUTION

$$6.1 \quad c_0 = c_A + c_B + c_C + c_D = 28.2 + 7.8 + 8.3 + 1.8 = 46.1 \text{ mmol dm}^{-3}$$

$$6.2 \quad k = \frac{1}{0.4343 t} \log\left(\frac{c_0}{c_A}\right) = \frac{1}{0.4343 \times 5} \log\left(\frac{46.1}{28.2}\right) = 0.0983 \text{ s}^{-1}$$

$$6.3 \quad t = \tau_{1/2} = \frac{1}{0.4343 k} \log \frac{c_0}{\frac{c_0}{2}} = \frac{1}{0.4343 \times 0.0983} \log 2 = 7.05 \text{ s}$$

6.4

$$v_1 = \frac{\Delta c_B}{\Delta t} = k_1 c_A$$

$$v_2 = \frac{\Delta c_C}{\Delta t} = k_2 c_A$$

$$v_3 = \frac{\Delta c_D}{\Delta t} = k_3 c_A$$

$$v = v_1 + v_2 + v_3 = k c_A$$

$$(1) \quad k_1 + k_2 + k_3 = k = 0.0983 \text{ s}^{-1}$$

$$(2) \quad \frac{\Delta c_B}{\Delta c_C} = \frac{c_B - 0}{c_C - 0} = \frac{c_B}{c_C} = \frac{k_1}{k_2} = \frac{7.8}{8.3} = 0.940$$

$$(3) \quad \frac{\Delta c_B}{\Delta c_D} = \frac{c_B - 0}{c_D - 0} = \frac{c_B}{c_D} = \frac{k_1}{k_3} = \frac{7.8}{1.8} = 4.33$$

From equations (1) – (3):

$$k_1 = 0.0428 \text{ s}^{-1}$$

$$k_2 = 0.0455 \text{ s}^{-1}$$

$$k_3 = 0.00988 \text{ s}^{-1}$$

6.5 At $t = \tau_{1/2} = 7.05 \text{ s}$

$$(4) \quad c_A = \frac{c_0}{2} = c_B + c_C + c_D = 23.05 \text{ mmol dm}^{-3}$$

From equations (2) – (4):

$$c_B = 10.0 \text{ mmol dm}^{-3}$$

$$c_C = 10.7 \text{ mmol dm}^{-3}$$

$$c_D = 2.32 \text{ mmol dm}^{-3}$$

PRACTICAL PROBLEMS**PROBLEM 1 (practical)**

Fourteen numbered test tubes contain solutions of pure inorganic substances. Each test tube contains only one substance. The samples contain the following ions:

cations K^+ , Na^+ , Hg_2^{2+} , Ag^+ , NH_4^+ , Ba^{2+} , Sr^{2+} , Fe^{3+} ;

anions OH^- , NO_3^- , Cl^- , SCN^- , I^- , CO_3^{2-} , $Cr_2O_7^{2-}$, CrO_4^{2-} , $Fe(CN)_6^{4-}$, $Co(NO_2)_6^{3-}$.

Determine the contents of the test tubes. In addition to reactions between samples, the only other possible reagent is a solution of hydrochloric acid with a concentration of 2 mol dm^{-3} .

Fill in the following information on the sheet provided:

1. The chemical formulae of the individual samples and the numbers of the corresponding test tubes.
 2. The chemical formulae in ionic form on the basis of which you demonstrated the presence of individual cations present in the samples.
-
-

PROBLEM 2 (practical)

Determine the samples in the test tubes using the following reagents:

FeCl₃ (2.5 % aqueous solution), water, 2,4-dinitrophenylhydrazine, Lucas' reagent (ZnCl₂ – HCl), NaOH (5 % aqueous solution), NaHCO₃ (5 % aqueous solution), HCl (conc.), Fehling's solution (an alkaline aqueous solution containing Cu²⁺ ions; this is prepared immediately prior to use by mixing identical volumes of Fehling's solutions I and II), Tollen's reagent (prepared immediately prior to use by mixing identical volumes of 10 % solution of AgNO₃ and an NaOH solution with a concentration 2 mol dm⁻³). Finally, ammonia is added dropwise to complete dissolution of silver dioxide.

Write the results of your observations during testing the unknown substances with the reagents into the table provided.

Write the (IUPAC) names and structural formulae for the substances in the test tubes.

Write the chemical equations for the reactions on the basis of which the individual substances were identified. Write only a reaction scheme where this not possible.

PROBLEM 3 (practical)Volumetric determination of sodium carbonate and sodium hydrogen carbonate simultaneously.A) *Procedure:*

1. Determination of the precise concentration of an HCl solution (0.1 mol dm^{-3}) using borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$ as a standard.

Principle:

An aqueous solution of sodium tetraborate reacts with hydrochloric acid to form trihydrogenboric acid.

Procedure:

25.00 cm^3 of a standard borax solution with a concentration of about 0.05 mol dm^{-3} (the exact borax concentration is written on the label on the volumetric flask; the solution needs not be diluted with water to a volume of 100 cm^3) is transferred into a titration flask, 1 to 2 drops of methyl red are added and the solution is titrated to the first orange coloration of the yellow solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated by symbol V_1 .

2. Volumetric determination of Na_2CO_3 and NaHCO_3 simultaneously.

Procedure:

The sample in a volumetric flask (250 cm^3) should be diluted to the mark with distilled water from which the carbon dioxide has been removed by boiling, and mix.

- a) Part of the solution (25 cm^3) is titrated with an HCl solution using methyl orange (2 drops) to the first red coloration of the originally yellow solution. The sample is boiled 2 to 3 minutes to release carbon dioxide. Then the solution is cooled and the titration is continued to a clear red coloration of the solution. The titration should be carried out at least twice. The consumption of hydrochloric acid should be designated as V_2 (average of titration values).
- b) A further part of the sample (25.00 cm^3) is transferred to an Erlenmeyer flask and mixed with 25.00 cm^3 of the NaOH solution with a concentration of 0.1 mol dm^{-3} . Add 10 cm^3 of a 10 % solution of BaCl_2 and 2 drops of phenolphthalein. Excess hydroxide should be titrated immediately in the presence of a white precipitate formed, using an HCl solution whose precise concentration has been determined

- c) in part 1. The consumption of hydrochloric acid should be denoted as V_3 (average values of at least two titrations).
- d) Carry out the same titration as in part b) without the sample (blank). The consumption of HCl is designated as V_4 (average of two titrations).

Use the results of the above experiments to calculate the amounts of Na_2CO_3 and NaHCO_3 in the sample.

B) Results

The results should be written into the form provided in which you should note the following:

- a) The ionic equation for the reaction according to which the concentration of the HCl solution was determined.
- b) The ionic equation for the reaction used in the determination of Na_2CO_3 and NaHCO_3 simultaneously.
- c) The volume of hydrochloric acid consumed in the titration of 25.00 cm^3 of borax solution.
- d) Calculation of the HCl concentration (in mol dm^{-3}).
- e) Consumption of the HCl solution – V_2 , V_3 , and V_4 .
- f) Mass amounts of Na_2CO_3 and NaHCO_3 in the sample in grams.

$$M(\text{Na}_2\text{CO}_3) = 105.989 \text{ g mol}^{-1}$$

$$M(\text{NaHCO}_3) = 84.007 \text{ g mol}^{-1}$$

14th



**7 theoretical problems
3 practical problems**

THE FOURTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 3–12 JULY 1982, STOCKHOLM, SWEDEN

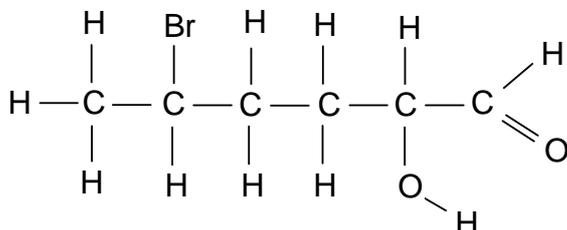
THEORETICAL PROBLEMS

PROBLEM 1

A. The IUPAC name of the compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ is

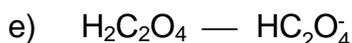
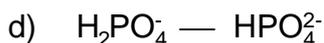
- cobalt(II) hexaammonia dichlorine,
- cobalt(II) hexaammonia dichloride,
- hexaammincobalt(II) chloride.
- hexaamminedichlorocobalt(II)
- cobalt(II) chloride-hexaammonia

B. The IUPAC name of the compound



is:

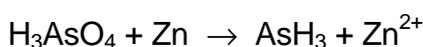
- 5-bromo-1-hexanoic acid
 - 5-bromo-2-hydroxy-1-hexanal
 - 2-bromo-5-hydroxy-6-hexanal
 - 2-bromo-2-hydroxy-1-hexanal
 - 5-bromo-2-hydroxy-1-hexanone
- C. Which of the following acid-base pairs is most suitable for keeping the pH constant at 9 in an aqueous solution?
- $\text{CH}_3\text{COOH} \text{ — } \text{CH}_3\text{COO}^-$
 - $\text{NH}_4^+ \text{ — } \text{NH}_3$
 - $\text{H}_2\text{CO}_3 \text{ — } \text{HCO}_3^-$



D. One of the following statements cannot be correct. State which one.

a) A water-soluble solid contains Mg^{2+} , Cr^{3+} , and Br^- .b) A solid soluble in a sodium hydroxide solution contains Al^{3+} , K^+ , and SO_4^{2-} .c) A solid soluble in aqueous ammonia solution contains Ag^+ , Cu^{2+} , and Cl^- .d) A solid soluble in nitric acid contains Ba^{2+} , Fe^{2+} , and CO_3^{2-} .e) A solution neutral to litmus contains Na^+ , Ca^{2+} , and PO_4^{3-} .

E. Complete the following equation:



The reaction is carried out in an acid solution. Fill in the missing particles and balance the reaction equation.

F. State the degree of protolysis of acetic acid with concentration of 0.25 mol dm^{-3} .

$$K_a(\text{HAc}) = 1.8 \times 10^{-5}$$

a) 0.021 %; b) 0.21 %; c) 0.84 %; d) 1.3 %; e) 8.4 %

G. A solution with a volume of 1.00 dm^3 is saturated with lead iodide, PbI_2 . The concentration of iodide ions is 2.7 mol dm^{-3} . Determine the solubility product of PbI_2 .a) 3.6×10^{-6} ; b) 2.0×10^{-8} ; c) 9.8×10^{-9} ; d) 2.5×10^{-9} ; e) 4.9×10^{-9} .

H. The following standard enthalpies of formation are given:

Compound	ΔH°
Acetic acid	$-0.50 \text{ MJ mol}^{-1}$
Carbon dioxide	$-0.40 \text{ MJ mol}^{-1}$
Water	$-0.30 \text{ MJ mol}^{-1}$

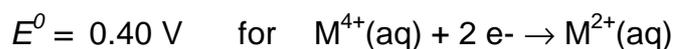
The ΔH° of combustion of acetic acid is:a) 0.90 MJ mol^{-1} ; b) $-0.90 \text{ MJ mol}^{-1}$; c) $-0.20 \text{ MJ mol}^{-1}$;d) -2.1 MJ mol^{-1} ; e) 0.20 MJ mol^{-1} I. $\text{COCl}_2(\text{g})$ is introduced in an empty vessel at a pressure of a . It dissociates and the following equilibrium is established at constant temperature:

If x represents the partial pressure of $\text{CO}_2(\text{g})$ at equilibrium, what is the equilibrium expression?

$$\text{a) } \frac{4x^3}{(a-2x)^2} = K_p \quad \text{b) } \frac{2x^4}{(a-2x)^2} = K_p \quad \text{c) } \frac{2x^3}{(a-x)^2} = K_p$$

$$\text{d) } \frac{4x^3}{(a-x)^2} = K_p \quad \text{e) } \frac{x^3}{(a-3x)^2} = K_p$$

K. For a metal M the following redox data are known:

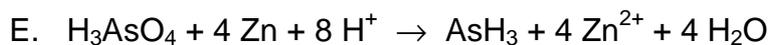


The E^0 for $\text{M}^{4+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{M}^+(\text{aq})$ is then:

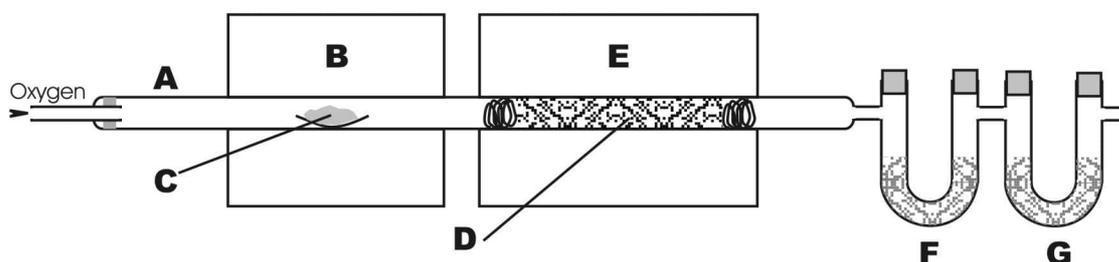
- a) -0.20 V b) -1.00 V c) 1.00 V d) 0.07 V e) -0.07 V

SOLUTION

A. c) B. b) C. b) D. e)



F. c) G. c) H. b) I. a) K. d)

PROBLEM 2

Quantitative analysis for carbon and hydrogen was originally carried out using a technique and apparatus (see figure) originally developed in 1831 by the famous chemist Justus Liebig. A carefully weighed sample of organic compound (C) is placed in a combustion tube (A) and vaporized by heating in a furnace (B). The vapours are swept by a stream of oxygen through a heated copper oxide packing (D) and through another furnace (E), which ensures the quantitative oxidation of carbon and hydrogen to carbon dioxide and water. The water vapour is absorbed in a weighed tube (F) containing magnesium perchlorate and the carbon dioxide in another weighed tube (G) containing asbestos impregnated with sodium hydroxide.

A pure liquid sample containing only carbon, hydrogen and oxygen is placed in a 0.57148 g platinum boat, which on reweighing weights 0.61227 g. The sample is ignited and the previously weighed absorption tubes are reweighed. The mass of the water absorption tube has increased from 6.47002 g to 6.50359 g, and the mass of the carbon dioxide tube has increased from 5.46311 g to 5.54466 g.

2.1 Calculate the mass composition of the compound.

2.2 Give the empirical formula of the compound.

To estimate the molar mass of the compound, 1.0045 g was gasified. The volume, measured at a temperature of 350 K and a pressure of 35.0 kPa, was 0.95 dm³.

2.3 Give the molar mass and the molecular formula of the compound.

2.4 Draw possible structures corresponding to the molecular formula excluding cyclic structures, stereo isomers, peroxides and unsaturated compounds. There are about 15 possibilities. Give 10 of them.

When the compound is heated with a sodium hydroxide solution, two products are formed. Fractional distillation of the reaction mixture yields one of the substances. The other substance is purified by distillation after acidification and appears to be an acid.

2.5 What structures are possible for compound C?

0.1005 g of the acid are dissolved in water and titrated with a sodium hydroxide solution with a concentration of $0.1000 \text{ mol dm}^{-3}$. The indicator changes colour on addition of 16.75 cm^3 of hydroxide solution.

2.6 What was the original substance C?

SOLUTION

2.1 Mass percentage composition: 54.56 % C; 9.21 % H; 36.23 % O

2.2 Empirical formula: $\text{C}_2\text{H}_4\text{O}$

2.3 Molar mass: 88 g mol^{-1}

Molecular formula: $\text{C}_4\text{H}_8\text{O}_2$

2.4 Possible structures:

- | | |
|--|--|
| 1. $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$ | 11. $\text{CH}_2(\text{OH})\text{-CH}(\text{CH}_3)\text{-CHO}$ |
| 2. $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-COOH}$ | 12. $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CHO}$ |
| 3. $\text{CH}_3\text{-O-CO-CH}_2\text{-CH}_3$ | 13. $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CHO}$ |
| 4. $\text{CH}_3\text{-CH}_2\text{-O-CO-CH}_3$ | 14. $\text{CH}_3\text{-O-CH}(\text{CH}_3)\text{-CHO}$ |
| 5. $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CO-H}$ | 15. $\text{CH}_3\text{-CH}_2\text{-CO-CH}_2\text{-OH}$ |
| 6. $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-O-CO-H}$ | 16. $\text{CH}_3\text{-CH}(\text{OH})\text{-CO-CH}_3$ |
| 7. $\text{CH}_3\text{-CH}_2\text{-CH}(\text{OH})\text{-CHO}$ | 17. $\text{CH}_2(\text{OH})\text{-CH}_2\text{-CO-CH}_3$ |
| 8. $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_2\text{-CHO}$ | 18. $\text{CH}_3\text{-O-CH}_2\text{-CO-CH}_3$ |
| 9. $\text{CH}_2(\text{OH})\text{-CH}_2\text{-CH}_2\text{-CHO}$ | |
| 10. $\text{CH}_3\text{-C}(\text{OH})(\text{CH}_3)\text{-CHO}$ | |

2.5 The possible structures are 3, 4, 5, 6.

2.6 The structure of the compound C is $\text{CH}_3\text{-CH}_2\text{-O-CO-CH}_3$.

PROBLEM 3

In a chemical factory in which formaldehyde is produced by oxidation of methanol, aqueous solutions containing methanol and formaldehyde are to be analyzed. In order to test the method, experiments are first carried out with known amounts of both methanol and formaldehyde. The following aqueous solutions are used:

Methanol, 5.00 g dm^{-3}

Formaldehyde, 5.00 g dm^{-3}

Potassium dichromate, $3.000 \times 10^{-2} \text{ mol dm}^{-3}$

Ammonium iron(II) sulphate, $0.2000 \text{ mol dm}^{-3}$

Iodine, $0.1000 \text{ mol dm}^{-3}$

Sodium thiosulphate, $0.2000 \text{ mol dm}^{-3}$.

- I. 10.00 cm^3 methanol solution and 100.00 cm^3 potassium dichromate solution are mixed, approximately 100 cm^3 concentrated sulphuric acid is added and the solution is allowed to stand for about 30 minutes. Excess dichromate ions are then titrated with iron(II) ions with diphenylamine sulphonic acid as a redox indicator (colour change from red-violet to pale green). The volume of the iron(II) solution consumed is 43.5 cm^3 .
 - II. 10.00 cm^3 of formaldehyde solution and 50.00 cm^3 of iodine solution are mixed. Sodium hydroxide solution is added to alkaline reaction and the mixture is left standing for about 10 minutes. Hydrochloric acid is then added to a neutral reaction, and the excess iodine is determined by titration with thiosulphate, with starch as an indicator. The volume of the thiosulphate solution required is 33.3 cm^3 .
- 3.1** Using the analysis data in I and II calculate the reacting amounts and the molar ratios of methanol/dichromate ions and formaldehyde/iodine.
- 3.2** Write balanced equations for all reactions described in experiments I and II.
- III. It is checked that iodine does not react with methanol. From a solution containing both methanol and formaldehyde, two 10.00 cm^3 samples are taken.

One sample is mixed with 100.00 cm^3 of potassium dichromate solution and concentrated sulphuric acid as in I. Excess dichromate ions consume 4.8 cm^3 of iron(II) solution.

The other sample is mixed with 50.00 cm³ of iodine solution and treated as in II. Excess iodine consumes 16.50 cm³ of thiosulphate solution.

3.3 Give balanced equations for the reactions and calculate the contents of methanol and formaldehyde in the solution. Give your answer in g dm⁻³.

SOLUTION

3.1 Amounts of substance:

methanol	1.56 mol
dichromate ions	3.00 mol
iron(II) ions	8.70 mol

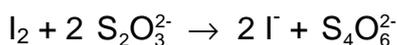
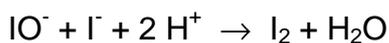
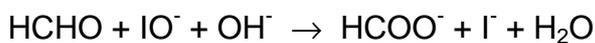
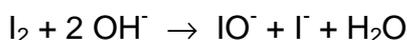
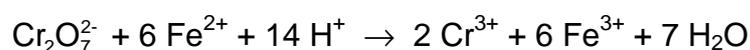
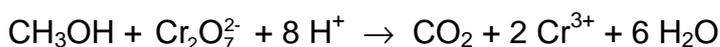
Molar ratio methanol/dichromate: $1 \text{ mol CH}_3\text{OH} \Rightarrow 1 \text{ mol Cr}_2\text{O}_7^{2-}$

Amounts of substance:

formaldehyde	1.67 mol
iodine	5.00 mol
thiosulphate ions	6.66 mol

Molar ratio formaldehyde/iodine: $1 \text{ mol HCHO} \Rightarrow 1 \text{ mol I}_2$

3.2 Chemical equations:



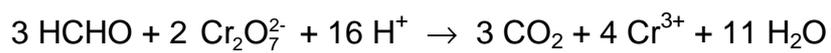
In (3), (5), and (6), I₃ may participate instead of I₂.

As an alternative to (4)



3.3 Chemical equations

To the chemical equations above is added



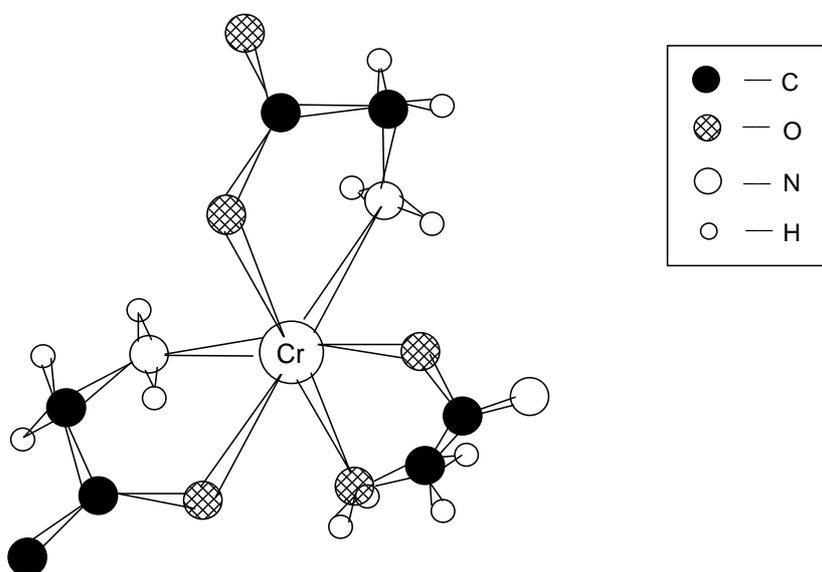
Content of methanol: 1.9 g dm^{-3}

Content of formaldehyde: 10.1 g dm^{-3}

PROBLEM 4

A transition metal atom or ion may be directly bonded to a number of atoms or molecules that surround it (ligands), forming a characteristic pattern. This is the essential structural feature of an important class of so-called coordination or complex compounds. If two or more atoms from one individual ligand form bonds to the same central atom then the ligand is said to form a chelate (Greek chele = crab' claw).

The glycinate ion, $\text{NH}_2\text{-CH}_2\text{-COO}^-$, is a bidentate chelate ligand which can form, for instance, tris-glycinato-chromium(III) complexes. The figure shows one possible structure of such a complex. Oxygen and nitrogen are forced to coordinate to adjacent octahedral positions, as the N-C-C-O chain is too short to "embrace" the chromium ion.



- 4.1 How many different configurational isomers of the complex are possible, not counting optical isomers?
- 4.2 Which of these isomers can be further resolved into optical isomers?

Another coordination compound of chromium was analyzed and found to have the following mass composition: 19.5 % Cr, 40.0 % Cl, 4.5 % H, and 36.0 % O. A 0.533 g sample of the compound was dissolved in 100 cm³ of water, and 10 cm³ of nitric acid (2 mol dm⁻³) was added. Excess of silver nitrate solution was then added and the precipitate formed was then filtered, washed, dried and weighed. Its mass was found to be 0.287 g.

When a 1.06 g sample was gently heated to 100 °C in a stream of dry air, 0.144 g of water was driven off.

The freezing point of a solution prepared from 1.33 g of the compound and 100 cm³ of water, was found to be -0.18 °C. (Molar freezing point depression of water is 1.82 K kg mol⁻¹).

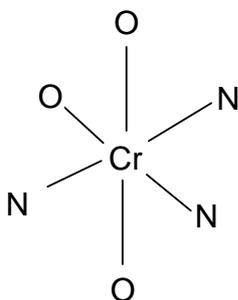
Use all the experimental information to solve the following problems:

- 4.3 Derive the empirical formula of the compound.
- 4.4 Deduce formula for the compound showing the ligands of the chromium ion. Give molar ratios to support your result.
- 4.5 Sketch all possible steric arrangements of the ligands about the chromium ion.

SOLUTION

4.1 Two geometrical isomers of the complex are possible:

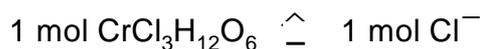
- i) the facial, which is the one illustrating the problem,
- ii) the meridional, with oxygen and nitrogen positions as shown:



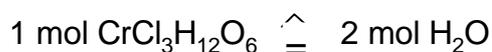
4.2 It is clearly seen that any complex with three bidentate ligands attached octahedrally as shown, lacks mirror symmetry. Hence, both stereoisomers are further resolvable into optical isomers.

4.3 The empirical formula is CrCl₃H₁₂O₆.

4.4 The reaction with silver ions indicates that

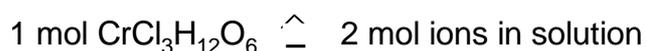


Gentle heating gives

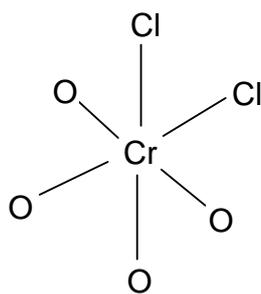


These results support the coordination [CrCl₂(H₂O)₄]Cl · 2 H₂O.

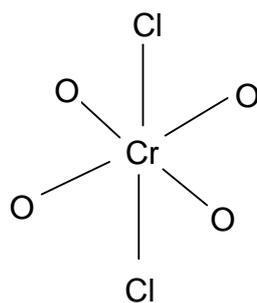
This formula is supported by the freezing point experiment showing that



4.5 Possible steric arrangements of the ligands about the chromium atom:



cis-form



trans-form

PROBLEM 5

Iodine is soluble to a certain extent in pure water. It is, however, more soluble in solutions containing iodide ions. By studying the total solubility of iodine as a function of iodide concentration, the equilibrium constants of the following reactions can be determined:

Equation	Equilibrium constants
$I_2(s) \rightleftharpoons I_2(aq)$	k_1 (1)
$I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$	k_2 (2)
$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$	k_3 (3)

5.1 Give the equilibrium equations for (1) – (3).

Solutions of known potassium iodide concentration $[I^-]_{tot}$ were equilibrated with solid iodine. Subsequent titration with sodium thiosulphate solution served to determine the total solubility of iodine $[I_2]_{tot}$.

The experiments yielded the following results:

$[I^-]_{tot} / \text{mmol dm}^{-3}$	10.00	20.00	30.00	40.00	50.00
$[I_2]_{tot} / \text{mmol dm}^{-3}$	5.85	10.53	15.11	19.96	24.82

5.2 Plot $[I_2]_{tot}$ versus $[I^-]_{tot}$ in a diagram.

5.3 Derive a suitable algebraic expression relating $[I_2]_{tot}$ and $[I^-]_{tot}$.

5.4 Use the graph to determine values of the equilibrium constants k_1 , k_2 , and k_3 .

SOLUTION

5.1 Equilibrium equations

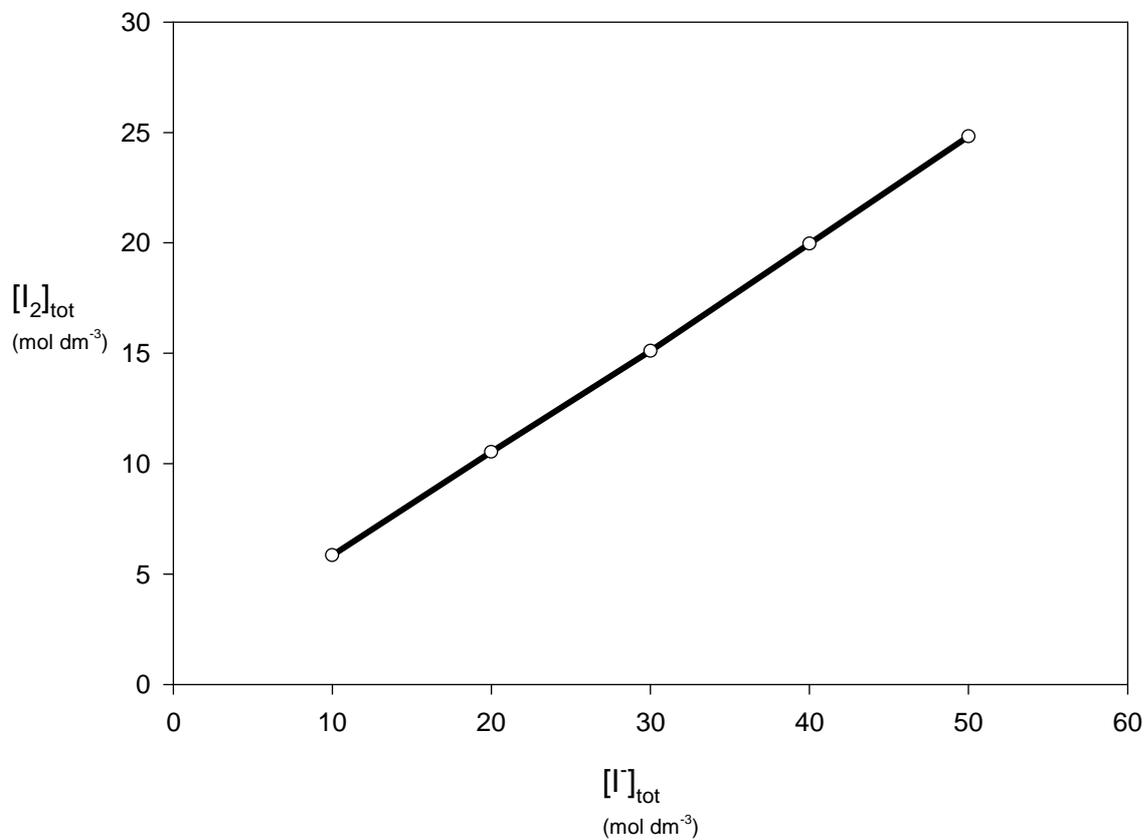
The following relations are valid for the concentrations of the aqueous solutions:

$$[I_2] = k_1$$

$$\frac{[I_3^-]}{[I^-]} = k_2$$

$$\frac{[I_3^-]}{[I_2][I^-]} = k_3 = \frac{k_2}{k_1}$$

5.2 See diagram on the next page.



5.3 The relation between $[I_2]_{\text{tot}}$ and $[I^-]_{\text{tot}}$ is as follows:

$$[I_2]_{\text{tot}} = k_1 + \frac{k_2}{1 + k_2} [I^-]_{\text{tot}}$$

5.4 $k_1 = 1.04 \times 10^{-3} \text{ mol dm}^{-3}$ $k_2 = 0.90$ $k_3 = 8.6 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$

(These values are calculated by the least square method.)

PROBLEM 6

A white solid organic acid, **A**, contains only carbon, hydrogen and oxygen. To obtain an approximate value for the molar mass, 10.0 g of the acid were dissolved in water. Crushed ice was added and vigorous shaking caused a decrease in temperature to $-2.5\text{ }^{\circ}\text{C}$. The ice was quickly removed. The mass of the solution was 76.1 g, and its pH value was determined to be 1.4. In a handbook the molar freezing point depression constant for water was found to be $1.86\text{ K kg mol}^{-1}$. A more precise determination of the molar mass of the acid was then carried out. 0.120 g of the acid was titrated with a sodium hydroxide solution with a concentration of 0.100 mol dm^{-3} . Phenolphthalein was used as an indicator, and when 23.4 cm^3 of hydroxide solution was added the indicator turned red.

6.1 Give the molar mass and the structure of acid **A**.

Liquid **B** dissolves in water up to 10 %. The pH value of the solution is about 4. **B** is not easily oxidized, but following the iodoform reaction and subsequent acidification it is oxidized to acid **A**. 0.10 g of **B** consumes 1.5 g of iodine.

When **B** reacts with sodium, hydrogen is evolved and a metal organic compound is formed. The molar mass of **B** is approximately 100 g mol^{-1} .

6.2 Write the chemical equation for the iodoform reaction and for the reaction with sodium. For the organic molecules structural formulas should be used.

Compound **C** in aqueous solution has a conductivity which differs very little from that of pure water. Alkaline hydrolysis of **C** yields ammonia. 0.120 g of **C** was treated with hot, dilute sodium hydroxide solution and the gas formed was led into 50.0 cm^3 hydrochloric acid with a concentration of 0.100 mol dm^{-3} . The excess acid was titrated with 10.0 cm^3 sodium hydroxide solution with a concentration of 0.100 mol dm^{-3} .

Acid hydrolysis of **C** yields carbon dioxide. From the freezing point depression, the molar mass of **C** is estimated to be between 40 g mol^{-1} and 70 g mol^{-1} .

6.3 Give the structure of **C**. Write reaction equations for both the alkaline and the acid hydrolysis.

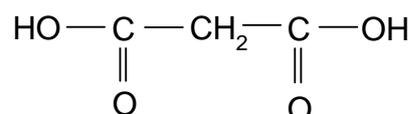
If **C** is allowed to react with the ethyl ester of acid **A** in the presence of a strong alkaline catalyst, ethanol and compound **D** are formed. The composition of **D** is 37.5 % C, 3.1 % H, 21.9 % N, and the remainder is oxygen. The compound is an acid.

6.4 Give the structure for **D**. Which is the "acid" hydrogen atom? Mark it with * in the structure.

SOLUTION

6.1 Molar mass of **A**: 103 g mol^{-1}

Structure of **A**:



6.2 $\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3 + 6 \text{I}_2 + 8 \text{OH}^- \rightarrow \text{O}^-\text{-CO-CH}_2\text{-CO-O}^- + 2 \text{CHI}_3 + 6 \text{I}^-$

$\text{O}^-\text{-CO-CH}_2\text{-CO-O}^- + 2 \text{H}^+ \rightarrow \text{HO-CO-CH}_2\text{-CO-OH}$

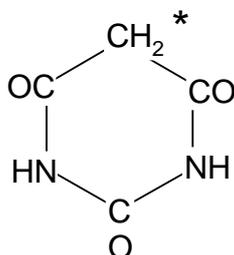
$2 \text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3 + 2 \text{Na} \rightarrow 2 \text{CH}_3\text{-CO-CH}^-\text{-CO-CH}_3 + \text{H}_2 + 2 \text{Na}^+$

6.3 $\text{H}_2\text{N-CO-NH}_2$

$\text{H}_2\text{N-CO-NH}_2 + 2 \text{OH}^- \rightarrow 2 \text{NH}_3 + \text{CO}_3^{2-}$

$\text{H}_2\text{N-CO-NH}_2 + 2 \text{H}^+ + \text{H}_2\text{O} \rightarrow 2 \text{NH}_4^+ + \text{CO}_2 \text{ CO}_3^{2-}$

6.4



* - "acid" hydrogen

PROBLEM 7

Calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is a sparingly soluble salt of analytical and physiological importance. The solubility product is 2.1×10^{-9} at 25 °C. Oxalate ions can protolyse to form hydrogen oxalate ions and oxalic acid. The pK_a values at 25 °C are 1.23 ($\text{H}_2\text{C}_2\text{O}_4$) and 4.28 (HC_2O_4^-). At 25 °C the ionic product of water is 1.0×10^{-14} .

- 7.1** State those expressions for the equilibrium conditions which are of interest for the calculation of the solubility of calcium oxalate monohydrate.
- 7.2** State the concentration conditions which are necessary for the calculation of the solubility s (in mol dm^{-3}) of calcium oxalate in a strong acid of concentration C .
- 7.3** Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in a plant cell in which the buffer system regulates the pH to 6.5.
- 7.4** Calculate the solubility (in g dm^{-3}) of calcium oxalate monohydrate in hydrochloric acid with a concentration of $0.010 \text{ mol dm}^{-3}$. Give the concentration of hydrogen ions in the solution.
- 7.5** Calculate the equilibrium concentrations of all other species in solution d).

SOLUTION

$$\text{7.1} \quad [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = K_s \quad (1) \qquad [\text{H}^+][\text{OH}^-] = K_w \quad (2)$$

$$\frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = K_{a1} \quad (3) \qquad \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = K_{a2} \quad (4)$$

$$\text{7.2} \quad s = [\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] \quad (5)$$

$$C = [\text{H}^+] + [\text{HC}_2\text{O}_4^-] + 2[\text{H}_2\text{C}_2\text{O}_4] - [\text{OH}^-] \quad (6)$$

Equations (5) or (6) may be replaced by

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{OH}^-] + C \quad (7)$$

- 7.3** The solubility of calcium oxalate monohydrate is 6.7×10^{-3} . (Calculated according to equation (8)).

7.4 Elimination of the concentrations of oxalate species using equations (1), (3), and (4) yields the following expressions for (5) and (6). (The concentration of hydroxide ions can be neglected.)

$$s_2 = K_s + \frac{[\text{H}^+] K_s}{K_{a2}} + \frac{[\text{H}^+]^2 K_s}{K_{a1} K_{a2}} \quad (8)$$

$$C = [\text{H}^+] + \frac{[\text{H}^+] K_s}{s K_{a2}} + \frac{2[\text{H}^+]^2 K_s}{s K_{a1} K_{a2}} \quad (9)$$

Elimination of s from (8) and (9) results in 4th order equation. For this reason, an iterative method is to be preferred. The first approximation is $[\text{H}^+] = C$. This value of $[\text{H}^+]$ can be used to calculate:

- i) solubility s from (8),
- ii) the last two terms in (9), which are corrections. Now a new value for $[\text{H}^+]$ obtained from (9) may be used as a starting value for the next approximation. Two repeated operations give the following value for s :

$$s = 6.6 \times 10^{-4} \text{ mol dm}^{-3} = 9.6 \times 10^{-2} \text{ g dm}^{-3}$$

$$[\text{H}^+] = 9.3 \times 10^{-3} \text{ mol dm}^{-3}$$

7.5 $[\text{Ca}^{2+}] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{C}_2\text{O}_4^{2-}] = 3.2 \times 10^{-6} \text{ mol dm}^{-3}$

$[\text{Cl}^-] = 0.010 \text{ mol dm}^{-3}$

$[\text{HC}_2\text{O}_4^-] = 5.7 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{OH}^-] = 1.1 \times 10^{-12} \text{ mol dm}^{-3}$

$[\text{H}_2\text{C}_2\text{O}_4] = 9.0 \times 10^{-5} \text{ mol dm}^{-3}$

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

A pH buffer solution has a well defined acidity which changes only very slightly upon addition of moderate quantities of strong acid or base. The larger is the quantity of acid or base that must be added to a certain volume of a buffer solution in order to change its pH by a specific amount, the better is its action. A buffer solution is prepared by mixing a weak acid and its conjugate base in appropriate amounts in a solution. An example of a useful buffer system in aqueous solution is the phosphate system.

Your task is to prepare a phosphate buffer with properties specified by the following two conditions:

- (1) pH = 7.20 in the buffer solution,
- (2) pH = 6.80 in a mixture of 50.0 cm³ of the buffer solution and 5.0 cm³ hydrochloric acid with a concentration of 0.100 mol dm⁻³.

Chemicals and equipment

Aqueous solution of phosphoric acid, sodium hydroxide solution of known concentration, hydrochloric acid (0.100 mol dm⁻³), solution of bromocresol green, distilled water.

Burettes, pipettes (25 and 5 cm³), Erlenmeyer flasks (100 and 250 cm³), volumetric flask (100 cm³), beaker, and funnel.

Procedure

Determine the concentration of the phosphoric acid solution by titration with a sodium hydroxide solution using bromocresol green as an indicator (pH range 3.8 < pH < 5.4).

Make a buffer solution by mixing calculated volumes of phosphoric acid and sodium hydroxide solutions in the volumetric flask and filling the flask to the mark with distilled water.

Mix in an Erlenmeyer flask 50.0 cm³ of the buffer solution with 5.0 cm³ of the hydrochloric acid.

Hand in your answer sheet to the referee who will also measure the pH of your two solutions and note your results.

The pK_a values for phosphoric acid are:

$$pK_{a1} = 1.75, \quad pK_{a2} = 6.73, \quad pK_{a3} = 11.50$$

SOLUTION

The buffer solution must contain

H₂PO₄⁻ (concentration **a** mol dm⁻³) and

HPO₄²⁻ (concentration **b** mol dm⁻³).

The concentrations should satisfy the condition

$$\frac{\mathbf{b}}{\mathbf{a}} = \frac{10^{-6.73}}{10^{-7.20}}$$

After addition of HCl the condition will be

$$\frac{50.0\mathbf{b} - 0.50}{50.0\mathbf{a} + 0.50} = \frac{10^{-6.73}}{10^{-6.80}}$$

From these equations,

$$\mathbf{a} = 0.0122 \quad \mathbf{b} = 0.0361$$

Total concentration of the phosphate system = 0.0483 mol dm⁻³

Total concentration of Na⁺ = (**a** + 2 **b**) mol dm⁻³ = 0.0844 mol dm⁻³

If the concentration of both phosphoric acid and sodium hydroxide solution are 0.500 mol dm⁻³, then 100.0 cm³ buffer solution will require:

$$\text{volume of H}_3\text{PO}_4 \text{ solution} = \frac{0.0483 \times 0.1000}{0.500 \text{ dm}^3} = 9.7 \text{ cm}^3$$

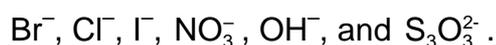
$$\text{volume of NaOH solution} = \frac{0.0844 \times 0.1000}{0.500 \text{ dm}^3} = 16.9 \text{ cm}^3$$

PROBLEM 2 (practical)

Each of 8 numbered test tubes contains a solution of one salt. In the solutions the following positive ions can be found (a maximum of one in each test tube):



and the following negative ions (at most one in each test tube)



A test plate, test tubes in a rack, dropping pipettes, indicator paper, and a gas burner are also provided.

Determine by means of mutual reactions which salt is dissolved in each test tube. Confirm your conclusions by carrying out as many reactions as possible. It may be necessary to use combinations of solutions and reagents.

Give a list of numbers and corresponding formulae of the substances, indicate the formation of a precipitate by a downward arrow, and gas evolution by an upward arrow in the square array provided for reporting the reactions.

Write chemical equations for all the reactions observed.

SOLUTION

Numbers of solutions mixed	Chemical equation for the observed reaction
1 + 2	$\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}$
2 + 3	$2 \text{OH}^- + 2 \text{Ag}^+ \rightarrow \text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}$
2 + 3 + 1	$\text{Ag}_2\text{O}(\text{s}) + 4 \text{NH}_4^+ + 2 \text{OH}^- \rightarrow 2 \text{Ag}(\text{NH}_3)_2^+ + 3 \text{H}_2\text{O}$
2 + 4	$\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_2(\text{s}) \leftrightarrow \text{Zn}(\text{OH})_2(\text{s}) + 2 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-}$
2 + 5	$\text{Al}^{3+} + 3 \text{OH}^- \rightarrow \text{Al}(\text{OH})_3(\text{s}) \leftrightarrow \text{Al}(\text{OH})_3(\text{s}) + \text{OH}^- \rightarrow \text{Al}(\text{OH})_4^-$

Reactions to distinguish Zn^{2+} from Al^{3+} :

Numbers of solutions mixed	Chemical equation for the observed reaction
2 + 4 + 1	$\text{Zn}(\text{OH})_4^{2-} + 4 \text{NH}_4^+ \rightarrow \text{Zn}(\text{NH}_3)_4^{2+} + 4 \text{H}_2\text{O}$
2 + 5 + 1	$\text{Al}(\text{OH})_4^- + 2 \text{NH}_4^+ \rightarrow \text{Al}(\text{OH})_3(\text{s}) + \text{NH}_3 + \text{H}_2\text{O}$
2 + 6	$\text{Cu}^{2+} + 2 \text{OH}^- \rightarrow \text{Cu}(\text{OH})_2(\text{s})$

2 + 6 + 1	$\text{Cu}(\text{OH})_2(\text{s}) + 4 \text{NH}_4^+ + 2 \text{OH}^- \rightarrow \text{Cu}(\text{NH}_3)_4^{2+} + 4 \text{H}_2\text{O}$
3 + 4	$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(\text{s})$
3 + 6	$\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}(\text{s})$
3 + 7	$\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}(\text{s})$
3 + 8	$2 \text{Ag}^+ + \text{S}_2\text{O}_3^{2-} \rightarrow \text{Ag}_2\text{S}_2\text{O}_3(\text{s}) \leftrightarrow \text{Ag}_2\text{S}_2\text{O}_3(\text{s}) + 3 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$

Reactions to distinguish Cl^- from Br^- and from I^-

3 + 4 + 1 + 2	$\text{AgCl}(\text{s}) + 2 \text{NH}_4^+ + 2 \text{OH}^- \rightarrow \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^- + \text{H}_2\text{O}$
3 + 4 + 8	$\text{AgCl}(\text{s}) + 2 \text{S}_2\text{O}_3^{2-} \rightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{Cl}^-$
3 + 6 + 1 + 2	AgBr(s) does not dissolve
3 + 6 + 8	$\text{AgBr}(\text{s}) + 2 \text{S}_2\text{O}_3^{2-} \rightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{Br}^-$
3 + 7 + 8	AgI(s) does not dissolve
6 + 7	$2 \text{Cu}^{2+} + 4 \text{I}^- \rightarrow 2 \text{CuI}(\text{s}) + \text{I}_2$
6 + 7 + 8	$\text{I}_2(\text{s}) + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}$

	1	2	3	4	5	6	7	8
1		↑						
2	↑		↓	↓	↓	↓		
3		↓		↓		↓	↓	↓
4		↓	↓					
5		↓						
6		↓	↓				↓	
7			↓			↓		
8			↓					

List of numbers and corresponding formulae for the substances:

- | | |
|-----------------------------|--------------------------------------|
| 1. NH_4NO_3 | 5. $\text{Al}(\text{NO}_3)_3$ |
| 2. NaOH | 6. CuBr_2 |
| 3. AgNO_3 | 7. NaI |
| 4. ZnCl_2 | 8. $\text{Na}_2\text{S}_2\text{O}_3$ |
-
-

PROBLEM 3 (practical)*Determination of the solubility product of lead(II) chloride*

Shake solid lead(II) chloride:

- with water,
 - with three solutions of sodium chloride of different concentrations,
- until equilibrium is attained. Then determine the lead ion concentration by titration with EDTA. Calculate the solubility product of lead(II) chloride.

Equipment and chemicals

Volumetric flask (100 cm³), pipettes (20 cm³ and 10 cm³), graduated cylinder (100 cm³ and 25 cm³), 4 Erlenmeyer flasks (200 – 250 cm³) with stoppers, spatula, 4 filter funnels, filter papers, thermometer, 4 Erlenmeyer flasks (100 cm³), titrating flasks (200 – 250 cm³), beakers, stand with burette (50 cm³), burette funnel, wash bottle with distilled water, glass rod.

Standard solutions of sodium chloride (0.1000 mol dm⁻³) and EDTA (0.01000 mol dm⁻³), solid lead(II) chloride, xylene orange solution in a dropping bottle (0.5 % in water), solid hexamine (urotropine), nitric acid (2.5 mol dm⁻³) in a dropping bottle.

Procedure

- Prepare 100 cm³ of sodium chloride solutions with concentrations of 0.0600 mol dm⁻³, 0.0400 mol dm⁻³, and 0.0200 mol dm⁻³, respectively. Place the solutions in Erlenmeyer flasks with stoppers. Place 100 cm³ of water in the fourth flask with a stopper. Add 5 spatulas of solid lead(II) chloride (about 2 g) to each, stopper the flasks and shake vigorously. Let the flasks stand for 30 minutes. Shake them occasionally. Prepare for filtration and titration in the meanwhile.
- Measure the temperatures of the lead(II) chloride solutions and report them in the table of results. Filter the solutions through dry filters into small, dry Erlenmeyer flasks.
- Using a pipette, transfer 10.00 cm³ of the filtrate into a titration flask. Dilute with approximately 25 cm³ of water, add 3 drops of xylene orange (indicator) and 5 drops of nitric acid. Then add 5 spatulas (about 0.5 g) of solid hexamine (a weak base) and swirl gently until the solution is clear. Titrate with EDTA.

4. Calculate the concentration of lead ions and that of chloride ions in the solutions and give the solubility product K_s . Report the results in the table.
5. Answer the questions in the answer sheet.

Questions

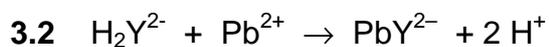
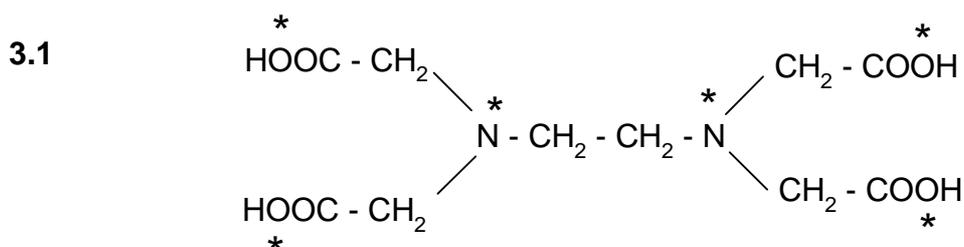
- 3.1 Give the structure of EDTA. Mark those atoms which can coordinate to a metal ion with an asterisk (*).
- 3.2 Give the equation for the filtration reaction. EDTA may be written as H_2X^{2-} .

SOLUTION

A typical result:

$c(\text{NaCl})$ (mol dm^{-3})	Temperature ($^{\circ}\text{C}$)	Volume EDTA solution (cm^3)	$[\text{Pb}^{2+}]$ (mol dm^{-3})	$[\text{Cl}^-]$ (mol dm^{-3})	K_s
0.0600	21	18.7	0.0187	0.0974	1.77×10^{-4}
0.0400	21	22.7	0.0227	0.0854	1.66×10^{-4}
0.0200	21	27.8	0.0278	0.0756	1.59×10^{-4}
-	21	34.2	0.0342	0.0684	1.60×10^{-4}

Answers to the questions:



15th



International Chemistry Olympiad

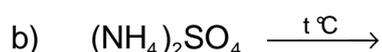
**7 theoretical problems
3 practical problems**

THE FIFTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 2–11 JULY 1983, TIMISOARA, ROMANIA

THEORETICAL PROBLEMS

PROBLEM 1

A) Describe the thermal decomposition of the following ammonium salts in terms of chemical equations:



B) Indicate the right answer:

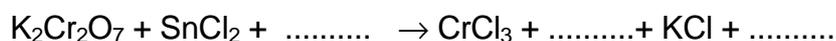
a) Can the molar mass be determined by measuring the density of a gaseous compound at a given temperature and pressure?

1. Yes, under any conditions.
2. Yes, if the gaseous compound does not dissociate and associate.
3. Yes, if the gaseous compound does not dissociate.
4. Yes, if the gaseous compound does not associate.

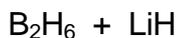
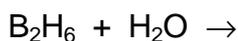
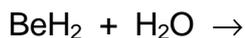
b) Is a liquid boiling at a constant temperature (at a given pressure) a pure substance?

1. Yes, if the liquid is not azeotropic.
2. Yes, if the liquid is azeotropic.

C) Complete and balance the following equation: (in H_2O)

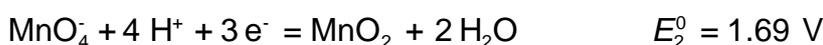
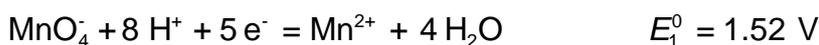


- D) The solubility of Hg_2Cl_2 in water is 3.0×10^{-5} g/100 ml solution.
- What is the solubility product?
 - What is the solubility (in mol dm^{-3}) of this substance in a 0.01 M NaCl solution?
 - What is the volume of a 0.01 M NaCl solution which dissolves the same quantity of mercurous chloride as that dissolved in one litre of pure water?
- $A_r(\text{Hg}) = 200.61$ $A_r(\text{Cl}) = 35.45$
- E) Which of the following groups contains solid compounds at 10 °C?
- H_2O , NH_3 , CH_4
 - F_2 , Cl_2 , Br_2
 - SO_3 , I_2 , NaCl
 - Si , S_8 , Hg
- F) Which of the following salts forms an acidic aqueous solution?
- CH_3COONa
 - NH_4Cl
 - Na_2HPO_4
 - Na_2CO_3
 - NaHCO_3
- G) Write the electronic formulas for the following compounds so that the nature of the chemical bonds is evident:
- NaClO_3 , b) HClO_3 , c) SiF_4 , d) NH_3 , e) CaF_2 , f) H_2O
- H) Solid perchloric acid is usually written as $\text{HClO}_4 \cdot \text{H}_2\text{O}$. Based on experimental data showing four equal bonds, suggest a structure accounting for the experimental result.
- I) The compounds of the second row elements with hydrogen are as follows: LiH , BeH_2 , B_2H_6 , CH_4 , NH_3 , H_2O , HF .
- Which compounds are solid at room temperature? Explain.
 - Which of them are ionic?
 - Which are polymeric?
 - Which ones do not react with water under normal conditions?
 - Give products of the following reactions.

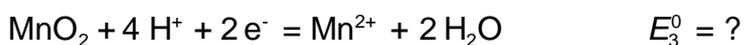


- f) Supposing that NH_3 , H_2O and HF are acids under some conditions, write their corresponding conjugated bases and arrange them in order of increasing basic strength.

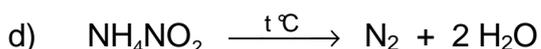
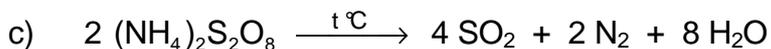
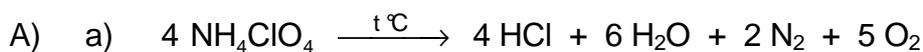
- J) The following E^0 values are given for the half-reactions:



Calculate E^0 for the following reaction:

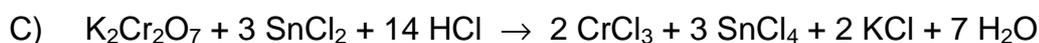


SOLUTION



- B) a) 1, 2, 3, 4

- b) 1, 2



D) a) $s = 3.0 \times 10^{-5} \text{ g}/100 \text{ cm}^3 = 3.0 \times 10^{-4} \text{ g dm}^{-3} =$
 $= \frac{3.0 \times 10^{-4} \text{ g dm}^{-3}}{472 \text{ g mol}^{-1}} = 6.3 \times 10^{-7} \text{ mol dm}^{-3}$



$$K_s = 4 s^3 = 4 (6.3 \times 10^{-7})^3 = 1.0 \times 10^{-18}$$

- b) $c(\text{Cl}^-) = 0.01 \text{ mol dm}^{-3}$

$$s = \frac{K_s}{[\text{Cl}^-]^2} = \frac{1.0 \times 10^{-18}}{(0.01)^2} = 1.0 \times 10^{-14}$$

$$s = 1.0 \times 10^{-14} \text{ mol dm}^{-3}$$

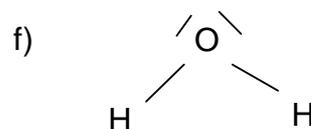
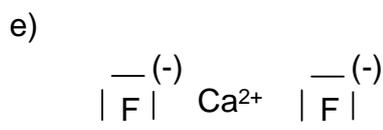
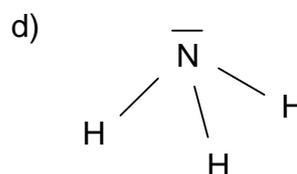
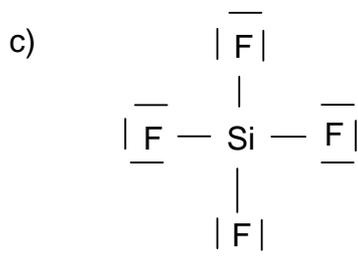
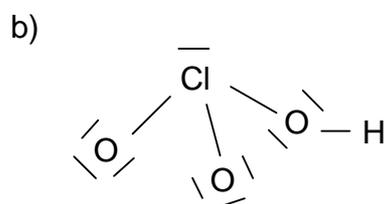
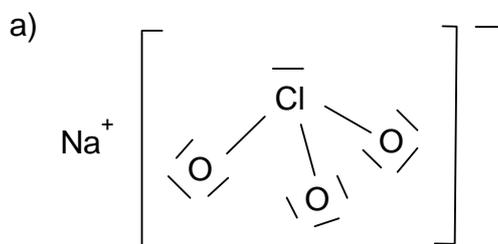
- c) The volume of 0.01 M NaCl solution in which dissolves the same quantity of Hg_2Cl_2 as in 1 dm³ of water, is as follows:

$$V = \frac{6.3 \times 10^{-7}}{1.0 \times 10^{-14}} = 6.3 \times 10^7 \text{ dm}^3$$

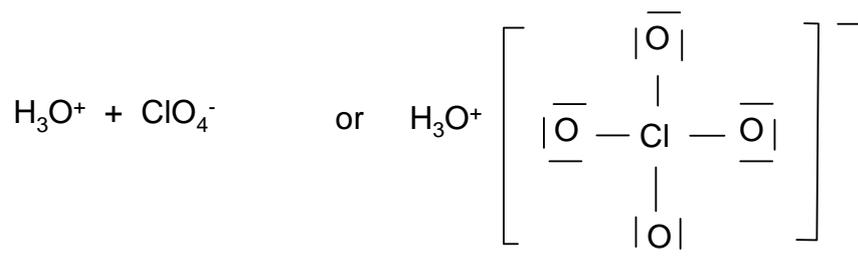
E) c) SO_3 , I_2 , NaCl

F) b)

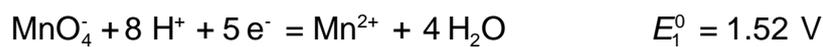
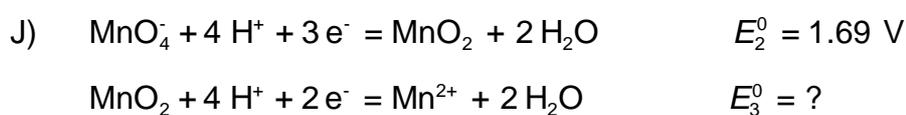
G)



H)



- I) a) LiH, (BeH₂)_n polymer
 b) LiH
 c) (BeH₂)_n
 d) CH₄
 e) BeH₂ + 2 H₂O → Be(OH)₂ + 2 H₂
 B₂H₆ + 6 H₂O → 2 B(OH)₃ + 6 H₂
 B₂H₆ + 2 LiH → 2 Li[BH₄]
 f) NH₂⁻ > OH⁻ > F⁻



$$5 E_1^0 = 3 E_2^0 + 2 E_3^0$$

$$7.60 = 5.07 + 2 x$$

$$x = 1.26 \text{ V}$$

PROBLEM 2

In a gaseous mixture of CO and CO₂, a mass ratio of carbon : oxygen = 1 : 2 was determined.

- 2.1 Calculate the mass percent composition.
- 2.2 Calculate the volume percent composition.
- 2.3 Indicate values of the carbon: oxygen ratios for which both gases cannot be present simultaneously.

SOLUTION

Write x = number of moles of CO in 100 g

y = number of moles of CO₂ in 100 g

$$28x + 44y = 100$$

$$\frac{12(x+y)}{16(x+2y)} = \frac{1}{2}$$

$$x = 1.389 \text{ mol CO}$$

$$y = 1.389 \text{ mol CO}_2$$

$$2.1 \quad \frac{1.389 \times 44}{100} \times 100 = 61.11 \% \text{ CO}_2$$

$$\frac{1.389 \times 28}{100} \times 100 = 38.89 \% \text{ CO}$$

$$2.2 \quad X = y \quad 50 \% \text{ CO}_2 + 50 \% \text{ CO (by volume)}$$

2.3 The two gases cannot be simultaneously present in the mixture if:

$$\frac{\text{carbon mass}}{\text{oxygen mass}} = \frac{12}{16} \text{ which corresponds to pure CO}$$

$$\frac{12}{32} \text{ which corresponds to pure CO}_2$$

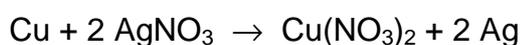
PROBLEM 3

A sample containing a mixture of sodium chloride and potassium chloride weights 25 g. After its dissolution in water 840 ml of AgNO₃ solution ($c = 0.5 \text{ mol dm}^{-3}$) is added. The precipitate is filtered off and a strip of copper weighing 100.00 g is dipped into the filtrate. After a given time interval the strip weights 101.52 g.

Calculate the mass percent composition of the mixture.

SOLUTION

$$A_r(\text{Cu}) = 63.5 \quad A_r(\text{Ag}) = 108$$



$$y \quad \quad \quad x$$

x = the quantity of deposited silver

y = the quantity of dissolved copper

$$\frac{63.5}{y} = \frac{2 \times 108}{x}$$

$$x - y = 101.52 - 100 \quad x = 1.52 + y$$

$$\frac{63.5}{y} = \frac{2 \times 108}{1.52 + x} \quad y = 0.63 \quad x = 2.15 \text{ g Ag}^+$$

Mass of silver nitrate:

$$\frac{840}{1000} \times 0.5 \times 170 = 71.4 \text{ g AgNO}_3$$

$$\frac{170 \text{ g AgNO}_3}{108 \text{ g Ag}} = \frac{71.4}{x} \quad x = 45.36 \text{ g Ag}^+$$

Silver consumed for participation

$$45.36 - 2.15 = 43.21 \text{ g Ag}^+$$

Total mass of chloride

$$\frac{108 \text{ g Ag}^+}{35.5 \text{ g Cl}^-} = \frac{43.2}{x} \quad x = 14.2 \text{ g Cl}^-$$

$$M_r(\text{NaCl}) = 58.5 \quad M_r(\text{KCl}) = 74.6$$

x = mass of NaCl in the mixture

y = mass of KCl in the mixture

$$\text{mass of Cl}^- \text{ in NaCl: } \frac{35.5 x}{58.5}$$

$$\text{mass of Cl}^- \text{ in KCl: } \frac{35.5 y}{74.6}$$

$$\frac{35.5 x}{58.5} + \frac{35.5 y}{74.6} = 14.2$$

$$x + y = 25$$

$$x = 17.6 \text{ g NaCl} \quad 70.4 \% \text{ NaCl}$$

$$y = 7.4 \text{ g KCl} \quad 29.6 \% \text{ KCl}$$

PROBLEM 4

The following data were gathered for the alkaline hydrolysis of certain chlorinated compounds:

- a) A certain volume of a solution of the neutral potassium salt of chlorosuccinic acid is mixed with an equal volume of hydroxide solution. The initial concentration of each solution is 0.2 mol dm^{-3} . The potassium hydroxide concentration in the reaction mixture was determined at different time intervals at $25 \text{ }^{\circ}\text{C}$. The following values were obtained:

t (minutes)	10	20	30	45	60	80	100
c(KOH) (mol dm^{-3})	0.085	0.074	0.065	0.056	0.049	0.042	0.036

The experiment was repeated with the same initial solutions at $35 \text{ }^{\circ}\text{C}$. The hydroxide concentration is reduced to one half after 21 minutes.

- b) In the hydrolysis of 3-chloro-3-methylhexane with potassium hydroxide, the concentration of potassium hydroxide was found to have been reduced to one half after 32 minutes at $25 \text{ }^{\circ}\text{C}$ or 11 minutes at $35 \text{ }^{\circ}\text{C}$, regardless of the initial reactant concentrations (identical).
- c) In the alkaline hydrolysis of 3-chloro-2,4-dimethyl-3-isopropylpentane an identical reaction mechanism as for reaction b was found but the reaction rate was about 100 times faster under the same reaction conditions.

Considering the above data answer the following questions:

- 4.1 What is the reaction order in cases a, b, and c?
- 4.2 What is the rate constant at $25 \text{ }^{\circ}\text{C}$ for reaction a? Indicate the units.
- 4.3 Calculate the activation energies for reactions a and b.
- 4.4 If in reaction a dipotassium salt of L-chlorosuccinic acid (which is levorotatory,) is used, what type of optical rotation will be exhibited by the corresponding salt of malic acid formed by hydrolysis?
- 4.5 If the levorotatory isomer is also used in reaction b, what optical rotation will be exhibited by 3-methyl-3-hexanol formed in the hydrolysis reaction?

4.6 Why is the rate of reaction c much faster than that of reaction b when both reactions are of the same type and occur under the same temperature and concentration conditions?

SOLUTION

4.1 For reaction a the reaction order is estimated as follows:

- assuming the first-order reaction:

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

t (°C)	10	20	30	45	60	80	100
k · 10 ²	1.625	1.505	1.436	1.288	1.189	1.084	1.022

k is not constant, hence the reaction is not of the first-order.

- for the second-order reaction (with reactant concentrations equal at time zero):

$$k = \frac{1}{t} \left(\frac{a}{a-x} - \frac{1}{a} \right)$$

t (°C)	10	20	30	45	60	80	100
k	0.176	0.176	0.179	0.175	0.173	0.173	0.178

As k has almost a constant value the condition for a second-order reaction is fulfilled.

The half-life of reaction b is independent on the initial concentrations, i. e. it is a first-order reaction:

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{t_{1/2}} \ln \frac{a}{a-\frac{a}{2}} = \frac{1}{t_{1/2}} \ln 2$$

Reaction c has the same mechanism as reaction b. Therefore, it will also be a first-order reaction.

4.2 The rate constant of reaction a is an average of the above calculated values.

$$k = 0.176 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

4.3 In order to determine the activation energy, the rate constant, k , at 35 °C is to be calculated.

For the second-order reactions the relationship between the rate constants and half-lives is as follows:

$$k = \frac{1}{t} \left(\frac{a}{a-x} - \frac{1}{a} \right) = \frac{1}{t_{1/2}} \left(\frac{1}{a-\frac{a}{2}} - \frac{1}{a} \right) = \frac{1}{t_{1/2}} \frac{1}{a}$$

The half-life at 35 °C and the initial concentration, $a = 0.1 \text{ mol dm}^{-3}$, are known. (By mixing equal volumes of the two solutions the concentration of each reacting species is reduced to a half.)

Calculation of the rate constant at 35 °C:

$$k' = \frac{1}{21} \cdot \frac{1}{0.1} = 0.476 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

The activation energy of reaction a will be:

$$E_a = R \ln \frac{k' \cdot T' \cdot T}{k \cdot T' - T} = 8314 \ln \frac{0.476 \cdot 308 \cdot 298}{0.176 \cdot 308 - 298} = 7.592 \times 10^7 \text{ J mol}^{-1}$$

For reaction b that is a first-order reaction, the rate constants at the two temperatures are calculated from the half-lives:

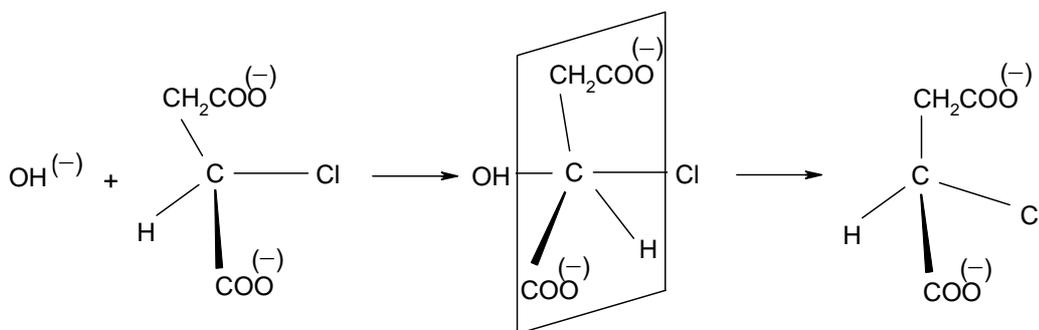
$$\text{at } 25 \text{ °C: } k = \frac{\ln 2}{32} = 2.166 \times 10^{-2} \text{ min}^{-1}$$

$$\text{at } 35 \text{ °C: } k' = \frac{\ln 2}{11} = 6.301 \times 10^{-2} \text{ min}^{-1}$$

Hence the activation energy is:

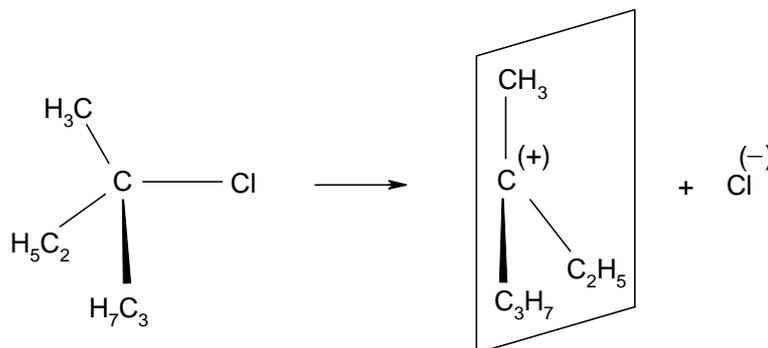
$$E_a = 8314 \ln \frac{6.301 \times 10^{-2} \cdot 308 \cdot 298}{2.166 \times 10^{-2} \cdot 308 - 298} = 8.149 \times 10^7 \text{ J mol}^{-1}$$

4.4 The product of the hydrolysis reaction a will become dextrorotatory as a result of configuration inversion.



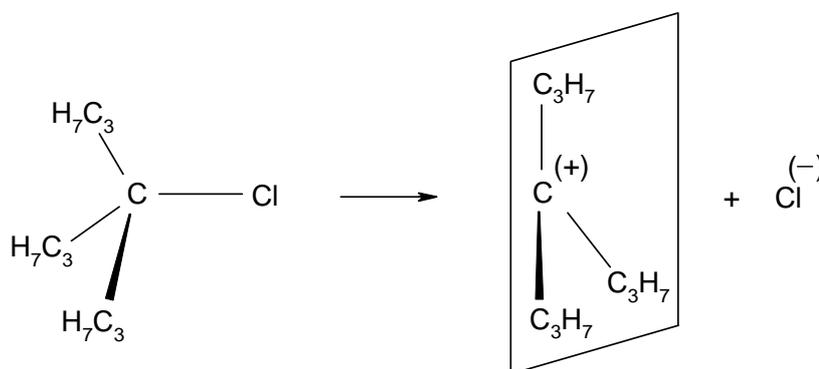
As an S_N2 type reaction, it involves a transition state in which the inversion of the configuration of the asymmetric carbon atom occurs. Thus, if the substrate is levorotatory, the product will become dextrorotatory.

- 4.5 The reaction b is a unimolecular S_N1 reaction and involves the transient formation of an almost stable carbonium ion in the rate-determining step.



The most probable structure of the carbonium ion is planar. The carbonium ion may be attacked by the nucleophilic reagent (the OH⁻ ion) on both sides of the plane with the same probability. The product will result as a racemic mixture, with no optical activity, inactive by intermolecular compensation.

- 4.6 The same is true for the reaction c, the only difference being a more marked repulsion among bulkier substituents. The tendency towards carbonium ion formation with a planar structure and reduced repulsions is increased.



The rate of the carbonium ion formation, and therefore the overall reaction rate, is consequently increased.

PROBLEM 5

On passing ethanol over a catalyst at 400 K, a dehydration reaction occurs resulting in the formation of ethylene:



At the above temperature and $p_0 = 101.325 \text{ kPa}$, the conversion of ethyl alcohol is 90.6 mol %.

- 5.1 Calculate the equilibrium constant K_p of the reaction under given conditions.
- 5.2 Calculate the values of the equilibrium constants K_x and K_c at the above temperature.
- 5.3 Calculate the ethanol conversion at the following pressures:
5 p_0 , 10 p_0 , 50 p_0 , 100 p_0 , and 200 p_0 .
- 5.4 Plot the graph for the variation of conversion vs. pressure.

SOLUTION

The reaction: $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$

Moles:

initial:	1	0	0	
at equilibrium:	$1 - x$	x	x	total: $1 + x$

	Molar fraction	Partial pressure
Ethanol	$\frac{1-x}{1+x}$	$\frac{1-x}{1+x} p$
Ethylene	$\frac{x}{1+x}$	$\frac{x}{1+x} p$
Water	$\frac{x}{1+x}$	$\frac{x}{1+x} p$

$$p = \frac{p'}{p} \quad p' - \text{total pressure, } p_0 = 101.325 \text{ kPa}$$

$$K_p = \frac{p_{\text{C}_2\text{H}_4} \cdot p_{\text{H}_2\text{O}}}{p_{\text{C}_2\text{H}_5\text{OH}}} = \frac{\left(\frac{x}{1+x} p\right) \left(\frac{x}{1+x} p\right)}{\frac{1-x}{1+x} p} = \frac{x^2}{1-x^2} p$$

5.1 $p' = 101.325 \text{ kPa}$

$$K_p = \frac{x^2}{1-x^2} = \frac{0.906^2}{1-0.906^2} = 4.56$$

5.2 $K_x = K_p p^{-\Delta n}$; $p' = 101.325 \text{ kPa}$; $\Delta n = 1$; $K_x = 4.56$

$$K_c = K_p \left(\frac{c_0 RT}{p_0} \right)^{\Delta n} \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}; \quad c^0 = 1 \text{ mol dm}^{-3}; \quad T = 400 \text{ K}$$

$$K_c = 0.139$$

5.3 $\frac{x^2}{1-x^2} = \frac{K_p}{p} = \frac{4.56}{p}$

a) $\frac{x^2}{1-x^2} = \frac{4.56}{5} = 0.912 \quad x = 0.69$

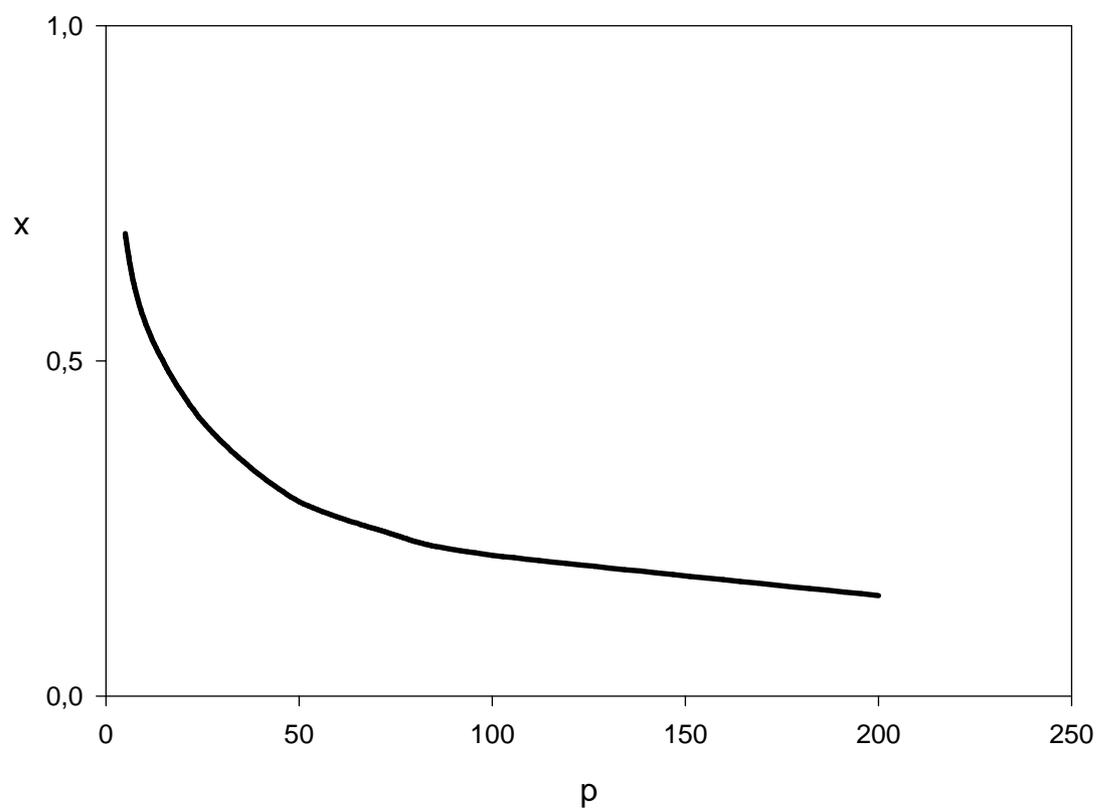
b) $\frac{x^2}{1-x^2} = \frac{4.56}{10} = 0.456 \quad x = 0.56$

c) $\frac{x^2}{1-x^2} = \frac{4.56}{50} = 0.0912 \quad x = 0.29$

d) $\frac{x^2}{1-x^2} = \frac{4.56}{100} = 0.0456 \quad x = 0.21$

e) $\frac{x^2}{1-x^2} = \frac{4.56}{200} = 0.0228 \quad x = 0.15$

5.4

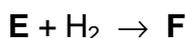


PROBLEM 6

One mole of compound **A** reacts successively with 3 moles of compound **B** in aqueous solution in the presence of a basic catalyst (such as $\text{Ca}(\text{OH})_2$):



Hydrogenation of compound **E** yields compound **F**:



F has the composition: C = 44.18 %, H = 8.82 %, O = 47.00 %.

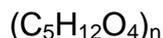
Its molar mass: $M = 136 \text{ g mol}^{-1}$

Knowing that 13.6 g of **F** reacts with 40.8 g acetic anhydride to form product **G** and acetic acid write down all chemical equations and assign the letters **A**, **B**, **C**, **D**, **E**, **F**, and **G** to particular formulas of compounds.

SOLUTION

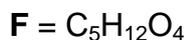
The molecular formula of **F**:

$$\text{C} : \text{H} : \text{O} = \frac{44.18}{12} : \frac{8.82}{1} : \frac{47.00}{16} = 1.25 : 3 : 1 = 5 : 12 : 4$$



Since $M(\mathbf{F}) = 136$

$$\text{and } (5 \times 12) + (12 \times 1) + (4 \times 16) = 136$$



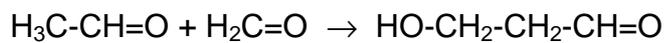
Since **F** reacts with acetic anhydride it could be a mono- or polyhydroxy alcohol. If it were a monohydroxy alcohol, 136 g of **F** (1 mol) could react with 102 g (1 mol) of acetic anhydride. In fact 13.6 g of **F** (i. e. 0.1 mol) reacts with 40.8 g of acetic anhydride ($40.8 / 102 = 0.4 \text{ mol}$), i. e. **F** is a polyol (tetrahydroxy alcohol).

F is formed by the reduction of **E**, so that **E** has one carbonyl and three OH groups.

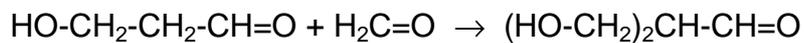
E is formed from 3 molecules of **B** and one molecule of **A**.

Since compound **E** has three OH groups and one CO group and the reaction conditions used are typical for aldol condensation, it is clear that **A** is acetaldehyde and **B**

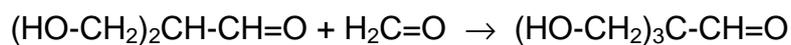
is formaldehyde. **C** and **D** are the products of successive aldol condensation of acetaldehyde with formaldehyde:



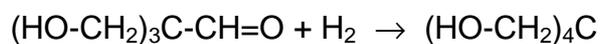
A **B** **C**



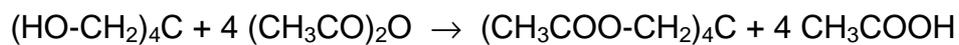
C **B** **D**



D **B** **E**



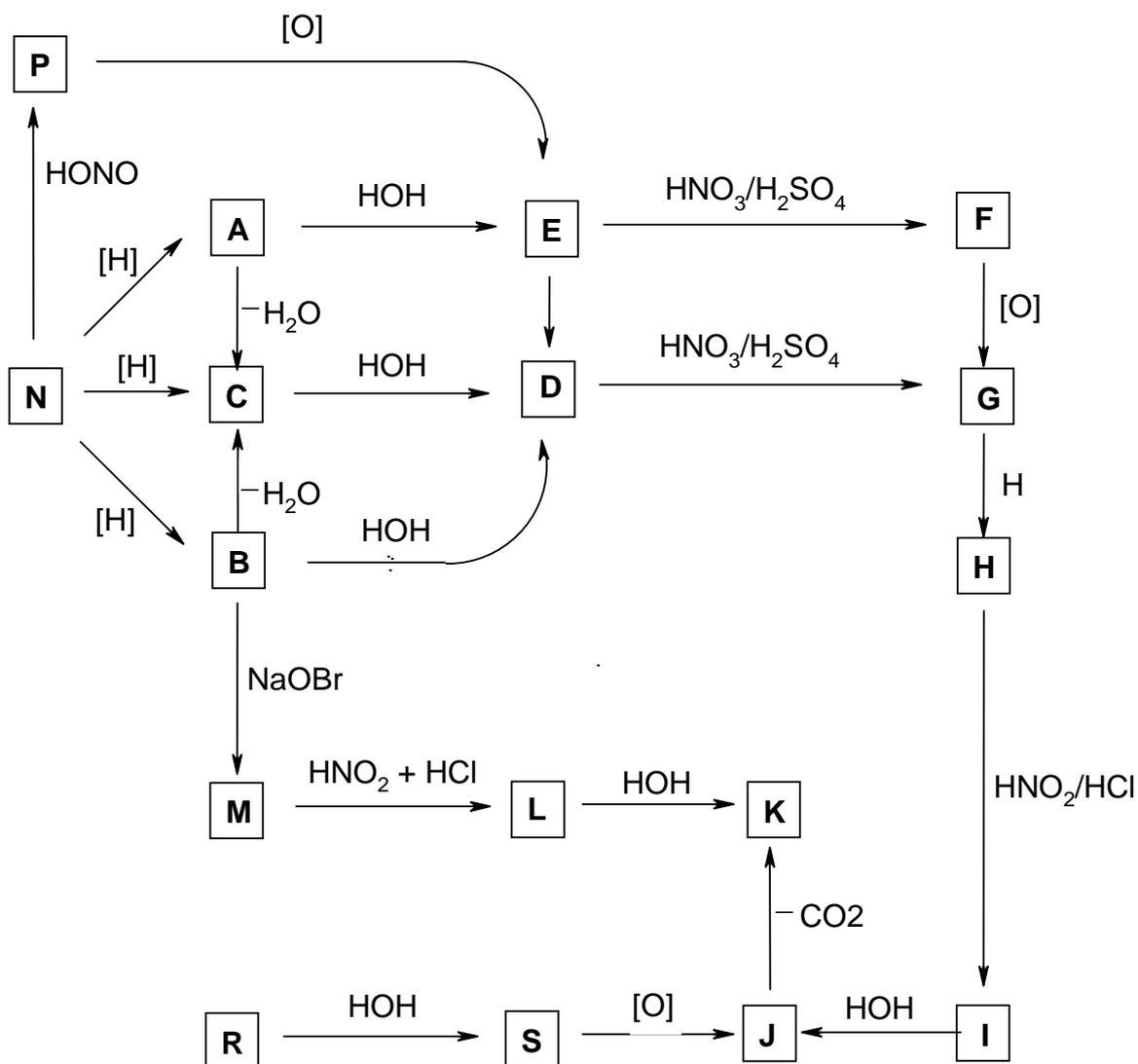
E **F**



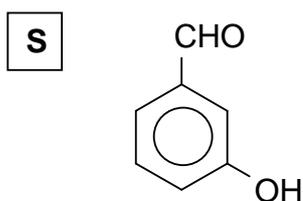
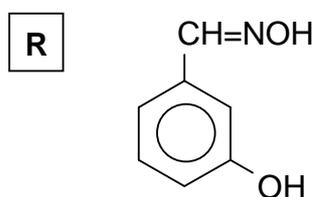
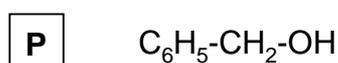
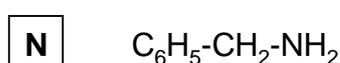
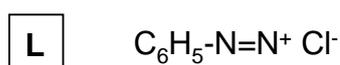
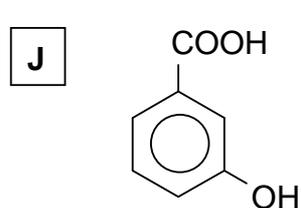
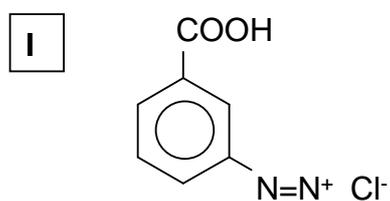
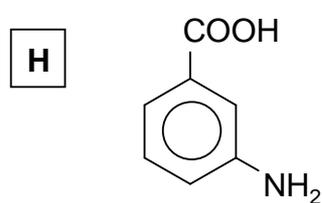
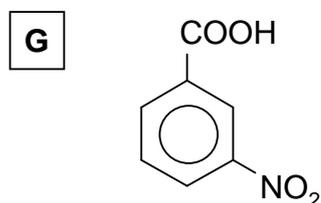
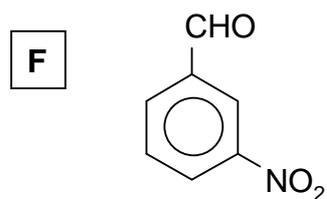
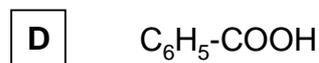
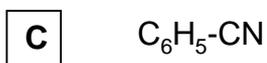
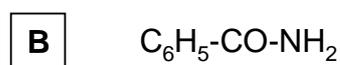
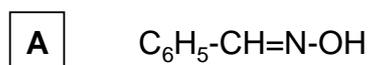
G

PROBLEM 7

Knowing that compounds **A** and **B** are isomers with the molecular formula C_7H_7NO and the relative molecular mass of compound **M** is 93, determine the formulae of compounds **A** to **S** taking in account the reactions given in the following reaction scheme:



SOLUTION



PRACTICAL PROBLEMS

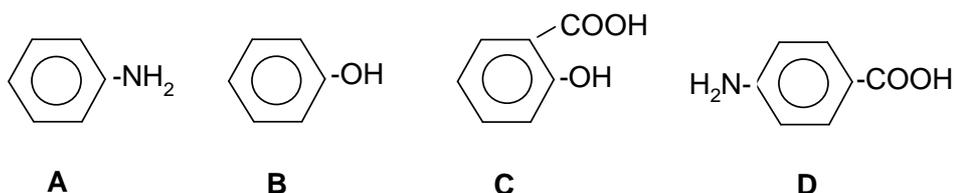
PROBLEM 1 (practical)

In test tubes **A**, **B**, **C**, and **D** there are four benzene derivatives containing one or two functional groups of three distinct types. Identify the functional groups of compounds **A**, **B**, **C**, and **D** using the available reagents.

- Justify your choice by writing down the identification reactions.
- Using as reagents the four compounds **A**, **B**, **C**, and **D** synthesize four organic dyes and write the equations for the reactions performed.

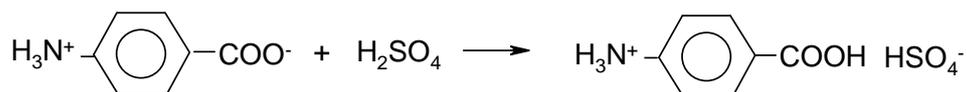
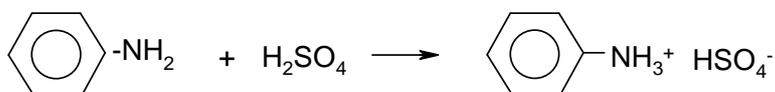
SOLUTION

The four compounds are as follows:

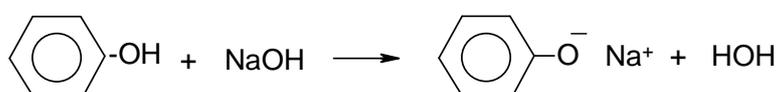


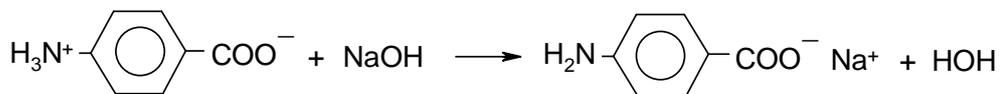
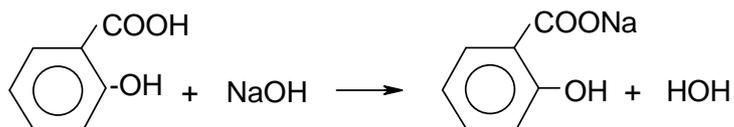
The identification reactions:

a) With H_2SO_4 :

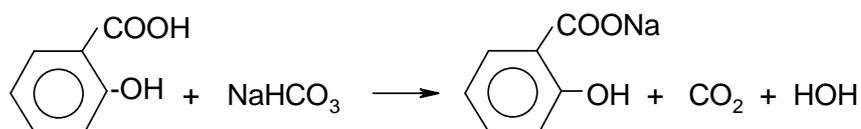


b) With NaOH :

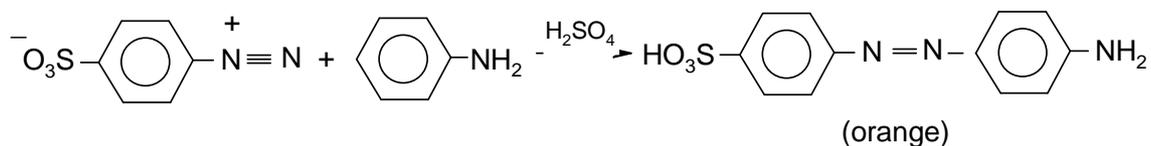
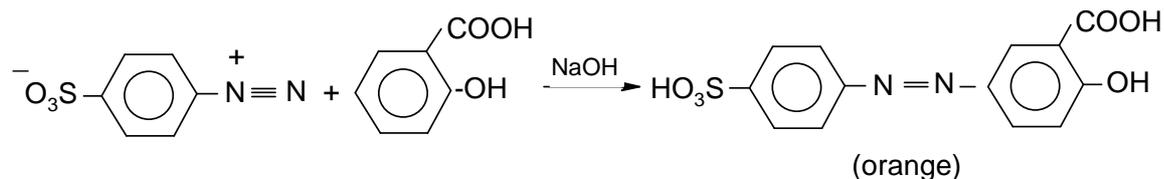
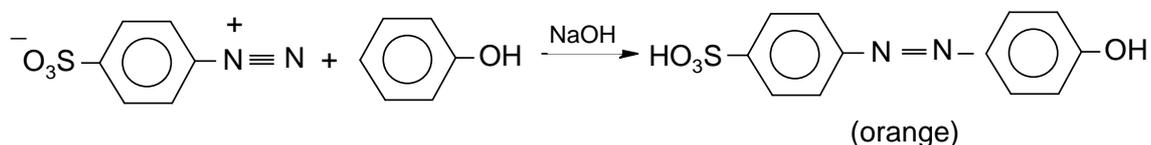
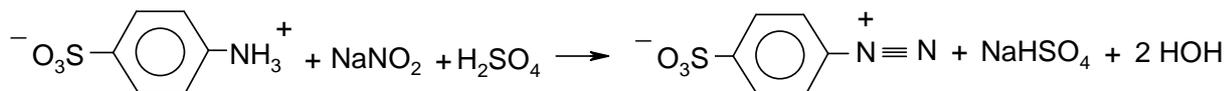




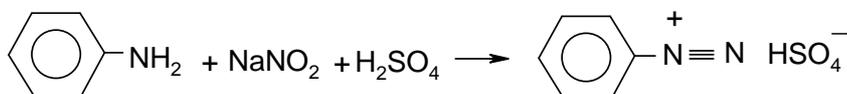
c) With NaHCO_3 :

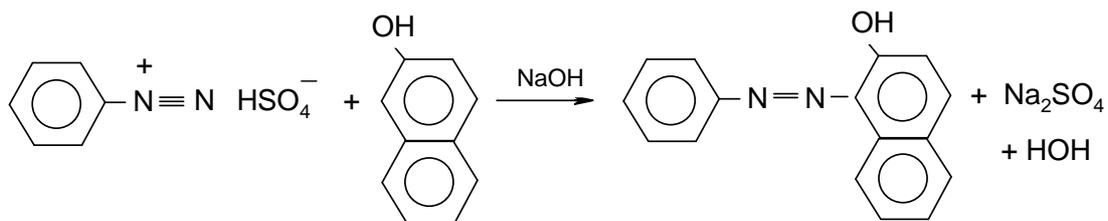


d) With $\text{NH}_2 \text{C}_6\text{H}_4 \text{SO}_3\text{H}$

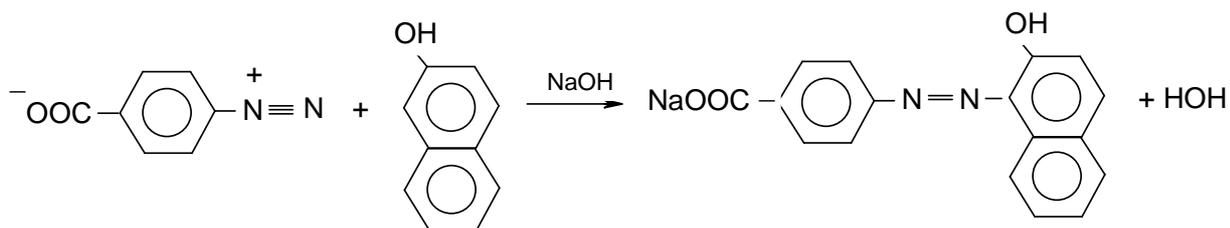
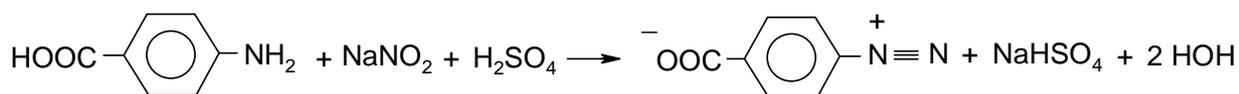


II. e) With β -naphthol:



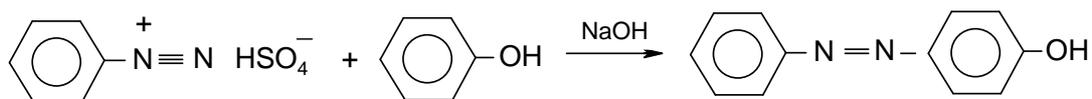


yellow - orange

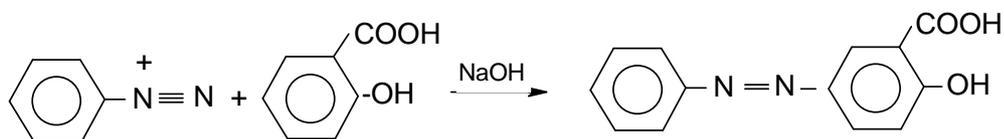


red

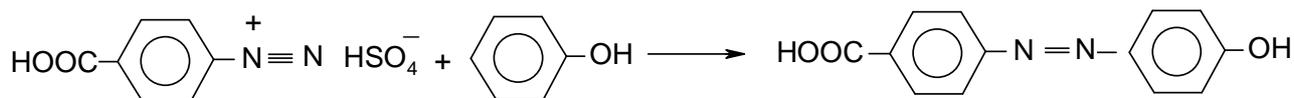
The following dyes can be obtained:



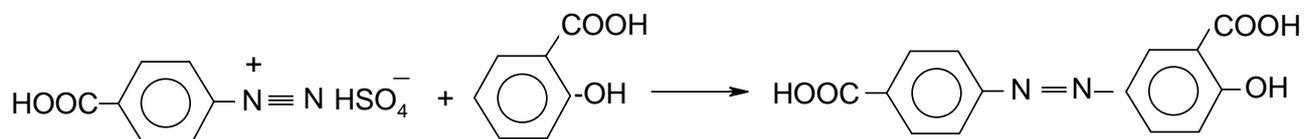
(red - orange)



(red - orange)



(red - orange)



(red - orange)

PROBLEM 2 (practical)

A solution in a graduated flask contains a mixture of oxalic acid and ammonium oxalate.

One of the bottles denoted X, Y, and Z contains a solution of a calibration substance with reducing character at a concentration of $0.1000 \text{ mol dm}^{-3}$.

You are required to solve the following tasks:

- Determine the quantity of oxalic acid and of ammonium oxalate in the solution in the graduated flask. (The result will be given in grams.)
- Write the formula for the substance with reducing character and the equations of the chemical reactions which led to its determination.

In order to carry out the analyses the following solutions are available:

HCl ($c = 0.1000 \text{ mol dm}^{-3}$), NaOH ($c = 2 \text{ mol dm}^{-3}$), KMnO_4 ($c = 0.02 \text{ mol dm}^{-3}$), 25 % H_2SO_4 , HNO_3 ($c = 2 \text{ mol dm}^{-3}$), 5 % BaCl_2 , 5 % AgNO_3 , 5 % $\text{Hg}_2(\text{NO}_3)_2$, phenolphthalein 0.1 %, methyl red 1 %.

- Describe the procedure used in the individual steps, indicators employed and partial results.

$$M_r(\text{H}_2\text{C}_2\text{O}_4) = 90.04$$

$$M_r((\text{NH}_4)_2\text{C}_2\text{O}_4) = 124.11$$

SOLUTION

ANSWER SHEET:

A₁ – Identification of the solution with the reducing substance X, Y, Z: $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$

A₂ – Identification reactions for the ions of the substance

- $\text{Fe}^{2+} + 2 \text{NaOH} \rightarrow \text{Fe}(\text{OH})_2 + 2 \text{Na}^+$
- $\text{NH}_4^+ + \text{NaOH} \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} + \text{Na}^+$
- $4 \text{NH}_3 + 2 \text{Hg}_2(\text{NO}_3)_2 + \text{H}_2\text{O} \rightarrow \text{O}(\text{Hg})_2\text{NH}_2.\text{NO}_3 + 3 \text{NH}_4\text{OH}$
- $\text{SO}_4^{2-} + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2 \text{Cl}^-$

B₁– Preparation of the 0.1 M NaOH solution

..... cm^3 in 200.0 cm^3

B₂ – Concentration of the NaOH in its solution: M

Indicator used:

C – Concentration of KMnO₄ in its solution M

D₁ – Mass of oxalic acid in the initial solution g

Indicator used

D₂ – Mass of ammonium oxalate in the initial solution g

S o l u t i o n

A₁ – 1-2 cm³ of solution X, Y and Z are put into three test tubes. 6 N H₂SO₄ and a drop of KMnO₄ solution are added. The solution which loses colour is the one with reducing character.

A₂ – Establishment of the formula:

. + NaOH – greenish white precipitate ⇒ Fe²⁺

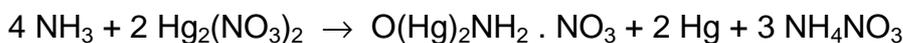
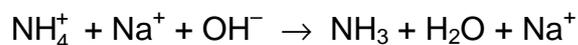
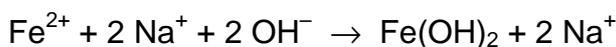
. + NaOH at the upper end of the test-tube, filter paper with a drop of Hg₂(NO₃)₂, black spot ⇒ NH₄⁺

. + BaCl₂ – white precipitate ⇒ SO₄²⁻

. + AgNO₃ + HNO₃ ⇒ Cl⁻ is absent

Accordingly the substance used is Fe(NH₄)₂(SO₄)₂.

The chemical reactions:



B₁ – 5 cm³ 2 M solution ⇒ 100 cm³ 0.1 M solution

B₂ – V cm³ 0.1000 N HCl + 0.1 N NaOH in the presence of phenolphthalein.

C – V cm³ solution X + 10.0 cm³ H₂SO₄ + H₂O is titrated at elevated temperature with KMnO₄.

D₁ – The solution which is to be analyzed is filled to the mark; $V \text{ cm}^3$ of this solution is titrated with NaOH in the presence of methyl red. The quantity of oxalic acid (moles and g) is calculated.

D₂ – $V \text{ cm}^3$ solution to be analyzed + 10.0 cm^3 6 N H_2SO_4 + H_2O are heated and titrated with KMnO_4 solution.

The total amount of oxalate is calculated (in mol).

The difference gives the amount of ammonium oxalate (moles and g).

PROBLEM 3 (practical)

Six test-tubes contain aqueous solutions of FeSO_4 , H_2SO_4 , $\text{Mn}(\text{NO}_3)_2$, H_2O_2 , $\text{Pb}(\text{NO}_3)_2$, NaOH .

- a) Identify the content of each test-tube without using other reagents. Write the results in tabular form. Write the equations for the chemical reactions used for the identification.
- b) After identification, perform four reactions each time using three of the identified compounds and write the equations.

SOLUTION

	FeSO_4	H_2SO_4	$\text{Mn}(\text{NO}_3)_2$	H_2O_2	$\text{Pb}(\text{NO}_3)_2$	NaOH
1) FeSO_4		–	–	$\text{Fe}(\text{OH})\text{SO}_4$ yellowish	$\text{PbSO}_4 \downarrow$ white	$\text{Fe}(\text{OH})_2 \downarrow$ white-greenish \downarrow $\text{Fe}(\text{OH})_3 \downarrow$ brown-redish
2) H_2SO_4	–		–	–	$\text{PbSO}_4 \downarrow$ white	–
3) $\text{Mn}(\text{NO}_3)_2$	–	–		–	–	$\text{Mn}(\text{OH})_2 \downarrow$ white \downarrow $\text{MnMnO}_3 \downarrow$ brown black
4) H_2O_2	$\text{Fe}(\text{OH})\text{SO}_4$ yellowish	–	–		–	–
5) $\text{Pb}(\text{NO}_3)_2$	$\text{PbSO}_4 \downarrow$ white	$\text{PbSO}_4 \downarrow$ white	–	–		–
6) NaOH	$\text{Fe}(\text{OH})_2 \downarrow$ white-greenish \downarrow $\text{Fe}(\text{OH})_3 \downarrow$ brown-redish	–	$\text{Mn}(\text{OH})_2 \downarrow$ white \downarrow $\text{MnMnO}_3 \downarrow$ brown black	–	$\text{Pb}(\text{OH})_2 \downarrow$ white \downarrow $\text{Pb}(\text{OH})_4^{2-}$	

	Reactions	Observation
(1) + (4)	$\text{FeSO}_4 + \text{H}_2\text{O}_2 \rightarrow 2 \text{Fe}(\text{OH})\text{SO}_4$	Colour change - yellowish (Fe^{3+})
(1) + (5)	$\text{FeSO}_4 + \text{Pb}(\text{NO}_3)_2 \rightarrow \text{PbSO}_4 \downarrow + \text{Fe}(\text{NO}_3)_2$	Appearance of a white precipitate.
(1) + (6)	$\text{FeSO}_4 + 2 \text{NaOH} \rightarrow \text{Fe}(\text{OH})_2 \downarrow + \text{Na}_2\text{SO}_4$ $\text{Fe}(\text{OH})_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3$	Appearance of a greenish white precipitate $\text{Fe}(\text{OH})_2$ which after oxidation by air turns into a reddish brown precipitate $\text{Fe}(\text{OH})_3$.
(2) + (5)	$\text{H}_2\text{SO}_4 + \text{Pb}(\text{NO}_3)_2 \rightarrow \text{PbSO}_4 \downarrow + 2 \text{HNO}_3$	Appearance of a white precipitate PbSO_4 .
(3) + (6)	$\text{Mn}(\text{NO}_3)_2 + 2 \text{NaOH} \rightarrow \text{Mn}(\text{OH})_2 + 2 \text{NaNO}_3$ $2 \text{Mn}(\text{OH})_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{MnMnO}_3 + 2 \text{H}_2\text{O}$ $\text{Mn}(\text{OH})_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{MnO}_2 + \text{H}_2\text{O}$	Appearance of a white precipitate $\text{Mn}(\text{OH})_2$ which after oxidation by air converts into a brown-black precipitate MnMnO_3 which eventually changes into MnO_2 – a black-brown precipitate.
(5) + (6)	$\text{Pb}(\text{NO}_3)_2 + 2 \text{NaOH} \rightarrow \text{Pb}(\text{OH})_2 + 2 \text{NaNO}_3$ $\text{Pb}(\text{OH})_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{Pb}(\text{OH})_4$	Appearance of a white precipitate $\text{Pb}(\text{OH})_2$ which dissolves in excess reagent.
b)		
(1) + (2) + (4)	$2 \text{FeSO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O}$	Colour change \rightarrow yellowish (Fe^{3+})
(1) + (4) + (6)	$2 \text{FeSO}_4 + \text{H}_2\text{O}_2 + 4 \text{NaOH} \rightarrow \text{Fe}(\text{OH})_3 +$ $+ 2 \text{Na}_2\text{SO}_4$	Appearance of a brown-reddish precipitate $\text{Fe}(\text{OH})_3$
(3) + (4) + (6)	$\text{Mn}(\text{NO}_3)_2 + \text{H}_2\text{O}_2 + 2 \text{NaOH} \rightarrow \text{MnO}_2 + 2 \text{NaNO}_3$ $+ 2 \text{H}_2\text{O}$	Appearance of a brown precipitate MnO_2
(5) + (4) + (6)	$\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}_2 + 2 \text{NaOH} \rightarrow \text{PbO}_2 + 2 \text{NaNO}_3$ $+ 2 \text{H}_2\text{O}$	Appearance of a brown precipitate PbO_2 .

16th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE SIXTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–10 JULY 1984, FRANKFURT AM MAIN, GERMAN FEDERAL REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

A)

The element carbon consists of the stable isotopes ^{12}C (98.90 percent of atoms) and ^{13}C (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope ^{14}C ($t_{1/2} = 5730$ years), which is continuously formed in the atmosphere by cosmic rays as CO_2 . ^{14}C mixes with the isotopes ^{12}C and ^{13}C via the natural CO_2 cycle.

The decay rate of ^{14}C is described by (N = number of ^{14}C atoms; t = time; λ = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \quad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0 e^{-\lambda t} \quad (2)$$

N_0 = number of ^{14}C atoms at $t = 0$

- 1.1 What is the mathematical relationship between the parameters α and $t_{1/2}$ (= half life)?
- 1.2 The decay rate of carbon, which is a part of the natural CO_2 cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the CO_2 cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

- 1.3 Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?
- 1.4 What is the isotope $^{12}\text{C}/^{14}\text{C}$ ratio of carbon, which takes part in the natural CO_2 cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 % ^{84}Sr ; 9.86 % ^{86}Sr ; 7.00 % ^{87}Sr ; 82.58 % ^{88}Sr (these isotopes are all stable).

Rubidium: 72.17 % ^{85}Rb (stable) ; 27.83 % ^{87}Rb (radioactive; $t_{1/2} = 4.7 \times 10^{10}$ years).

The radioactive decay of ^{87}Rb leads to ^{87}Sr .

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

- 1.5 What is the equation rate law describing the formation of ^{87}Sr from ^{87}Rb as a function of time?
- 1.6 Assume that the isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ (as determined by mass spectrometry) and the isotope ratio $^{87}\text{Rb} : ^{86}\text{Sr}$ are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

SOLUTION

A)

- 1.1 The relationship is:

$$\alpha = \frac{\ln 2}{t_{1/2}}$$

1.2

$$t = \frac{t_{1/2}}{\ln 2} \times \ln \left(\frac{N_0}{N} \right) = \frac{5730}{0.6930} \times \ln \left(\frac{13.6}{12.0} \right) = 1035 \text{ years}$$

- 1.3 For $N_0/N = 13.6/12.0$ $t = 1035$ years
 For $N_0/N = 13.6/12.2$ $t = 898$ years
 For $N_0/N = 13.6/11.8$ $t = 1174$ years

Thus, the tree was cut 1035 (+ 139/–137) years ago.

1.4

$$N = \frac{13.6 \times t_{1/2}}{\ln 2} = 5.91 \times 10^{10} \text{ atoms } ^{14}\text{C} / \text{g carbon}$$

$$1 \text{ g} \approx 0.989 \text{ g } ^{12}\text{C}; \quad 0.989 \text{ g } ^{12}\text{C} \approx (0.989/12) \times 6.023 \times 10^{23} \text{ atoms } ^{12}\text{C}$$

$$^{12}\text{C} / ^{14}\text{C} = \frac{0.989 \times 6.023 \times 10^{23}}{12 \times 5.91 \times 10^{10}} = 8.40 \times 10^{11} : 1$$

B)

1.5 Equation (2) describes the decay of the ^{87}Rb :

$$^{87}\text{Rb} = ^{87}\text{Rb}_0 \cdot \exp(-\lambda t)$$

The symbol ^{87}Rb stands for the number of atoms of this nuclide.

Consequently, one obtains for the formation of ^{87}Sr from ^{87}Rb :

$$^{87}\text{Sr} = ^{87}\text{Rb}_0 - ^{87}\text{Rb} = ^{87}\text{Rb} \cdot \exp(\lambda t) - ^{87}\text{Rb} \quad (\text{a})$$

1.6 The formation of the radiogenic ^{87}Sr follows equation (a).

One has to take into account that at time $t = 0$, when the mineral was formed, there was some non-radiogenic strontium in it already:

$$^{87}\text{Sr} = (^{87}\text{Sr})_0 + ^{87}\text{Rb} \cdot [\exp(\lambda t) - 1]$$

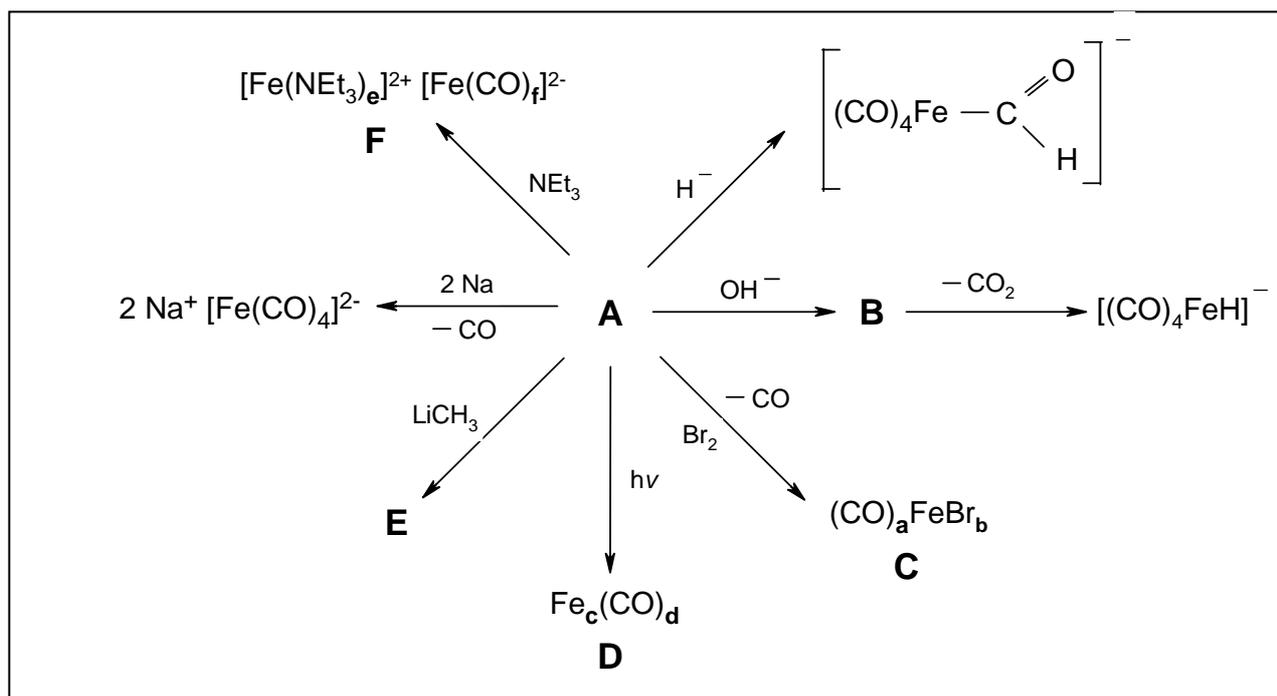
The isotope ratio $(^{87}\text{Sr} / ^{86}\text{Sr})_0$ follows from the isotope composition of strontium. The time t in this equation corresponds to the age of the gneiss.

PROBLEM 2

Ludwig Mond discovered before the turn of this century that finely divided nickel reacts with carbon monoxide forming tetracarbonylnickel, $\text{Ni}(\text{CO})_4$, a colourless, very volatile liquid. The composition of $\text{Ni}(\text{CO})_4$ provides an example of the noble gas rule ("EAN rule").

Problems:

- 2.1 Use the eighteen-electron rule (noble gas rule) to predict the formula of the binary carbonyls of $\text{Fe}(0)$ and $\text{Cr}(0)$.
- 2.2 What composition would the eighteen-electron rule predict for the most simple binary chromium(0)-nitrosyl compound?
- 2.3 Explain why $\text{Mn}(0)$ and $\text{Co}(0)$ do not form so-called mononuclear carbonyl complexes of the type $\text{M}(\text{CO})_x$ ($\text{M} = \text{metal}$), but rather compounds with metal-metal bonding.
- 2.4 Suggest structures of $\text{Ni}(\text{CO})_4$, $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$.
- 2.5 State whether $\text{V}(\text{CO})_6$ and the compounds mentioned in a) and d) are diamagnetic or paramagnetic.
- 2.6 Why are the carbon monoxide ligands bound to metals much more strongly than to boron in borane adducts (e.g. $\text{R}_3\text{B}-\text{CO}$; $\text{R} = \text{alkyl}$)?
- 2.7 Determine the composition of the compounds labeled **A** - **F** in the following reaction scheme:



Hints:

- C** has the following analysis: C, 14.75 % ; Br, 48.90 % .
- D** contains 30.70 % Fe; the molecular mass is 363.8 a.m.u.
- Excess triethylamine is used for the synthesis of **F**. **F** contains 5.782 % C and 10.11 % N.

2.8 Why is the compound **F** formed in the disproportionation reaction (given in g)), and not the compositional isomer $[\text{Fe}(\text{CO})_f]^{2+}[\text{Fe}(\text{NEt}_3)_e]^{2-}$?

2.9 The eighteen-electron rule is also satisfied by a compound prepared from elementary chromium and benzene.

- Draw the formula of this complex.
- Which complex with the analogous structure is prepared by the reaction of iron powder with cyclopentadiene? Write the chemical equation for its formation.

SOLUTION

2.1 $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$

2.2 $\text{Cr}(\text{NO})_4$

2.3 Explanation: the odd number of electrons in the $\text{Mn}(\text{CO})_5$ and $\text{Co}(\text{CO})_4$ fragments.

2.4 $\text{Ni}(\text{CO})_4$: tetrahedral geometry

$\text{Mn}_2(\text{CO})_{10}$: - octahedral $\text{Mn}(\text{CO})_5$ -structure having a Mn-Mn bond,

- relative orientation (conformation) of the carbonyl groups.

$\text{Co}_2(\text{CO})_{10}$: CO-bridges and Co-Co bond

2.5 $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Ni}(\text{CO})_4$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_{10}$ are diamagnetic,

$\text{V}(\text{CO})_6$ is paramagnetic.

2.6 Explanation using the so-called "back-bonding concept"

2.7 **A** = $[\text{Fe}(\text{CO})_5]$

B = $[\text{HOCOF}(\text{CO})_4]$

C = $[\text{FeBr}_2(\text{CO})_4]$

D = $[\text{Fe}_2(\text{CO})_9]$

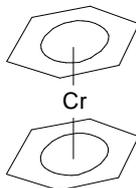
E = $[(\text{CO})_4\text{Fe}=\text{C}(\text{OLi})\text{CH}_3]$

F = $[\text{Fe}(\text{NEt}_3)_6][\text{Fe}(\text{CO})_4]$

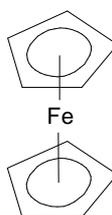
2.8 This observation is due to differing back bonding capability of NEt_3 and CO.

2.9

i) Structural formula of dibenzenechromium



ii) Structural formula of ferrocene.



PROBLEM 3

A weak acid of total concentration 2×10^{-2} M is dissolved in a buffer of pH = 8.8. The anion A^- of this acid is coloured and has a molar decadic absorption coefficient ε of $2.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$. A layer l of the solution with 1.0 cm thickness absorbs 60 percent of the incident luminous intensity I_0 .

- 3.1 What is the equation relating the extinction to the thickness of the absorbing layer?
 3.2 How large is the concentration of the acid anion in the buffer solution?
 3.3 How large is the pK_a of the acid?

SOLUTION

- 3.1 The Lambert-Beer law e.g.:

$$\log(I_0/I) = A = \varepsilon \cdot c \cdot l$$

- 3.2 $\log[(100-60)/100] = -2.1 \times 10^4 \times [A^-] \times 1$

$$[A^-] = 1.895 \times 10^{-5} \text{ mol cm}^{-3} = 1.895 \times 10^{-2} \text{ mol dm}^{-3}$$

- 3.3 According to the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log \frac{[A^-]_{\text{eq}}}{[HA]_{\text{eq}}}$$

and with the total concentration

$$[HA]_{\text{tot}} = [HA]_{\text{eq}} + [A^-]_{\text{eq}} = 2 \times 10^{-2} \text{ mol dm}^{-3}$$

$$8.8 = pK_a + \log \frac{1.895 \times 10^{-2}}{2 \times 10^{-2} - 1.895 \times 10^{-2}}$$

$$pK_a = 7.5$$

PROBLEM 4

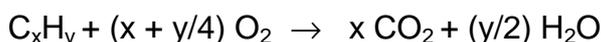
15 cm³ of a gaseous hydrocarbon C_xH_y are mixed with 120 cm³ oxygen and ignited. After the reaction the burned gases are shaken with concentrated aqueous KOH solution. A part of the gases is completely absorbed while 67.5 cm³ gases remain. It has the same temperature and pressure as the original unburned mixture.

- 4.1 What is the composition of the remaining gas? Explain.
- 4.2 How large is the change in the amount of substance per mole of a hydrocarbon C_xH_y when this is burned completely?
- 4.3 What is the chemical formula of the hydrocarbon used for the experiment? Give the steps of the calculation.

SOLUTION

4.1 The remaining gas is oxygen since the burning products CO₂ and H₂O are completely absorbed in concentrated KOH solution.

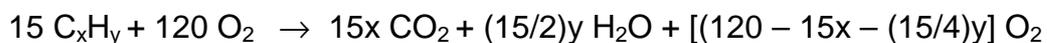
4.2 The general stoichiometric equation for complete combustion of a hydrocarbon C_xH_y is as follows:



The change in amount of substance per mole of hydrocarbon is

$$[x + (y/2) - (1 + x + y/4)] \text{ mol} = [(y/4) - 1] \text{ mol}$$

4.3 The equation of chemical conversion at the experimental condition is as follows:



For the residual oxygen:

$$(1) \quad 120 - 15x - (15/4)y = 67.5$$

and for the total balance of amount of substance:

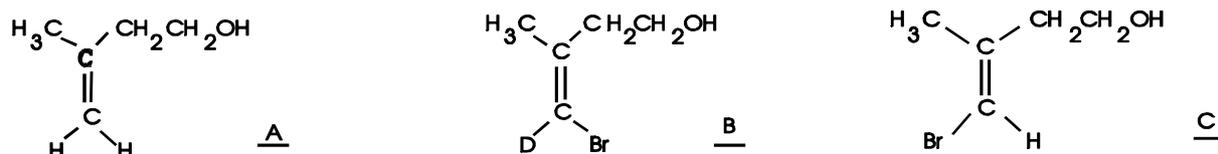
$$(2) \quad 15x + (15/2)y + 67.5 = 15 + 120 + 15[(y/4) - 1]$$

From equation (1) and (2) follows: $x = 2$ and $y = 6$.

The hydrocarbon in question is ethane.

PROBLEM 5

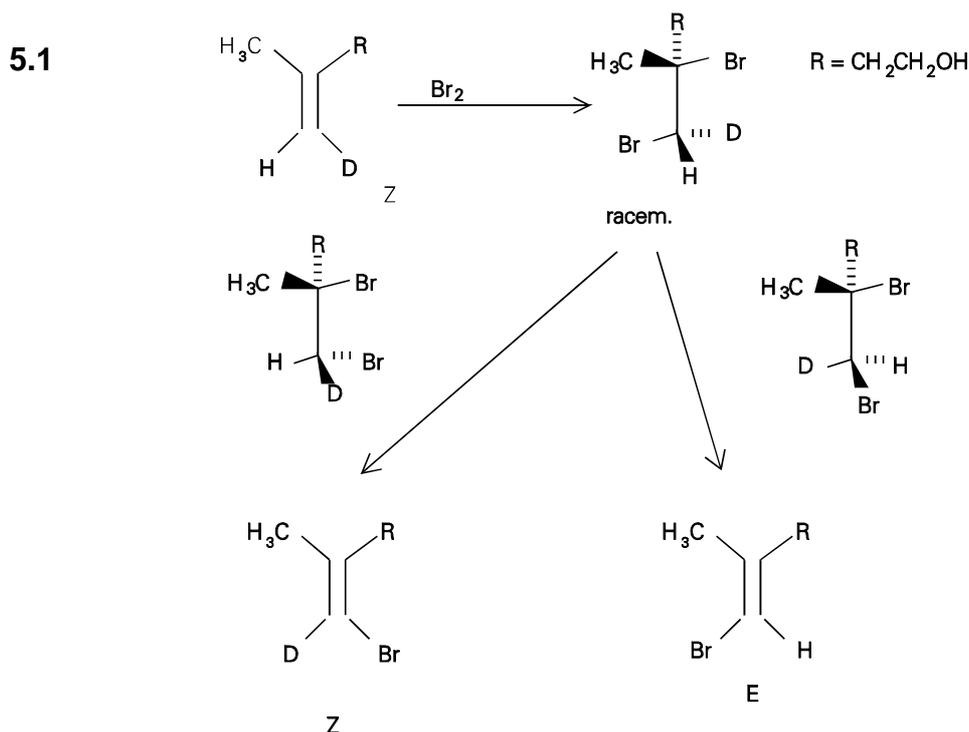
One of the diastereotopic methylene protons at the double bond of **A** was selectively substituted by deuterium. Bromination and subsequent dehydrobromation yields the



deuteriated product **B** and the non-deuteriated product **C**.

5.1 Which configuration follows for the monodeuteriated **A** from the given reaction products?

5.2 The solution of this question requires the formulation of the reaction and a short argumentation why only **B** and **C** are formed.

SOLUTION

5.2 The addition of bromine occurs trans (antarafacial). The elimination of HBr via an E2 mechanism also requires an anti-periplanar (= trans) arrangement of H and Br. The products given in this problem are only formed from a Z-configured adduct.

The bromination of **A** and subsequent dehydrobromination yield both E,Z isomeric bromoolefins that have to be separated. Substitution of the bromine by deuterium in the Z-isomer proceeds by treatment with a metal (best: Na/t-BuOD) under retention to **A**.

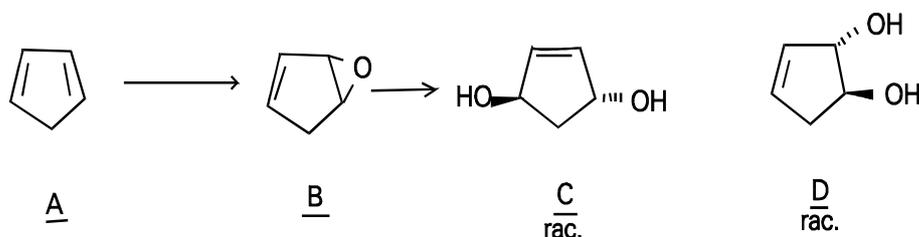
PROBLEM 6

A technical interesting C₅ hydrocarbon **A** is separated via dimerization from the for-runnings of the benzene-pyrolysis fraction. This is achieved either by heating to 140 – 150 °C under pressure or by heating over several hours at 100° C. Then it is distilled out at 200 °C. Treatment of **A** with peroxyacetic acid under neutral conditions (sodium acetate and sodium carbonate) in dichloromethane at 20° C yields a product **B**. **B** yields two isomeric products **C** and **D** (summary formula C₅H₈O₂) by the reaction with aqueous sodium carbonate solution. The main product **C** contains three different bound carbon atoms whereas in the minor product **D** five different carbon atoms are present. **C** is chiral.

- 6.1 Write the formulas of **A**, **B**, **C**, and **D** considering the stereochemical representation.
- 6.2 What is the name of the chemical reaction which is used for the above mentioned separation procedure?
- 6.3 Which stereochemical rules hold for the dimerization reaction?
- 6.4 Give the structure of the dimerization product.
- 6.5 Give the mechanism of the formation of **C** and **D** from **B**.
- 6.6 Which kind of isomers are **C** and **D** ?
- 6.7 How many stereoisomers of **C** and **D** are principally (regardless of their synthetic availability) possible? Give their mutual stereochemical relations. Write their structural formulas.

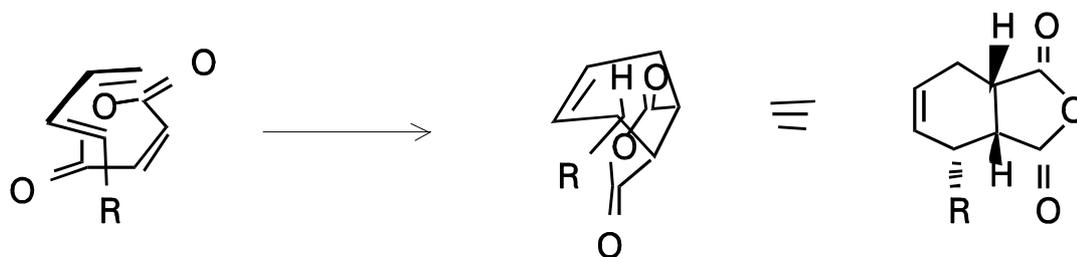
SOLUTION

6.1



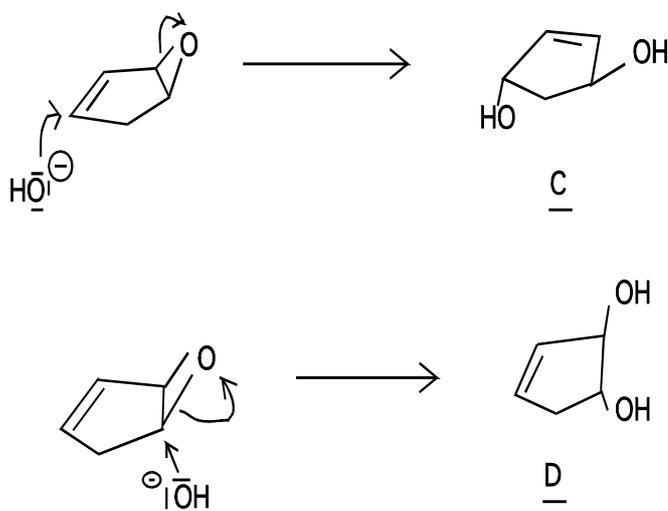
6.2 Diels-Alder-reaction, 4+2-cycloaddition

6.3 cis-addition = suprafacial addition with respect to diene and dienophile endo-rule: a substituent at the dienophile is oriented primarily toward the diene . E.g.



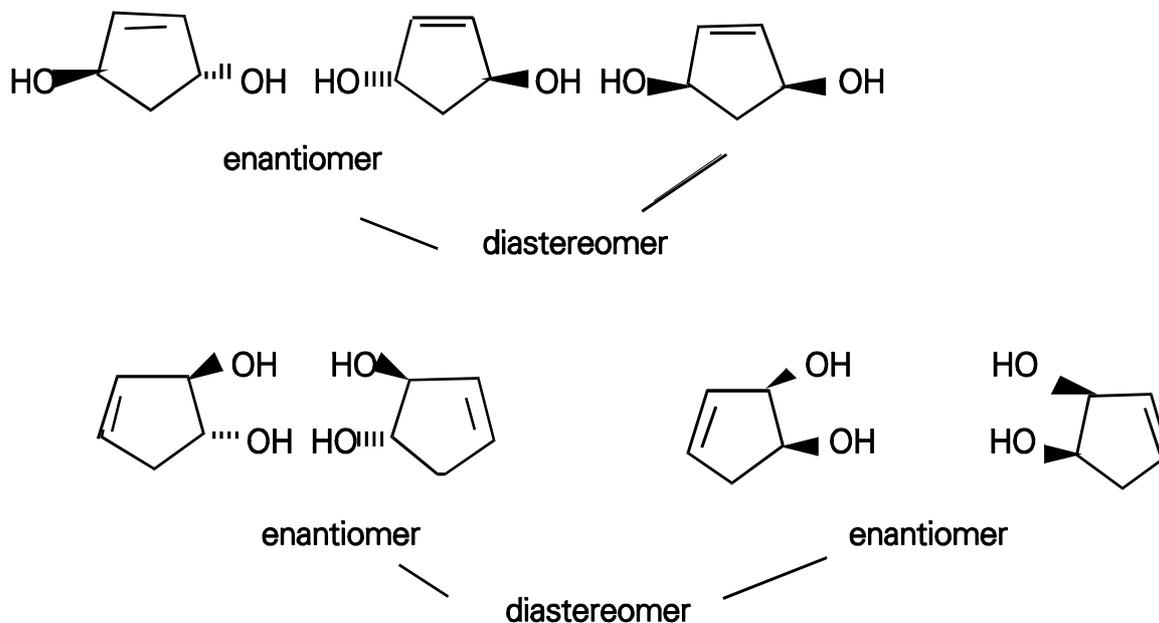
6.4

6.5 **C** is formed via a S_N2 reaction. This reaction can lead to a cis or a trans product. Because **C** is chiral, the trans product is formed. **D** is formed via S_N2 reaction.



6.6 **C** and **D** are constitutional isomers.

6.7 There exist two diastereomers (cis and trans) of **C**. The trans form is chiral, i.e. there exists a pair of enantiomers. The cis form is achiral (reduction of the number of stereoisomers caused by constitutional symmetry, meso-form). **D** forms two diastereomers, each of them is chiral.



PROBLEM 7

Deoxyribonucleic acid (DNA) represents the genetic program of all living beings. The human genetic program is subdivided into 23 chromosomes.

7.1 Calculate the mass of a DNA thread in grams, which reaches from earth to the moon (340,000 km). A mass of 1 g represents 1,000 nucleotide pairs.

One nucleotide pair (base pair) has a length of 0.34 nm.

7.2 Give estimation on how many nucleotide pairs are stored in the chromosome set of a human being. Human cells can synthesize 50,000 different proteins, which are on the average 300 amino acids long. Only 2 % of the DNA code for proteins.

7.3 The DNA of the bacteriophage M13 shows the following base composition:

A: 23 %, T: 36 %, G: 21 %, C: 20 % (mole %)

What does the base composition tell about the structure of the DNA?

SOLUTION

7.1 1. Number of nucleotide pairs as calculated from the given length

$$\frac{3.4 \times 10^8 \text{ m}}{3.4 \times 10^{-10} \text{ m}} = 10^{18} \text{ nucleotide pairs}$$

2. Calculation of the mass:

$$1,000 \text{ nucleotide pairs} = 10^{-18} \text{ g}$$

$$10^{18} \text{ nucleotide pairs} = 1 \text{ mg}$$

The mass of 340.000 km DNA is 1 mg.

7.2 Human DNA codes for $50,000 \times 300$ amino acids in form of proteins: Each amino acid is encoded by 3 nucleotides or due to the double stranded structure of DNA by 3 nucleotide pairs. This amounts to 4.5×10^7 nucleotide pairs. Since only 2% of the DNA code for proteins one can calculate the number of nucleotide pairs in human DNA to 2.25×10^9 nucleotide pairs.

7.3 The DNA has to be single stranded, since the ratio of adenine : thymine and guanine : cytosine is different from one.

PROBLEM 8

The sequence of the amino acids in a peptide can be determined by a combination of chemical and enzymatic methods. The peptide in question functions in the human body as a pain reliever.

- Hydrolysis of the peptide in 6 M HCl at 110° C followed by an analysis of the liberated amino acids, resulted in a molar ratio of Gly, Leu, and aromatic amino acids Phe, Tyr 2 : 1 : 1 : 1.
- Reacting the peptide with 2,4-dinitrofluorobenzene (DNFB), followed by hydrolysis and chromatographic analysis, yielded the tyrosine derivative.
- Partial hydrolysis with chymotrypsin yielded Leu, Tyr and a smaller peptide. After hydrolysis of this peptide Gly and Phe were identified in a ratio 2 : 1. Chymotrypsin is a protease which cleaves a peptide bond following an aromatic amino acid.

Problems:

- Determine the amino acid sequence from the given information.
 - Write the structural formula of the DNFB- and the dansyl derivative of tyrosine. What is the advantage of the dansylation in comparison to the DNFB-modification?
Dansyl means 5-N,N-dimethylaminonaphtalene-4-sulphonyl.
 - In a similar peptide which shows the same biological activity, leucine is replaced by methionine. Explain from the chemical structure of both amino acids why the replacement is possible without loss of biological activity.
-

SOLUTION

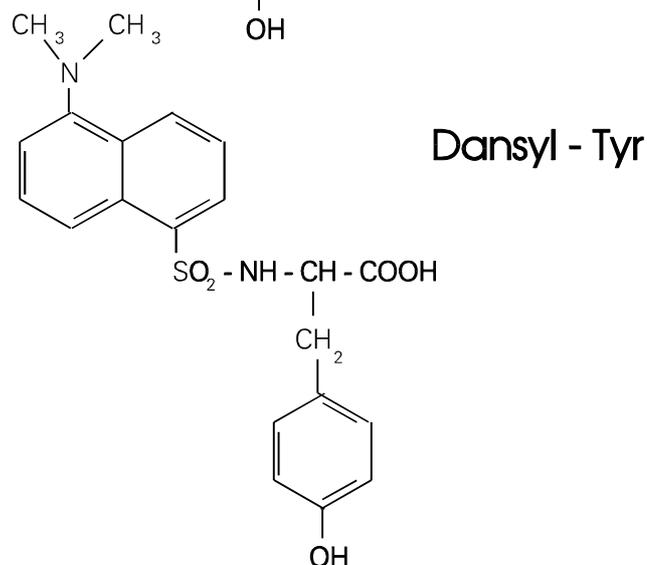
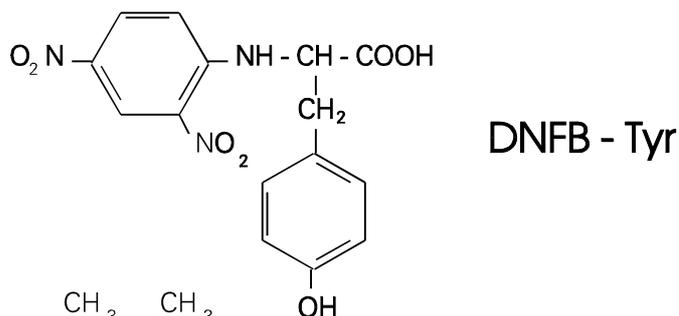
- It can be derived from data in part 1 that the net composition of the peptide is 2 Gly, 1 Leu, 1 Phe and 1 Tyr.

From part 2 one can conclude that the N-terminal amino acid has to be Tyr since DNFB is specific for the N-terminus.

Part 3 shows that the internal peptide has to be Gly-Gly-Phe.

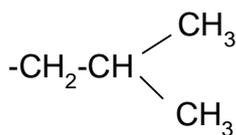
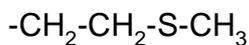
The sequence is Tyr-Gly-Gly-Phe-Leu.

8.2 The trivial name of the peptide is Leu-Enkephaline. It acts as a pain killer in the human body.



Dansyl derivatives give increased sensitivity since they are highly fluorescent.

8.3 The compound is Met-Enkephaline. Leu and Met are both non-polar amino acids. Both side chains show comparable van der Waals radii.



PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Nitration of phenacetine (4-ethoxyacetanilide) with nitric acid in acetic acid as solvent

Caution:

Both acetic acid and 65 % nitric acid attack the skin. If it happens, the skin must be rinsed with water immediately and washed with a saturated aqueous solution of sodium carbonate. Vapours of nitric acid damage the respiratory tract; moreover, nitric gases evolved in the reaction flask are very toxic.

The glass joints of the various apparatus must be only slightly greased.

Apparatus:

250 ml four-necked flask with laboratory stirrer, thermometer, reflux condenser with gas vent, water bath, Bunsen burner.

Preparation:

40 ml of acetic acid are placed with a glass syringe pipette in the four-necked round bottom flask. 2.0 g of phenacetine are then dissolved in the acetic acid. Also, 2.5 ml 65 % nitric acid are added by using a glass syringe pipette under an effective hood. This mixture is heated for five minutes in a water bath at 90 °C.

Isolation and purification:

The hot water bath is replaced by ice water. After ca. 10 minutes the gas vent is removed and ca. 120 ml of distilled water are added through the reflux condenser into the flask in order to dilute the original solution. Stirring is continued until a temperature of ca. 5 °C is reached.

The precipitated solid is filtered off and then washed with a total of 100 ml of cold water and finally dried at 60° C for 2.5 hours in a drying oven.

Evaluation of the experiment:

a) Melting points:

The melting point of phenacetine and its reaction product are to be determined and recorded in the note book. The melting point of phenacetine is higher than 120° C and that of the product is higher than 80° C.

b) Thin-layer chromatogram:

The relative position of the spots of the starting compound and its reaction product must be recorded. In order to reach it, little portions of the both samples must be dissolved in 1-2 ml of acetone. The solutions must be placed on the plate by using a capillary tube. To develop the chromatogram, a mixture of 90 ml toluene, 25 ml acetone, and 5 ml acetic acid is used.

After drying the spots are circled with a pen. The R_f -values must be recorded.

c) Developing reagent:

The developed TLC-plate must be sprayed under a hood with the available reagent solution consisting of iron(III) chloride and potassium hexacyanoferrate(III).

Interpretation of the results:

- 1.1 Which nitration product(s) has (have) been formed? The discussion should be focused on the relative position of the spots in your chromatogram; describe your arguments in the note book.
- 1.2 Explain why such "mild conditions" have been used here for the nitration reaction. Explain why the nitration reaction has proceeded in spite of these "mild conditions".
- 1.3 Explain the observed colour reaction of phenacetine with the developing reagent.
- 1.4 Make a brief proposal, how the filtrate should be prepared to avoid environmental damage.

Chemicals:

Acetic acid (analysis grade)

Nitric acid (analysis grade); $w = 65\%$ by mass

Phenacetine (analysis grade)

Toluene (analysis grade)

Acetone (analysis grade)

Developing reagent: 100 ml solution

200 ml solution

700 ml distilled water.

SOLUTION

a) Melting points:

4-ethoxy-N-acetylphenylamin (phenacetine) : 135 °C

4-ethoxy-2-nitroacetanilide : 103 °C (theoretical value)

b), c) Documentation, Thin-layer chromatogram

Interpretation of the results:

1.1 The R_f -value of the nitration product is almost twice as great as that of the starting compound phenacetine. Although nitration has occurred, the molecules exhibit less dipolar character that indicates intramolecular hydrogen bridges. This is only possible if the acetyl amino and nitro groups are located in 1.2-positions.

In accordance with the +M-effect of the acetyl amino group one should expect that the nitro group would be favoured in a (free) ortho-position because of the lowered activation energy. On the other hand, one would not expect multiple nitration because of the "mild reaction conditions" (see below) and also because of the electron withdrawing mesomeric effect (-M-effect) and the inductive electron withdrawal (-I-effect) of the nitro group that has entered the molecule.

Nitration product: 4-Ethoxy-2-nitroacetanilide

The melting point confirms this observation.

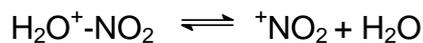
1.2 The nitration reaction is carried out relatively rapidly, at relatively low temperature in dilute solution and without using fuming nitric acid or "nitration acid".

Instead of sulphuric acid concentrated acetic acid is used. The molecules of the latter compound neither protonate the HNO_3 sufficiently nor do they do solvate the

NO_2^+ ions. As a result, the equilibrium reactions



and



are shifted far to the left. This effect is counterbalanced by the high reactivity (+M-effect) of phenacetine.

1.3 Phenacetine is oxidized by iron(III) ions and a molecule of p-quinone type and iron(II) ions are formed. The iron(II) ions react immediately with the hexacyanoferrate(III) ions to give Turnbull's Blue.

1.4 Neutralization with sodium or potassium hydroxide solution, use of calcium hydroxide solution and argumentation:

NO_3^- -ions, CH_3COO^- ions and 4-ethoxy-2-nitroacetanilide are removed by biological metabolism.

PROBLEM 2 (practical)Determination of the content of phosphoric acid in a cola drink*Apparatus:*

500 ml round-bottom flask with stirrer, reflux condenser, heating mantle, magnetic stirrer, water bath.

Preparation of the sample:

The content of a cola drink bottle is stirred for two or three minutes in a round-bottom flask. Afterwards, 6.0 g powdered active charcoal are added. The entire suspension is carefully heated to reflux and is maintained there for ten minutes. The glass joint of the reflux condenser must not be greased!

The heating mantle is then exchanged with an ice water bath. After the sample has been cooled to 20 °C, it is filtered through a double fluted filter paper. The initial filtrate should be recycled several times.

Adjustment of the pH-meter:

The pH-meter is adjusted to the working electrode by using two buffer solutions.

Titration:

150 ml of the unknown solution are titrated using pH indication with a standardized sodium hydroxide solution ($c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$).

The first equivalence point of the phosphoric acid is reached after about 6 ml of the NaOH solution have been consumed. The titration is to be continued until more than about 12 ml of sodium hydroxide solution have been added.

Results of the experiment:

- Draw the titration curve and determine the first equivalence point.
- Determine the pH value of the heated cola drink and the pH value at the first equivalence point.
- Calculate the concentration of phosphoric acid in the cola drink. Write the calculation and the result in your report.

Interpretation of the experiment:

1. Describe and explain your observations during the titration.
2. Is it possible that the active charcoal could have influenced your titration result? Give reasons for your presumption.

Chemicals:

Powdered active charcoal

Sodium hydroxide solution; $c(\text{NaOH}) = 0.0500 \text{ mol dm}^{-3}$

Buffer solutions

17th



International Chemistry Olympiad

**8 theoretical problems
1 practical problem**

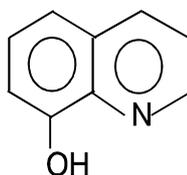
THE SEVENTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–8 JULY 1985, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A solution was formed from 0.5284 g of a sample of an alloy containing aluminium. The aluminium was then precipitated as aluminium 8-hydroxyquinolate. The precipitate was separated, dissolved in hydrochloric acid and the 8-hydroxyquinoline formed was titrated with a standard solution of potassium bromate containing potassium bromide. The concentration of the standard potassium bromate solution was 0.0200 M and 17.40 cm³ of it were required. The resultant product is a dibromo derivative of 8-hydroxyquinoline.

The structural formula of 8-hydroxyquinoline is:



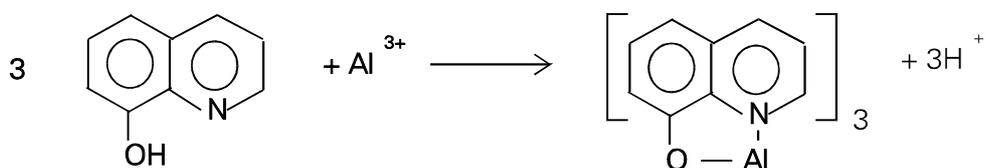
The relative atomic mass of aluminium is 26.98.

Problems:

- 1.1 Write the balanced equation for the reaction of the aluminium (III) ion with 8-hydroxyquinoline, showing clearly the structure of the products.
- 1.2 Give the name of the type of compound which is formed during the precipitation.
- 1.3 Write the balanced equation for the reaction in which bromine is produced.
- 1.4 Write the balanced equation for the reaction of bromine with 8-hydroxyquinoline.
- 1.5 Calculate the molar ratio of aluminium ions to bromate ions.
- 1.6 Calculate the percentage by weight of aluminium in the alloy.

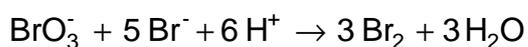
SOLUTION

1.1



1.2 Chelate

1.3



1.4



1.5 As $\text{Al} \triangleq \text{Al}(\text{oxine})_3 \triangleq 3 \text{ oxine} \triangleq 12 \text{ Br} \triangleq 12 \text{ e}$,
the chemical equivalent of Al equals $26.98/12 = 2.248$.

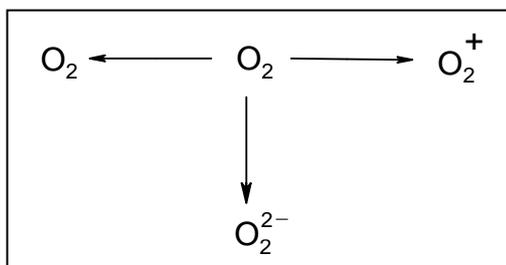
1.6 The percentage of the aluminium in the sample is

$$\% \text{Al} = \frac{17.40 \times 0.1000 \times 2.248 \times 100}{528.4} = 0.74$$

The alloy contains 0.74% of aluminium.

PROBLEM 2

It is possible to prepare compounds containing ions O_2^- , O_2^{2-} or even O_2^+ . These ions are usually formed from molecules of oxygen during various reactions, as indicated in the scheme below:



- 2.1** Indicate clearly which of the above reactions correspond to the oxidation and which to the reduction of the oxygen molecule.
- 2.2** For each of the ions in the scheme give the formula of a compound containing that particular ion.
- 2.3** It has been found that one of the species in the scheme is diamagnetic. Which one is it?
- 2.4** Copy out the following table:

Species	Bond order	Interatomic distance	Bonding energy
O_2			
O_2^+			
O_2^-			
O_2^{2-}			

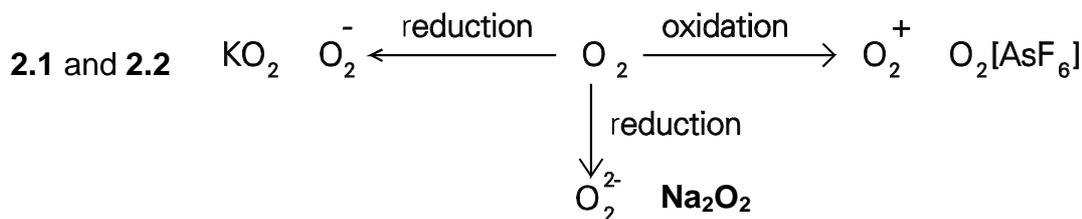
The interatomic distances, O-O, in the above species have the values 112, 121, 132 and about 149 pm. Write these values in the appropriate column in the table.

$$1 \text{ pm} = 10^{-12} \text{ m.}$$

- 2.5** Three of the bond energies, $E_{\text{O-O}}$, have the values approximately 200, 490 and 625 kJ mol^{-1} . The value for one of the species is uncertain and, therefore, not given. Write the values in the appropriate spaces in the table.

- 2.6 Determine the bond order for the individual species and write the answers in the table.
- 2.7 Is it possible to prepare compounds containing the F_2^{2-} ion? Give reasons for your answer.

SOLUTION



2.4 - 2.6

Species	Bond order	Interatomic distance (pm)	Bonding energy (kJ mol^{-1})
O_2	2	121	490
O_2^+	2.5	112	625
O_2^-	1.5	132	–
O_2^{2-}	1	149	200

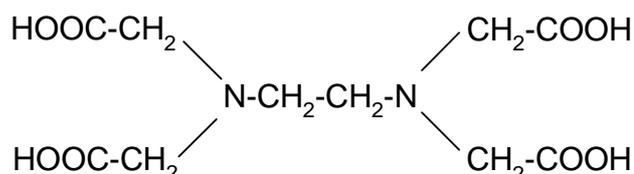
- 2.7 Ion F_2^{2-} does not exist. The number of electrons in the bonding and antibonding orbitals would be the same and thus, the bonding F–F cannot be formed. Therefore, there exists no compound containing ion F_2^{2-} .

PROBLEM 3

Calcium sulphate is a sparingly soluble compound. Its solubility product is given by:

$$K_s(\text{CaSO}_4) = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 6.1 \times 10^{-5}$$

Ethylenediaminetetraacetic acid (EDTA) has the formula $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$ and the structure:



The anion of this acid, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$, forms a stable complex $\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{2-}$ with calcium ions. The stability constant of this complex ion is given by:

$$K = \frac{[\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{2-}]}{[\text{Ca}^{2+}][\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}]} = 1.0 \times 10^{11}$$

EDTA is completely dissociated in strongly alkaline solution. The equation for this dissociation is:

Problems:

- 3.1** Calculate the concentration of calcium ions in a saturated solution of calcium sulphate.
- 3.2** Calculate the concentration of free Ca^{2+} cations in a solution of 0.1 M $\text{Na}_2(\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$. You should ignore any protonation of the ligand.
- 3.3** How many moles of calcium sulphate will dissolve in 1 litre of a strongly alkaline solution of 0.1 M $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$?
What would be the concentrations of the calcium and sulphate ions in the resulting solution?
- 3.4** Suggest a structure for the complex ion $[\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8]^{2-}$ assuming that it is approximately octahedral.
- 3.5** Is the structure you have suggested in 4) optically active?
If your answer is "yes" then draw the structure of the other optical isomer enantiomer).
- 3.6** Explain why the complexes formed by the anion $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$ are exceptionally stable.

SOLUTION

3.1 $[\text{Ca}^{2+}] = 7.8 \times 10^{-3} \text{ mol dm}^{-3}$

3.2 $[\text{Ca}^{2+}] = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$

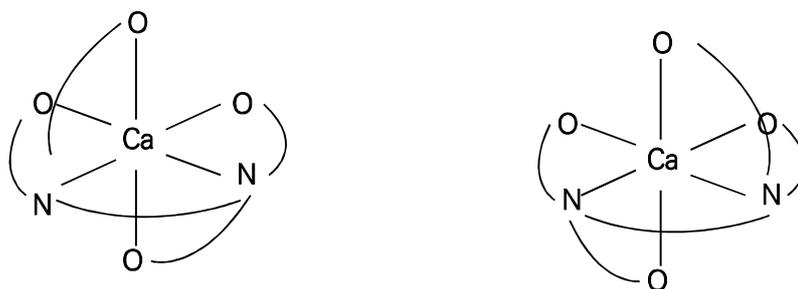
3.3 The CaSO_4 amount dissolved is 0.1 mol.

$[\text{SO}_4^{2-}] = 0.10 \text{ mol dm}^{-3}$.

$[\text{Ca}^{2+}] = 6.1 \times 10^{-4} \text{ mol dm}^{-3}$

3.4 + 3.5

The complex is optically active. The structures of both enantiomers are

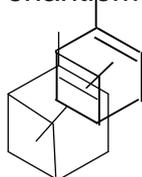


3.6 The high number of the chelate rings. Other factors also contribute to the complex ability, e.g. the character of the donor atoms, the magnitude and distribution of the charges in the anion, etc.

PROBLEM 4

At a temperature around 200 °C the racemisation of pinene can be followed in the gaseous phase by measuring the optical rotation.

If, for example, you take the (+)-enantiomer of α -pinene



an equilibrium is gradually established between the two enantiomers (optical isomers). The two opposing reactions are both of the first order.

In 1927 D. F. Smith obtained the following data in his study of racemisation of α -pinene:

T/K	α_1	α_2	t/min
490.9	32.75	18.01	579
490.9	29.51	15.59	587
503.9	30.64	8.74	371
505.4	12.95	8.05	120
510.1	23.22	6.15	216

α_1 and α_2 are the values for optical rotation in terms of the dimensions of the polarimeter scale; t is the time which has elapsed between the two measurements.

Problems:

4.1 What is the value for the equilibrium constant for the racemisation?

What is the corresponding value of $\Delta_r G^\circ$ (racemisation)?

What is the relationship between the forward and backward rate constants, k_1 and k_{-1} , in a state of dynamic equilibrium?

4.2 State the rate equation for the racemisation of pinene.

Derive a relationship which could be used to calculate the rate constant for the conversion of the (+)-enantiomer into the (-)-enantiomer using the data given in the table.

- 4.3 Calculate the rate constant for this reaction at the four temperatures given in the table.
- 4.4 Calculate the average value of the activation energy for this reaction. You should take the average of the values at a minimum of three temperatures or use a graphical method.

HINT:

If the loss of concentration of a substance obeys the rate equation:

$$-\frac{dc}{dt} = k(2c - \text{constant})$$

Then the dependence of concentration on time is given by:

$$\ln \frac{2c_0 - \text{constant}}{2c - \text{constant}} = 2kt$$

where c_0 is the initial concentration at time $t = 0$.

SOLUTION

- 4.1 The racemisation equilibrium constant equals unity at all temperatures and $\Delta_r G^\circ = 0$.
- 4.2 If the concentration of one enantiomer is c and that of the other is c' , then it holds for the rate of the loss of c that

$$-\frac{dc}{dt} = k_1c - k_{-1}c' = k(c - c') \text{ for } k_1 = k_{-1} = k$$

If the initial concentrations are c_0 and c_0' , then

$$c' = c_0 - c + c_0'$$

can be substituted for c' in the rate equation, obtaining

$$-\frac{dc}{dt} = k(2c - c_0 - c_0')$$

It then holds for concentrations c_1 and c_2 measured at times t_1 and t_2 , respectively, that

$$\ln \frac{2c_1 - c_0 - c_0'}{2c_2 - c_0 - c_0'} = 2k(t_2 - t_1)$$

and since $c_0 + c_0' = c_1 + c_1' = c_2 + c_2'$

$$\ln \frac{c_1 - c_1'}{c_2 - c_2'} = 2k(t_2 - t_1)$$

The measured optical rotation α is proportional to $c - c'$; hence $\ln \frac{\alpha_1}{\alpha_2} = 2k(t_2 - t_1)$

4.3

T/K	490.9	503.9	505.4	510.1
$10^4 k \text{ min}^{-1}$	5.3	16.9	19.8	30.7

$$4.4 \quad \ln \frac{k_2}{k_1} = \frac{E_A}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad E_A = \ln \frac{k_2}{k_1} \times \frac{R T_1 T_2}{T_2 - T_1}$$

If e.g. the value of k for 490.9 K (the average of two measurements) is combined with each of the remaining three values, three values of activation energy are obtained: 183400 J mol⁻¹, 177500 J mol⁻¹, 190500 J mol⁻¹. The average value equals 187100 J mol⁻¹.

PROBLEM 5

The equilibrium voltage of the cell,

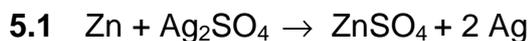


was measured at several temperatures and the results of the measurements are given in the following table:

t / °C	10	20	30
E / V	1.5784	1.5675	1.5566

Problems:

- 5.1 Give the equation for the reaction occurring in this galvanic cell.
- 5.2 Determine the value of the cell voltage at the temperature $T = 298 \text{ K}$.
- 5.3 Determine $\Delta_r G_{298}$ of the cell reaction.
- 5.4 Determine $\Delta_r H_{298}$ of the cell reaction.

SOLUTION

5.2 The temperature dependence is described by the equation,

$$E_T = E_{T_0} + \frac{dE}{dT} \cdot (T - T_0)$$

It follows from the plot for the slope,

$$\frac{dE}{dT} = -1.09 \times 10^{-3} \text{ V K}^{-1}$$

Hence,

$$E_{298} = 1.5675 - 1.09 \times 10^{-3} \times 5 = 1.562 \text{ V}$$

5.3 The relationship,

$$\Delta_r G = -nFE$$

holds for $\Delta_r G$. Then

$$\Delta_r G_{298} = -2 \times 96484.6 \times 1.563 = -301417.9 \text{ J mol}^{-1}$$

5.4 The equation,

$$\Delta G = \Delta H - T \Delta S,$$

is employed to calculate $\Delta_r H_{298}$, substituting

$$\Delta S = -\frac{dG}{dT}$$

Rearrangement yields the relationship

$$\Delta H = \Delta G - T \frac{dG}{dT}$$

As it holds that

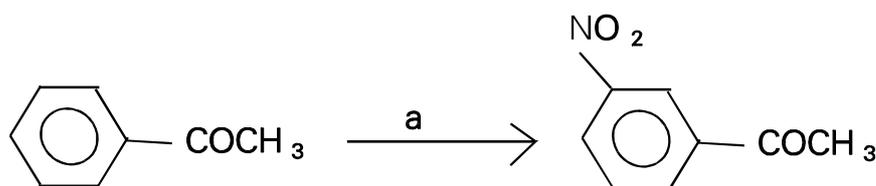
$$\frac{dG}{dT} = -nF \frac{dE}{dT}$$

the final expression is:

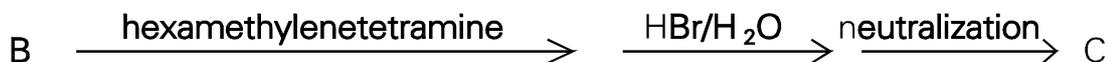
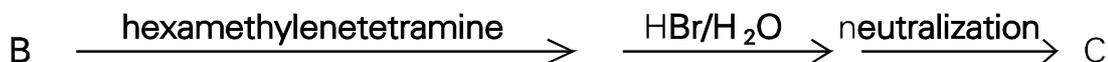
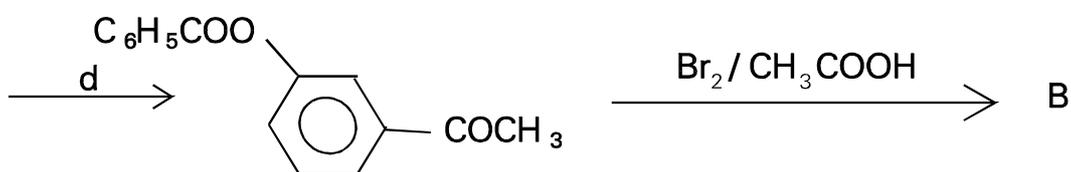
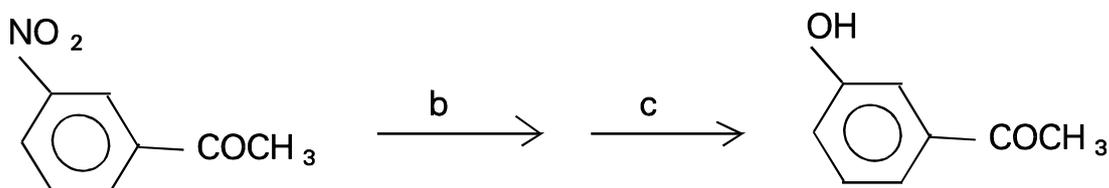
$$\begin{aligned}\Delta_r H_{298} &= \Delta G_{298} + nFT \frac{dE}{dT} \\ &= -301417.9 + [2 \times 96\,484.6 \times 298 \times (-1.09 \times 10^{-3})] = 364098.1 \text{ J mol}^{-1}\end{aligned}$$

PROBLEM 6

The following scheme describes the synthesis of a compound **D** (with sympathomimetic effects) whose skeleton consists of 2-phenylethylamine.



A Acetophenone



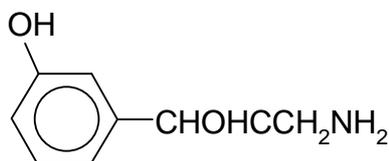
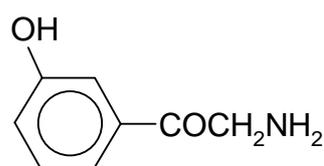
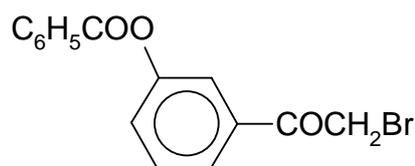
Problems:

- 6.1 What reagents were used in steps **a**, **b**, **c**, and **d**?
- 6.2 Give the structural formulae of compounds **B**, **C** and **D**.
- 6.3 Is it possible to prepare 3-hydroxyacetophenone from the reaction between phenol, acetylchloride and AlCl_3 ? Give reasons for your answer.
- 6.4 Give the formulae of the compounds that are formed by the reaction of compound **C** with a) 10% HCl and b) 10% NaOH.
- 6.5 By the asterisk denote the chirality centre in the formula of compound **D**.
- 6.6 Give the spatial formula of enantiomer (R) of compound **D**.

SOLUTION

- 6.1 a) $\text{HNO}_3/\text{H}_2\text{SO}_4$
 b) Fe/H^+
 c) NaNO_2/HCl
 d) benzoylchloride

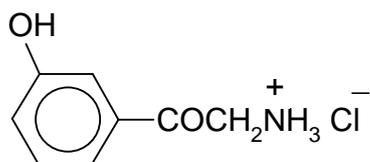
6.2



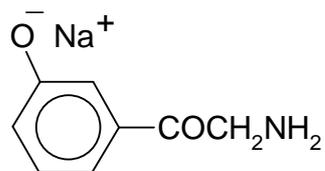
6.3 No

6.4

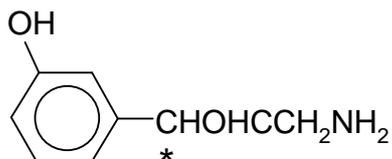
a)



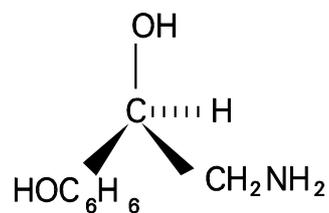
b)



6.5



6.6

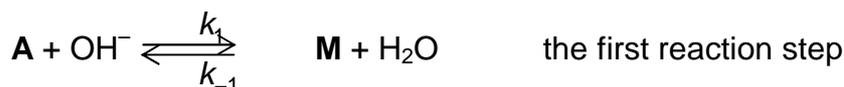


PROBLEM 7

Propanal, **A**, reacts in an aqueous-ethanolic solution of sodium hydroxide to yield compound **B** that is readily dehydrated to give compound **C** (C₆H₁₀O).

Problems:

- 7.1** Give the structural formulae of substances **B** and **C**.
- 7.2** Give the formula of intermediate **M** that is formed from propanal **A** by the action of hydroxide ions.
- 7.3** Give the formulae of the two most important mesomeric structures of intermediate **M** and denote the nonbonding electron pairs and the charge distribution.
- 7.4** The reaction of propanal **A** with sodium hydroxide, producing substance **B**, can be described by the scheme:



The rate of the formation of substance **B** is given by the equation:

$$v = k_2 [\text{M}] [\text{A}] \quad (1)$$

The above values of k are the rate constants for the individual reaction steps.

Assume that the concentration of intermediate **M** is small and constant during the reaction and express this fact by an equation involving terms with constants k_1 , k_{-1} and k_2 .

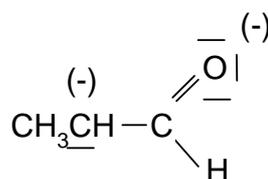
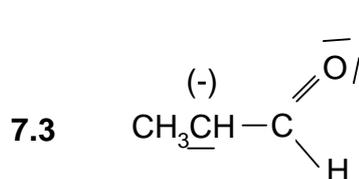
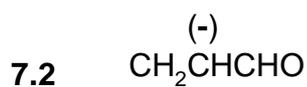
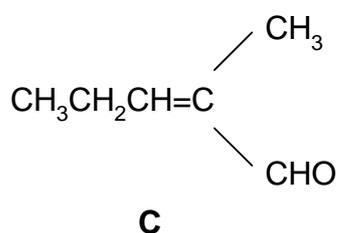
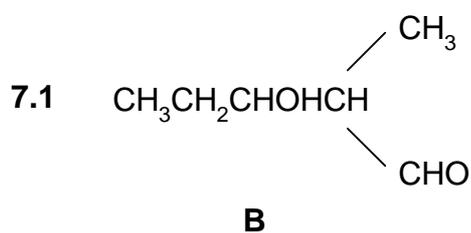
$$\frac{d[\text{M}]}{dt} = 0 \quad (2)$$

Derive an expression for the concentration of **M** from equation 2 and then substitute for **[M]** in equation 1. This gives equation 3 which is the complete rate equation for the formation of substance **B**.

If it is assumed that the second reaction step is rate determining, then the rearrangement of equation 3 gives equation 4, the rate equation.

Give equations 2, 3, and 4.

- 7.5** Determine the overall order of the reaction described by equation 4.

SOLUTION


7.4

$$\frac{d[\mathbf{M}]}{dt} = 0 = k_1[\mathbf{A}][\text{OH}^-] - k_{-1}[\mathbf{M}] - k_2[\mathbf{A}][\mathbf{M}] \quad (2)$$

$$[\mathbf{M}] = \frac{k_1[\mathbf{A}][\text{OH}^-]}{k_{-1} + k_2[\mathbf{A}]} \quad v = \frac{k_1 k_2 [\mathbf{A}]^2 [\text{OH}^-]}{k_{-1} + k_2[\mathbf{A}]} \quad (3)$$

for $k_2[\mathbf{A}][\mathbf{M}] \ll k_{-1}[\mathbf{M}]$ it holds, that

$$v = \frac{k_1 k_2 [\mathbf{A}]^2 [\text{OH}^-]}{k_{-1}} \quad (4)$$

7.5 Rate equation (4) corresponds to the overall reaction order of (3).

PROBLEM 8

The following reaction scheme represents part of anaerobic degradation of saccharides, i.e. the glycolysis, involving equilibrium constants K_1 and K_2 :



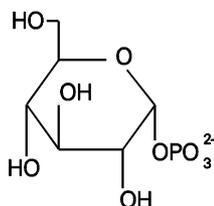
Problems:

- 8.1** Give the structural formulae for all the three reactants (compounds) that are mutually interconverted, i.e. α -D-glucose-1-phosphate, α -D-glucose-6-phosphate and α -D-fructose-6-phosphate.
- 8.2** In the beginning of the reaction the reaction mixture contained 1 mmol of glucose-6-phosphate. Calculate the amounts of glucose-6-phosphate, glucose-1-phosphate and fructose-6-phosphate in the mixture at equilibrium. (As the reaction take place in a constant volume, the ratio of the amounts of substances equals that of their concentrations.)

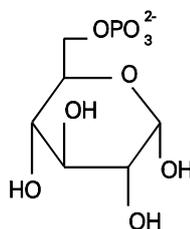
SOLUTION

8.1

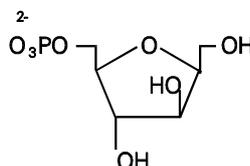
α -D-glucose-1-phosphate



α -D-glucose-6-phosphate



α -D-fructose-6-phosphate



8.2 It holds for the equilibrium constant of the successive reactions, that

$$\frac{\text{Fru-6-P}}{\text{Glc-1-P}} = 19 \times 0.5 = 9.5 \quad (\text{i})$$

If y mmoles of Glc-6-phosphate are converted into the same number of Glc-1-phosphate and another x mmoles of Glc-6-phosphate are converted into the same number of mmoles of Fru-6-phosphate, then $(1 - x - y)$ mmoles of Glc-6-phosphate remain in the reaction mixture at equilibrium. It follows from relationship (i) that

$$\text{Glc-1-phosphate} = y \quad x/y = 9.5$$

$$\text{Fru-6-phosphate} = x \quad x = 9.5 y$$

After substituting,

$$\text{Glc-6-phosphate} = 1 - x - y = 1 - 10.5y,$$

it is possible to write for the reaction mixture at equilibrium that

$$\frac{\text{Glc-6-P}}{\text{Glc-1-P}} = \frac{1 - 10.5y}{y} = 19 \quad 1 - 10.5y = 19 y$$

$$y = 1/29.5 = 0.034 \text{ mmoles Glc-1-phosphate}$$

It is further calculated that

$$x = 9.5y = 9.5 \times 0.034 \text{ or } 9.5/29.5 = 0.322 \text{ mmoles of Fru-6-phosphate}$$

$$1 - x - y = 1 - 0.322 - 0.034 = 0.644 \text{ mmoles of Glc-6-phosphate}$$

At equilibrium the reaction mixture contains 0.034 mmoles Glc-1-phosphate, 0.644 mmoles Glc-6-phosphate and 0.322 mmoles Fru-6-phosphate.

PRACTICAL PROBLEMS**PROBLEM 1 (practical)**

Determination of the relative molecular mass of a weak acid by acid-base titration in a non-aqueous solvent

Weak acid whose dissociation constants, K_a , are smaller than 1×10^{-7} can be satisfactorily titrated in ethanol or in a mixture of ethanol and benzene, using a standard ethanolic solution of potassium hydroxide or potassium alkoxide in the presence of phenolphthalein or thymolphthalein as an indicator.

Task:

Determine the molecular weight (chemical equivalent) of a weak monobasic acid by titration with potassium ethoxide in ethanolic solution using phenolphthalein as an indicator (the acid has the general formula $C_xH_yO_z$).

Chemicals and equipment:

Standard solution of potassium ethoxide in ethanol of concentration $c = 0.1000 \text{ mol dm}^{-3}$

Indicator: 0.1% solution of phenolphthalein in ethanol

Solvent: A mixture of ethanol and benzene

1.000 g of sample, accurately weighed,

3 titration flasks of volume 200 or 500 cm³, one 25 cm³ burette, one 50 cm³ pipette, one 250 cm³ volumetric flask, one 100 cm³ measuring cylinder, small funnels, beakers, filter paper.

Procedure:

You are provided with 1.000 g of the monobasic acid $C_xH_yO_z$. This sample is labelled with a number. This should be written clearly at the top of your answer paper.

Carefully transfer all the acid into the graduated (volumetric) flask and fill the solution in the flask with ethanol up to 250 ml. A portion of 50.00 ml of this solution should be titrated with the 0.1000 M alcoholic solution of potassium ethoxide using 5 drops of phenolphthalein as indicator. The first titration should be a rough titration for estimating the

approximate volume necessary to determine the endpoint. Subsequent titrations should be carried out with precision, using the same quantity of indicator each time.

Record all titration values. An extra titration should be carried out to eliminate any error that might be due to the action of the potassium hydroxide on the solvent, indicator or ethanol. This type of titration is known as a blank titration, its value should be recorded and used to correct the results of previous titrations. Care should be taken to use the same quantity of indicator as in previous titrations.

The correct titration values should be used to calculate the relative molecular mass (molecular weight) of the sample.

Note: The waste material containing organic solvents must not be discharged in a sink. Use labelled containers for this purpose.

Questions:

- 1) Suggest the name and formula of a common, monobasic acid which corresponds to the value you determined experimentally for your sample.
- 2) Write a general equation for the neutralisation of a monocarboxylic acid with:
 - i) potassium ethoxide,
 - ii) potassium hydroxide.
- 3) During the titration of some weak carboxylic (fatty) acids, similar to the titration that you have carried out, turbidity or cloudiness is observed. Suggest an explanation for this turbidity.
- 4) How would you produce 1 dm³ of a standard solution of 0.1 M potassium ethoxide? Which compound would you use, as a standard solution?
- 5) Why are the titrations of weak acids carried out in non-aqueous media?
- 6) Name another solvent which is suitable for use in the titration of weak acids.
- 7) How would you recover the organic solvent used in your experiment?
- 8) Sketch a schematic titration curve (pH as a function of volume) for the titration of 20 ml of a 0.1 M aqueous solution of a weak monobasic acid with a standard aqueous solution of 0.1 M potassium hydroxide.
- 9) Calculate the pH of 0.1 M aqueous solution of an acid which has a dissociation constant of 1×10^{-7} .

18th

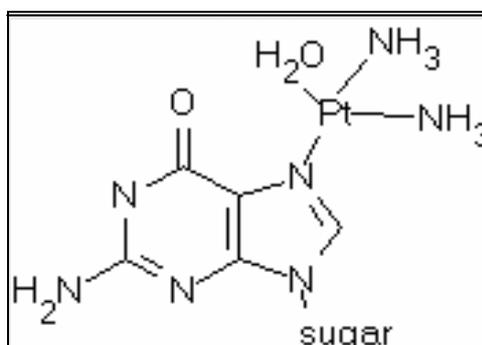


7 theoretical problems
2 practical problems

replaced relatively easily, but it is more difficult to replace the amine ligands, which usually requires heating.

- 1.5** Considering each of the isomers in the previous questions a-d, indicate which isomers can be converted to another at room temperature. Give both the original molecule and the products.
- 1.6** $\text{PtCl}_2(\text{en})$ reacts with Br^- in a molar proportion of 1:2 at room temperature. Which compound would you expect to form in what proportion? You can assume that the Pt-Br and Pt-Cl bonds are equally strong and that there is no perturbing influence from hydrolysis.
- 1.7** Using the equation to express chemical equilibrium, show that hydrolysis hardly ever occurs in blood but that it does occur in the cells. Note: $\text{PtCl}_2(\text{NH}_3)_2$ hydrolyses to and 2 Cl^- . In cells the Cl^- concentration is low; in blood it is fairly high.

After hydrolysis in the tumour cell a reactive platinum ion is formed to which two NH_3 groups are still bound, as it was found in the urine of patients treated with this compound. The reactive platinum ion appears to be bound to cellular DNA, where the bonding occurs via guanine to one of the N-atoms.

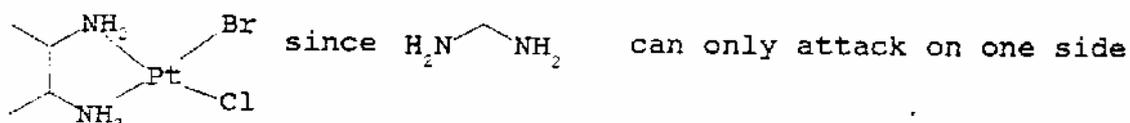
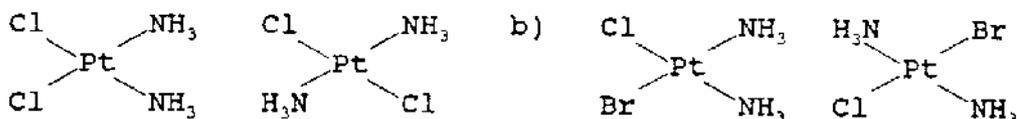


As a result of the two reactive sites of platinum and the two unreactive NH_3 ligands, it can form additionally a second bond to DNA. Research has shown that this happens in particular with a second guanine base from the same strand of DNA.

- 1.8** Show by calculations which of the two isomers in question a) can form this bond. (Note: Pt-N distance = 210 pm, DNA base distance = 320 pm).

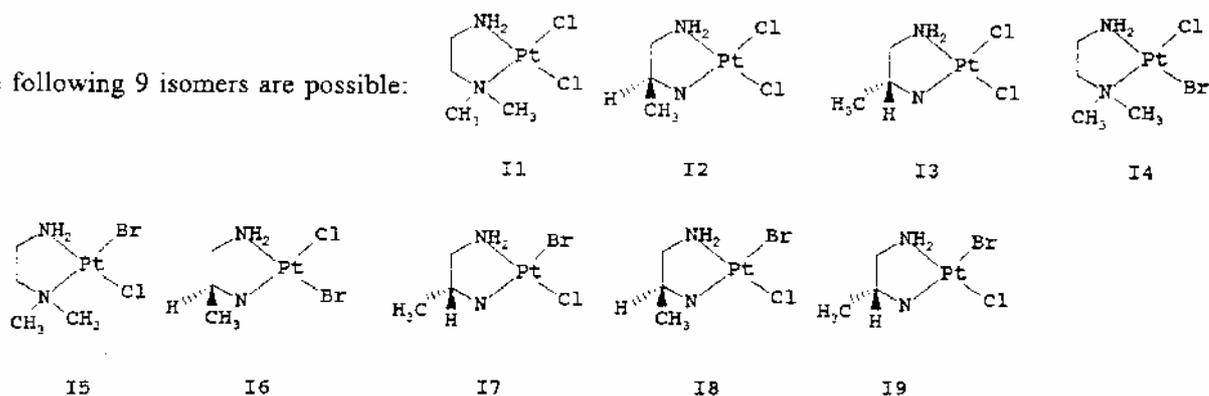
SOLUTION

1.1 - 1.3 The isomers are:



1.4

d) The following 9 isomers are possible:



1.5 In a-c) there is no change possible;

in d) I4 and I5, I6 and I7, I8 and I9 transform one into another. Via this isomerization also $\text{PtCl}_2(\text{dmen})$, $\text{PtBr}_2(\text{dmen})$, $\text{PtCl}_2(\text{pn})$ and $\text{PtBr}_2(\text{pn})$ can be formed, even though they are not isomers.

1.6 $\text{PtCl}_2(\text{en}) : \text{PtBr}_2(\text{en}) : \text{PtBrCl}(\text{en}) = 1 : 1 : 2$

1.7 $\text{PtCl}_2(\text{NH}_3)_2 \rightleftharpoons (\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2)^+ \rightleftharpoons \text{Pt}(\text{H}_2\text{O})_2(\text{NH}_3)_2^{2+}$

In blood the hydrolysis does not occur, because the concentration of Cl^- is rather high and the equilibrium is shifted to the left side.

1.8 The bond is formed by the cis-isomer, because in that case the distance between the bases (320 pm) has to change only to $210\sqrt{2} = 297$ nm, whereas in the case of the trans-compound the distant would be $210 \times 2 = 420$ nm.

PROBLEM 2

The compound $\text{Na}_5\text{P}_3\text{O}_{10}$ is used as an additive for detergents to bind the Ca^{2+} and Mg^{2+} ions present in water in order to prevent the precipitation of their fatty acid salts on the laundry.

- 2.1 Draw the structure of the ions $(\text{P}_3\text{O}_{10})^{5-}$ and $(\text{P}_3\text{O}_9)^{3-}$ assuming that P-P bonds do not occur.
- 2.2 Assuming an octahedral coordination of the Mg^{2+} ion give a drawing of the $\text{Mg}(\text{P}_3\text{O}_{10})(\text{H}_2\text{O})_n^{3-}$ ion also indicating the value for n.

The complex ions of Mg^{2+} and Ca^{2+} and triphosphate are well soluble in water. They are, among other things, responsible for the wild growth of algae in surface waters. They could be removed by precipitation as an insoluble compound.

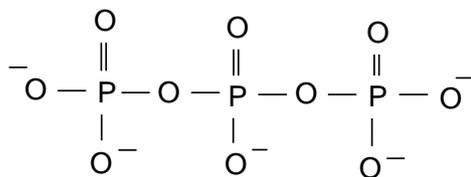
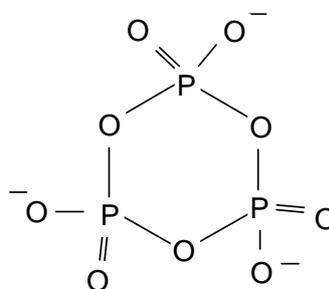
- 2.3 Give some possibilities (ions) to precipitate the triphosphates bound to Ca^{2+} or Mg^{2+} .
- 2.4 Calculate the mass of $\text{Na}_5\text{P}_3\text{O}_{10}$ (in grams) necessary in a washing machine to reduce the amount of Ca^{2+} in 20 litres of city water (0.225 g/l) to an acceptable maximum of 0.02 g/l. Effects of pH, the precipitation of $\text{Ca}(\text{OH})_2$, and possible effects by other positive ions, can be neglected. The following data is given:

$$K_1 = \frac{[\text{Ca}^{2+}][\text{P}_3\text{O}_{10}^{5-}]}{[\text{CaP}_3\text{O}_{10}^{3-}]} = 1.0 \times 10^{-6}$$

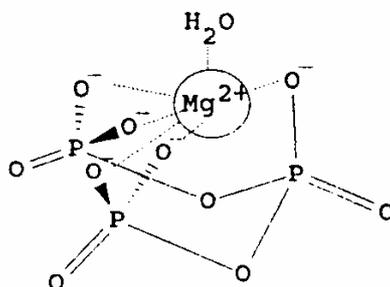
Molar mass of $\text{Na}_5\text{P}_3\text{O}_{10}$ is 366 g mol^{-1} , the molar mass of Ca is 40 g mol^{-1} .

SOLUTION

- 2.1 The structures are:


 $\text{P}_3\text{O}_{10}^{5-}$

 $\text{P}_3\text{O}_9^{3-}$

2.2 Since Mg^{2+} has the coordination number 6, one water molecule serves as the sixth ligand among the five O^- ligands already present in the $[\text{P}_3\text{O}_{10}]^{5-}$ - ligand:



2.3 Possible ions are Al^{3+} or Fe^{2+} because of their equal charge and similar size. The triphosphates are not soluble in water.

$$2.4 \quad [\text{Ca}^{2+}] + [\text{CaP}_3\text{O}_{10}]^{3-} = \frac{0.225}{40} \text{ mol dm}^{-3};$$

$$[\text{Ca}^{2+}] = \frac{0.020}{40} \text{ mol dm}^{-3} \Rightarrow [\text{CaP}_3\text{O}_{10}^{3-}] = \frac{0.205}{40} \text{ mol dm}^{-3}$$

$$[\text{P}_3\text{O}_{10}^{5-}] = \frac{K_1[\text{CaP}_3\text{O}_{10}^{3-}]}{[\text{Ca}^{2+}]} = 1.025 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{CaP}_3\text{O}_{10}^{3-}] + [\text{P}_3\text{O}_{10}^{5-}] = 5.135 \times 10^{-3} \text{ mol dm}^{-3} \equiv 37.6 \text{ g Na}_3\text{P}_3\text{O}_{10} \text{ in } 20 \text{ dm}^3 \text{ H}_2\text{O}$$

PROBLEM 3

In order to explain why dyes are coloured, they can be considered as rod-like, one-dimensional molecules over which the electrons are distributed. The wave lengths of the electrons should fit to the available space which is the length l . When absorbing light, an electron makes a transition from a lower to a higher energy state. The energy difference is given by:

$$\Delta E = h \times \text{cover} \lambda \text{ where } \lambda = \frac{h}{p}$$

- 3.1 Give a general expression for possible wavelengths of the electron as a function of the length l .

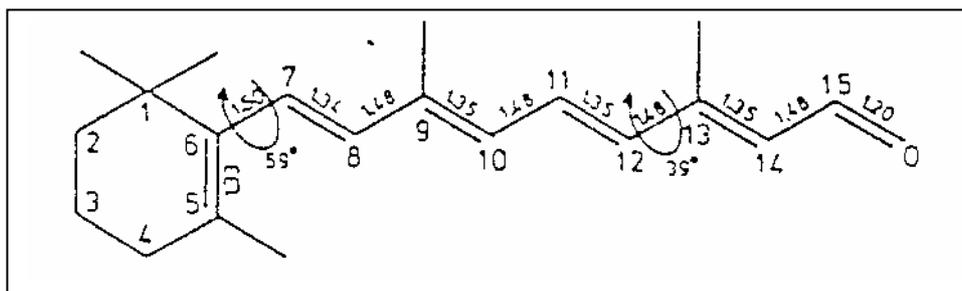
In the 'particle in the box' model, only the variations in the kinetic energy of the electrons are considered.

- 3.2 Give an expression for the possible energies that electrons in the molecule can have (as a function of l).
- 3.3 Show that for a chain of length l with k electrons, the longest wavelength absorption occurs at:

$$\lambda = \frac{8mc l^2}{h(k+1)} \text{ for even values of } k$$

- 3.4 Derive an expression for the wavelength of the first electronic transition as a function of the number of C-atoms for even values of n .
- 3.5 Calculate the minimum number of C-atoms (conjugated systems) to obtain a visible colour. C-C bond length is 142 pm.

The retina in the human eye contains rhodopsin, a light absorbent.



The molecule in the part of C-atoms 7 through 12 is planar. The angle between the bonds C5-C6, C7-C8, C11-C12 and C13-C14 is about 39°. According to the 'particle in the box' theory fragment C7 through C12 should absorb at about 213 nm. In reality the absorption of retinal occurs at 308 nm.

- 3.6 Give a reason for the longer wavelength that is observed in practice using the above mentioned theories.
- 3.7 When retinal is bound to opsin to form rhodopsin, the absorption occurs around 600 nm. Which atoms must be forced into one plane by the protein? Show by calculation that it's true.

SOLUTION

3.1 $\lambda = c\nu = 2l/n$ with $n = 1, 2, 3, \dots$

3.2 $E = \frac{hc}{\lambda} = \frac{mv^2}{2} = \frac{p^2}{2m}; p = \frac{h}{\lambda} = \frac{hn}{2l} \Rightarrow \Delta E_n = \frac{h^2 n^2}{8mI^2} = \frac{h^2}{8mI^2} \times (n_{\text{homo}}^2 - n_{\text{lumo}}^2)$

- 3.3 For k electrons and $k \equiv 0 \pmod{2}$, $k/2$ orbitals are possible, so $n_{\text{homo}} = k/2$ and $n_{\text{lumo}} = k/2 + 1$

$$\Delta E_n = \frac{h^2}{8mI^2} [(1/2k + 1)^2 - 1/2k^2] = \frac{h^2}{8mI^2} \times (k + 1) \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{8mcI^2}{h(k + 1)}$$

- 3.4 If N is the number of C-atoms, N is equal to $k+1$ for even number of electrons k , so

$$\lambda = \frac{8mcI^2}{Nh} = \frac{8mcI^2}{h(k + 1)}$$

for even N 's, the length of the box would be $a(N-1)$ with $k = N$ electrons, so

$$\lambda = \frac{8mc(N1)^2 a^2}{h(N+1)}$$

- 3.5 For a conjugated system N has to be even. To obtain a visible colour, the wavelength should be greater than 400 nm. Therefore:

$$\frac{8mc(N1)^2 a^2}{h(N+1)} \geq 4 \times 10^7 \text{ so accordingly : } \frac{(N1)^2}{N+1} \geq 6.02$$

The equation $N^2 - 6.02 N - 6.02 > 0$ derived from the equation above has the only positive solution $N = 8.60$. Since N must be even, the minimum number of C-Atoms is 10.

3.6 The angles between 5-6 and 7-8, as well as between 11-12 and 13-14 are smaller than 90° and therefore the effect of the double bonds between C5 and C6, C13, C14 and O cannot be neglected. They overlap to a small extent with the conjugated system C7 through C12 and enlarge the box significantly. A larger l leads to a larger λ , causing a shift towards a longer wavelength.

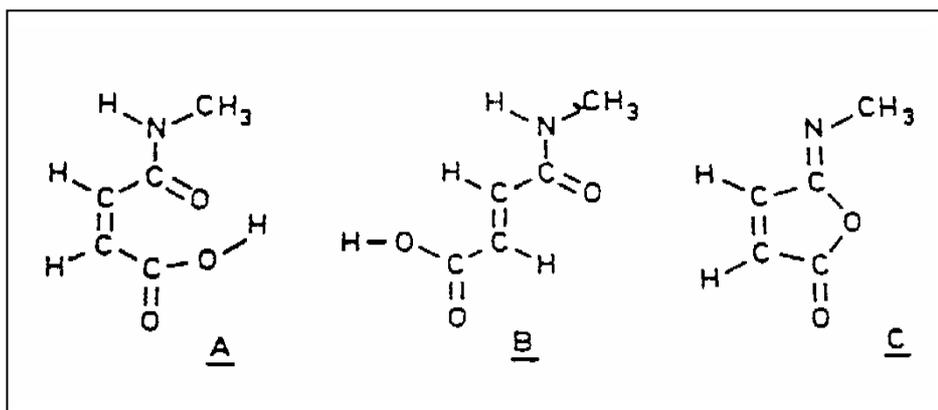
3.7 Obviously, the box must be much larger when bound to opsin. For $\lambda = 600$ nm the atoms C5 to O at the end of the chain must be forced into the plane:

$$l = 0.133 + 0.150 + 4(0.134 + 0.148) + 0.120 = 1.54 \text{ nm}; \quad k = 12;$$

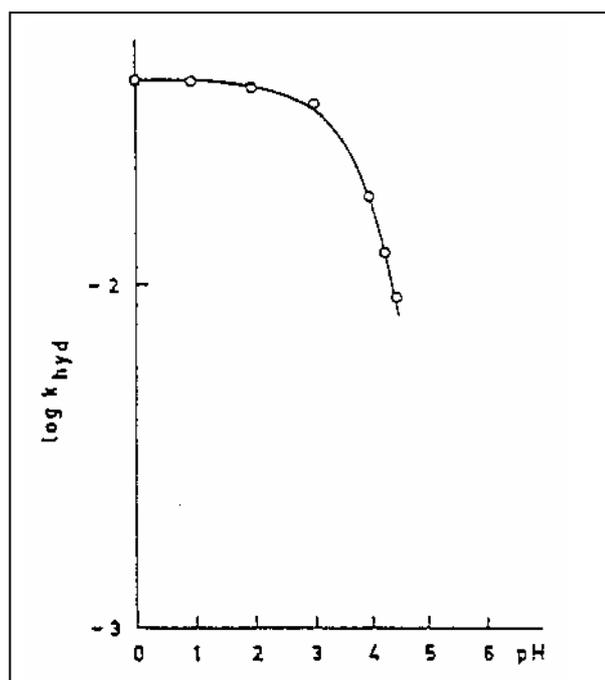
$$\lambda = 3.30 \times 10^{12} l^2 / (k + 1) = \underline{602 \text{ nm}}$$

PROBLEM 4

The high efficiency of catalysis by enzymes is mainly due to an enzyme-reactant complex in which the reacting group is placed in a favourable position for the reaction with respect to the catalyzing groups of the enzyme. Studies are carried out with model compounds in which a catalyzing group has been introduced in the proximity of the reaction centre of the molecule. As an example we consider the hydrolysis of the amide bond in compound **A**. This reaction proceeds in water at 39 °C and pH = 2 more than a million times faster than the hydrolysis of compound **B**.



The relation between the rate constant k_{hyd} and pH for the hydrolysis of **A** at 39 °C is shown in figure below.



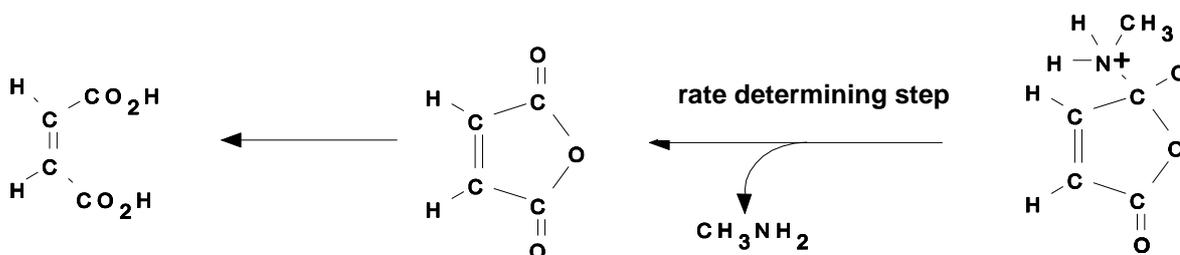
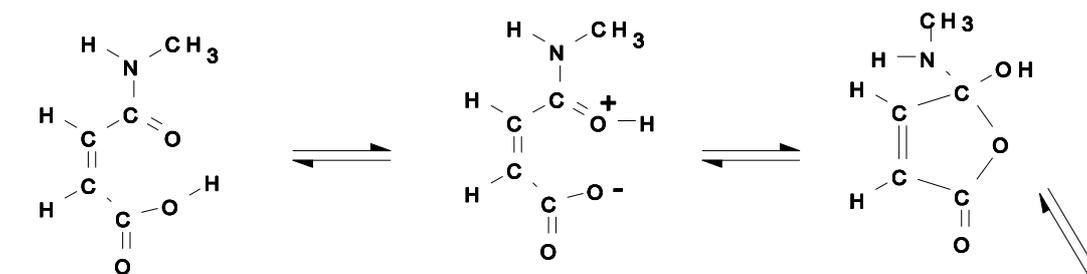
Further observation:

Addition of water to the iso-imide **C** gives a rapid reaction, which initially yields **A**. Subsequently, hydrolysis of **A** occurs. The amid carbonyl group in **A** is labelled with ^{13}C and the hydrolysis is allowed to take place in H_2^{18}O at $\text{pH} = 2$ and $39\text{ }^\circ\text{C}$. The diacid formed upon hydrolysis is isolated, converted into a disilver salt and completely decarboxylated with bromine in an anhydrous reaction medium. The carbon dioxide formed is a mixture of particles of masses 44, 45, 46 and 47 which are formed in equal amounts.

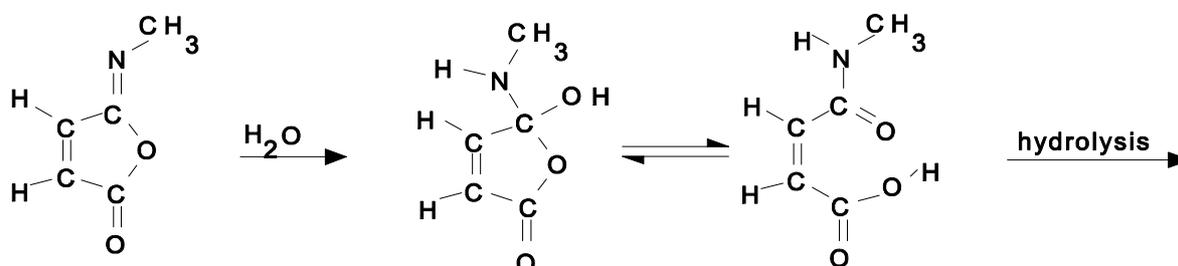
- 4.1 Why is the hydrolysis of **A** so much faster than that of **B**?
- 4.2 Explain why the rate of hydrolysis of **A** is independent on pH in the range between $\text{pH} = 0$ to $\text{pH} = 2$.
- 4.3 Why does k_{hyd} decrease so rapidly at pH values higher than 3.
- 4.4 Give a detailed reaction mechanism for the hydrolysis of **A**. Indicate which step in the reaction is rate determining.
- 4.5 Show that the observations further made are consistent with the reaction mechanism given under d.

SOLUTION

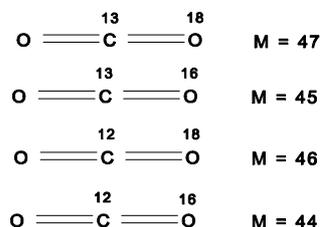
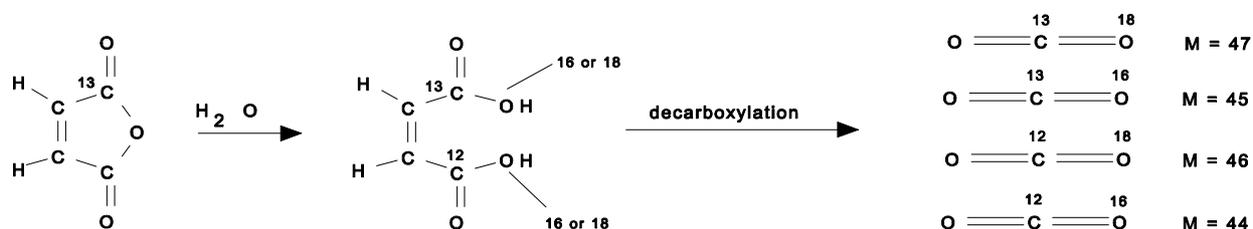
- 4.1 The high rate of hydrolysis of **A** is caused by intramolecular catalysis of the COOH group in the cis-position. In **B** the COOH group is situated in the trans-position with respect to the amide group and therefore too far away for intramolecular catalysis.
- 4.2 For $0 < \text{pH} < 2$ the COOH group is not ionized and therefore, it can act as an intramolecular catalyser. If the hydrolysis in that pH -range is only the result of catalysis by the COOH -group and not competing with H_3O^+ the rate constant in that range is pH independent.
- 4.3 At $\text{pH} > 3$ the COOH group deprotonates giving COO^- . Intramolecular acid catalysis, in which proton transfer plays an important role, is then not possible anymore.
- 4.4 The mechanism of hydrolysis is indicated below:



4.5



With the observation given, the rate determining step can be identified.



PROBLEM 5

Bacterial conversion of saccharose leads to (S)-(+)-2-hydroxypropanoic acid (L-(+)-lactic acid), which forms a cyclic ester out of two molecules. This dilactide can be polymerized to a polylactide, which is used in surgery.

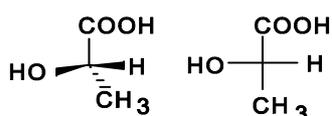
- 5.1 Give the spatial structures and Fischer projection of L-(+)-lactic acid and its dilactide.
- 5.2 Sketch the structure of the polylactide discussed above (at least three units). What is its tacticity (iso-, syndio- or atactic)?
- 5.3 Draw the isomeric dilactides formed out of racemic lactic acid. Show the configuration of the chiral centres.

L-(+)-lactic acid is used for the preparation of the herbicide Barnon that is used against wild oats. In this case (+)-lactic acid is esterified with 2-propanol and then the hydroxyl group is treated with methanesulfonyl chloride. The product is then submitted to a S_N2 -reaction with 3-fluoro-4-chloro-phenylamine, where the methanesulfonate group leaves as CH_3SO_3^- . Finally a benzoyl group is introduced with the help of benzoyl chloride.

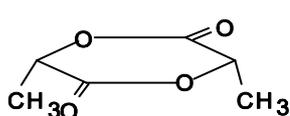
- 5.4 Draw the Fischer projection of the various consecutive reaction products.

SOLUTION

5.1

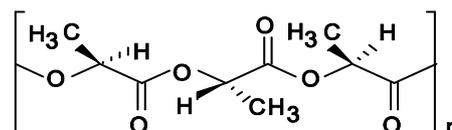


L-(+)-lactic acid and its Fischer projection



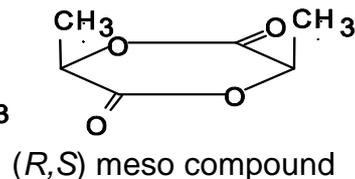
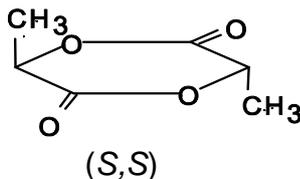
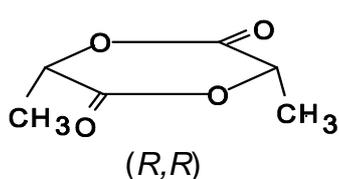
Dilactide of L-(+)-lactic acid - spatial formula

5.2



Polylactide of L-(+)-lactic acid

- 5.3 Dilactides of racemic lactic acid with the following configurations:

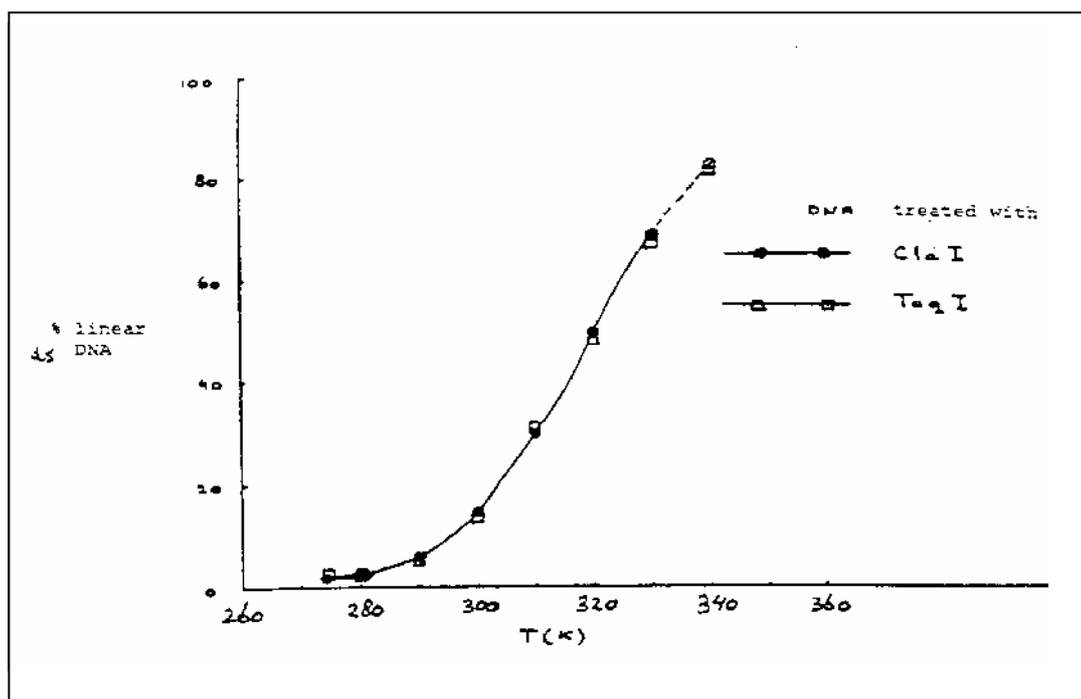


PROBLEM 6

In recombinant DNA technology specific endonucleases can recognize and hydrolyse the phosphoric ester bound in each of both strands. Cla I for example hydrolyses the bond between two nucleotides in the sequence:



- 6.1 Give the base sequence of the complementary strand in the 5' - 3' direction and indicate with arrows the location where the hydrolysis by Cla I would occur.
- 6.2 How often on average will this sequence occur in one strand of DNA molecule of 10^5 base pairs? You can assume that the four bases occur equally often and that they randomly distribute in the two chains.



Taq I hydrolyses a long double strand DNA molecule into fragments which are on average 256 base pairs long. The 3' end of these fragments treated by cleavage turns out to be a thymine(T)- and the 5' end a cytosine(C) -end.

- 6.3 How long is the sequence recognized by Taq I?
- 6.4 Give the two possible base sequences (in the direction 5' - 3') which form the recognition pattern for Taq I (must obviously have some symmetry).

The DNA of a phage which occurs as a close circle contains only 5'-pApTpCpGpApT-3' sequence in each of the two strands. After treatment with ClaI equilibrium is established: circular DNA \rightleftharpoons linear DNA.

6.5 Give a schematic drawing of the circular and linear molecules. Indicate the bases adjacent to the cleaving site in both strands. Indicate also the 3' and 5' ends.

In Fig. 1 the percentage of linear DNA is given as a function of temperature, measured in a solution of 0.15 M NaCl buffered with citrate at pH = 6.5. With Taq I as cleavage enzyme, the same curve is obtained.

6.6 Is the reaction as written endothermic or exothermic? Explain your answer.

6.7 Show, considering the information given, which of the two base sequences of the answer to **6.4** is the correct one.

6.8 What would look the curve for Taq I like if the recognition pattern would have been the other possibility of d)?

A large DNA molecule is cut into fragments with the aid of Cla I. One fragment is isolated, purified and mixed in the ratio of 1:1 with phage DNA which was also cleaved with Cla I. Thereby recombinant molecules can be formed through the reaction:



6.9 Would the enthalpy of this reaction be positive, negative or about zero? Explain your answer.

6.10 Which combination of temperature, DNA concentration and ionic strength (high or low in each case) will give the maximum percentage of recombinant molecules?

SOLUTION

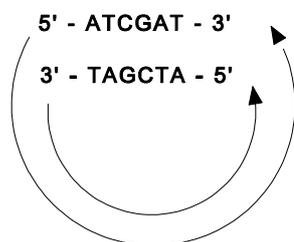
6.1 5' - pTpApGpCpT \pC

6.2 The probability of the sequence given is $(1/4)^6 = 1/4096$. Thus, this specific sequence may occur in the DNA $10^5/4096 = 24.4$ times on average

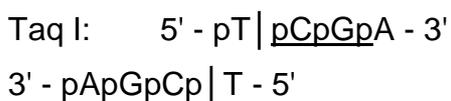
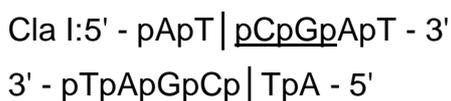
6.3 The sequence recognized by Taq I is 2 base pairs, that is 4 bases.

6.4 The sequence is 5' - pTpCpGpA - 3' or 5' - pGpApTpC - 3'

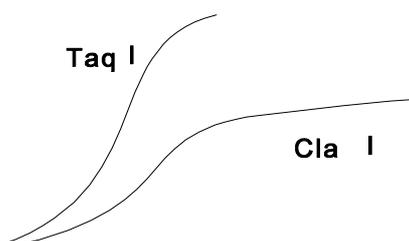
6.5



- 6.6** The reaction is endothermic. The reaction has a positive enthalpy, since the hydrogen bonds between the bases G and C in the complementary strands are broken.
- 6.7** The two relations show the same dependence on temperature. Therefore, the enthalpy of the two reactions is roughly the same. Then the interaction of the double helix must be identical and therefore we must choose TCGA for the first recognition sequence of question **6.4**. The cleavage in the two cases mentioned in d) occurs as follows:



- 6.8** The following curve would be obtained:

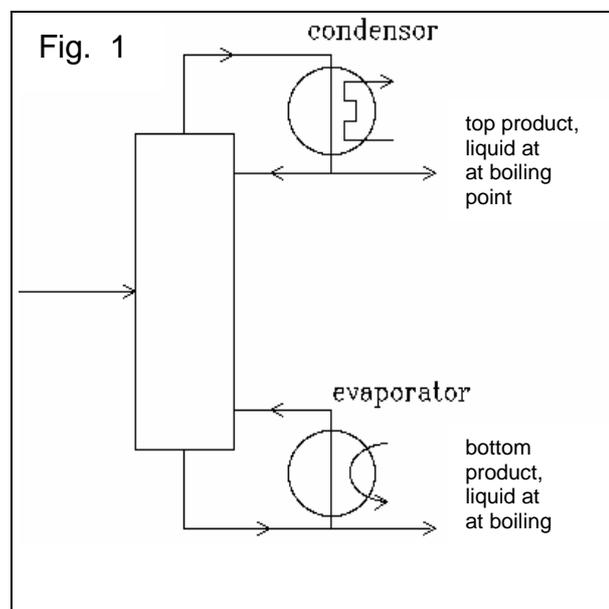


6.9 ΔH is negative.

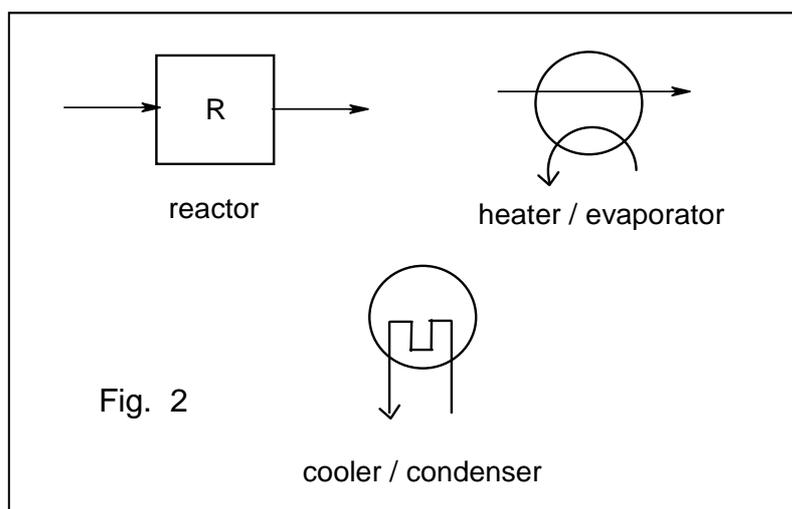
6.10 Low temperature, low DNA concentration and high ionic strength will give the maximum percentage of recombinant molecules.

PROBLEM 7

The equilibrium constant of the reaction $A_{(g)} + 2 B_{(g)} \rightleftharpoons 2 C_{(g)}$ is $K_p = 10.0 \text{ MPa}^{-1}$. The starting materials are supplied at 25 °C and heated to 100 °C where complete equilibration takes place. Below 100 °C the reaction rate is negligibly small. The whole process is executed continuously in a stationary state. The boiling points at 0.1 MPa of **A**, **B**, and **C** are 40 °C, 80 °C, and 60 °C, respectively. The three compounds have the same heat of evaporation: $q \text{ J mol}^{-1}$. The heat capacities of **A**, **B**, and **C** may be neglected. A schematic diagram of a distillation is shown below (Fig. 1).



The total heat used at each of the two distillations is $3q \text{ J mol}^{-1}$ (of the top product). Apart from distillation columns (each with its own evaporator and condenser) the pieces of apparatus shown of Fig. 2 are available.

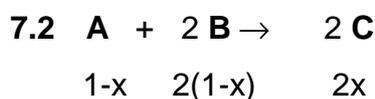
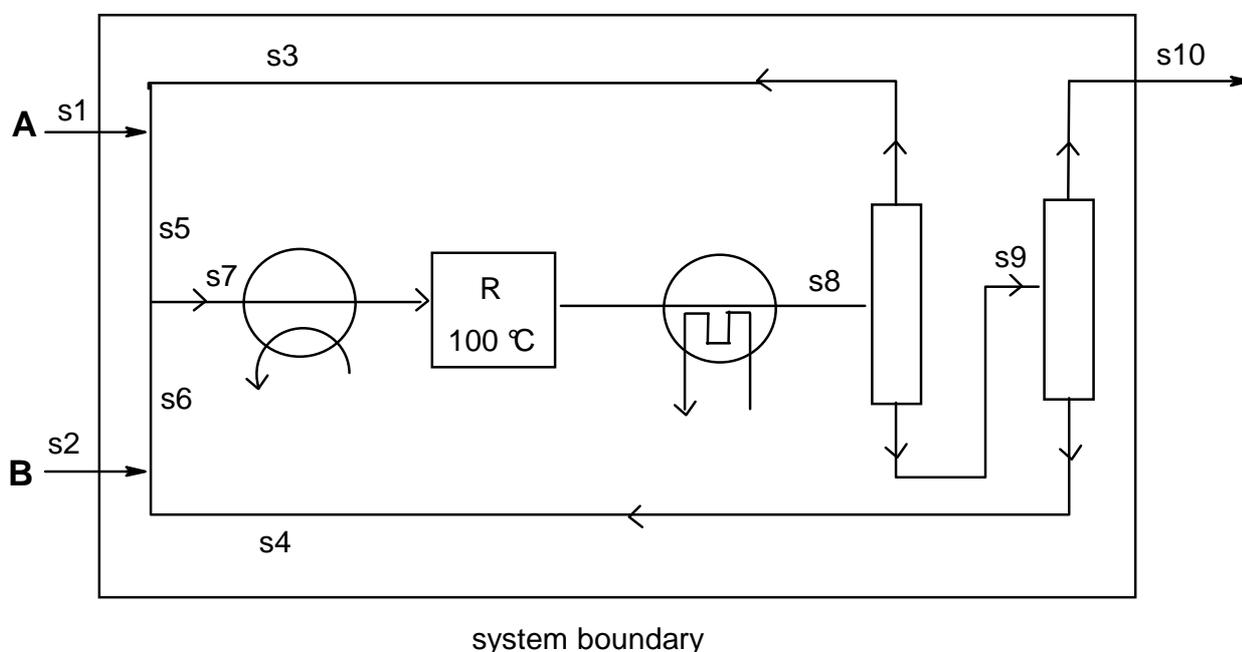


7.1 Draw a flow diagram of the process in which all flows are given (flow sheet) and in which the starting materials are used as efficiently as possible using as few pieces of apparatus as possible.

- 7.2 Express the equilibrium constant in terms of the degree of conversion and of total pressure for the case that the feed to the reactor is stoichiometric. What is the value of the degree of conversion when total pressure is 0.100 MPa?
- 7.3 Number all flows. Calculate the composition of each flow in mol s⁻¹ for a rate of production of 1 mole of **C** per second under the conditions of part b.
- 7.4 In what respect can the reaction conditions influence the composition of the mixture that leaves the reactor? (Refer to question b.)
- 7.5 The process requires energy. For the conditions of b explain where energy should be supplied in the flow diagram drawn in part a. Derive an expression for the total energy needed.

SOLUTION

- 7.1 In order to minimize the pieces of apparatus, the liquids A and B should evaporate together. For complete consumption of the starting materials, A and B are recirculated as feed for the reactor. The scheme of figure depicts the solution.



In total $3-x$ mol gases are present after conversion. Supposing that the input of **A** is a mol (S5) and the input of **B** b mol (S6) we can write for the equilibrium:

$$K_p = \frac{p_C^2}{p_A \times p_B^2} = 10.0$$

If x mol of **A** are converted, S8 contains $(a - x)$ mol of **A**, $(b - 2x)$ mol of **B** and $2x$ mol of **C**. Therefore S8 contains $(a - x) + (b - 2x) + 2x = (a + b - x)$ moles and we can write for the partial pressures of A and B:

$$p_A = \frac{a - x}{a + b - x} P \quad p_B = \frac{b - 2x}{a + b - x} P \quad p_C = \frac{2x}{a + b - x} P$$

Therefore the equilibrium can be written as

$$K_p = \frac{(2x)^2}{(a - x)(b - 2x)^2} \times \frac{a + b - x}{P} = 10$$

7.3 For $P = 0.10$ we obtain: $4x^2a + 4x^2b - 4x^3 = ab^2 - 4abx + 4ax^2 - xb^2 + 4x^2b - 4x^3$ and wherefrom:

$$0 = ab^2 - 4abx - xb^2 \text{ and since } b \neq 0: \quad 0 = ab - 4ax - bx$$

With a total inflow of 0.5 mol s^{-1} **A** (S1) and 1 mol s^{-1} **B** (S2), the amount of **C** leaving the reactor (S10) is 1 mol s^{-1} . So $2x = 1$ and $x = 0.5$. The relation between a and b can be written as: $a = b / (2b - 4)$. Since the feed is stoichiometric $a : b = 1 : 2$. This leads to $b = 3$ and $a = 1.5$.

All flows (mol/s) can be calculated now:

$$s_1 = 0.5 \text{ mol s}^{-1} \text{ A}$$

$$s_2 = 1 \text{ mol s}^{-1} \text{ B}$$

$$s_3 = 1.5 - 0.5 = 1 \text{ mol s}^{-1} \text{ A}$$

$$s_4 = 3 - 1 = 2 \text{ mol s}^{-1} \text{ B}$$

$$s_5 = a = 1.5 \text{ mol s}^{-1} \text{ A}$$

$$s_6 = b = 3 \text{ mol s}^{-1} \text{ B}$$

$$s_7 = 1.5 \text{ mol s}^{-1} \text{ A} + 3 \text{ mol s}^{-1} \text{ B}$$

$$s_8 = 1 \text{ mol s}^{-1} \text{ A} + 2 \text{ mol s}^{-1} \text{ B} + 1 \text{ mol s}^{-1} \text{ C}$$

$$s_{10} = 1 \text{ mol C}$$

$$s_{9_1} = 2 \text{ mol B} + 1 \text{ mol C}; \quad s_{9_2} = 1 \text{ mol A} + 1 \text{ mol C}$$

7.4 By increasing the pressure, the equilibrium is pushed towards the side with the smallest number of molecules that means to the right side. Another possibility is changing the ratio of the feed. i. e. $a : b$. According to $a = b / (2b - 4)$, b will be larger

if a decreases and vice versa. Because the net enthalpy change is 0, temperature has no effect.

7.5 Energy must be supplied for heating the evaporator and for the two distillation columns. The total energy consumed of the flow in scheme can be calculated as follows:

$$Q_1 = q \cdot S_7 + 3q \cdot S_3 + 3q \cdot S_{10} = 10.5 q$$

PRACTICAL PROBLEMS

Introduction:

The experimental assignment consists of the synthesis and subsequently, the analysis of amminenickel(II) chloride: $\text{NiCl}_x(\text{NH}_3)_y$.

The synthesis proceeds in three steps:

- Preparation of a solution of nickel nitrate from nickel and concentrated nitric acid (green solution), time required about 20 min.
- Preparation of amminenickel(II) nitrate (blue crystals)
- Preparation of amminenickel(II) chloride (blue-violet crystals)

The analysis encompasses the determination of the percentages of the three components (ammonia, nickel and chlorine) of the salt, according to the instructions given in 2.

PROBLEM 1 (practical)

Synthesis of the nickel(II) salt:

All work on the synthesis must be carried out in the fume hood. Use of (safety) glasses is obligatory. If necessary use other safety equipment, such as rubber gloves and pipetting balloons.

- Put a "dubbeltje" (Dutch coin of 10 c, containing 1.5 g of nickel), in a 100 ml conical flask (Erlenmeyer flask) and add 10 ml of concentrated nitric acid (65 %). Fit the flask with an "air cooled" condenser (no water) and heat the contents on a hot plate until a violent reaction occurs. Continue heating carefully until all metal is dissolved. Cool the green solution in an ice-water mixture.

Write in the report form the equation of the chemical reaction that has occurred.

- Add, under continuous cooling, in small portions 25 ml of ammonia solution (25 %) to the ice cold solution. As soon as about 15 ml has been added, salt crystals start to precipitate. Having added all ammonia solution, filter the cold solution through a sintered glass filtering crucible by applying a vacuum with an aspirator. Wash the crystals three times with small portions of a cold ammonia solution (25 %). Remove as much liquid as possible from the crystalline mass by maintaining the vacuum.

- c) Dissolve the moist crystalline mass in 10 ml of hydrochloric acid (18 %). Cool the blue solution in an ice-water mixture and then add slowly 30 ml of a solution of 30 g ammonium chloride in 100 ml of ammonia solution (25 %). This yields a blue-violet coloured crystalline mass. Cool the mixture and filter as in b). Wash with ammonia solution (25 %), then with ethanol and finally with diethyl ether. Leave the crystals on air until all ether has evaporated. Determine the mass of the dry product and record this on the report form.
-
-

PROBLEM 2 (practical)Analysis of the Nickel Salt:

For the analysis of the salt, only one sample solution is prepared. The determination of the components is achieved by titrating each time 25 ml of the sample solution in duplicate.

For the determination of the ammonia and chlorine content a back titration is carried out. For that purpose a certain amount of reagent is added in excess. The total amount of reagent, available for the sample, is determined by following the same procedure for 25 ml of a blank solution. This titration should not be carried out in duplicate.

Prepare the following solutions:

A) Sample solution:

Pipette 25.0 ml of 1.6 M nitric acid into a volumetric flask of 250 ml. Add a sample of about 1.2 g of the ammonienickel(II) chloride and dilute with water to a volume of 250 ml.

B) Blank solution:

Pipette 25.0 ml of the same 1.6 M nitric acid and dilute it with water to a volume of 250 ml.

Note:

- 1) For the chlorine determination use conical (Erlenmeyer) flasks with a ground glass stopper.
- 2) The nitric acid contains a small amount of hydrochloric acid. The total acid content is 1.6 M.

a) *Determination of the ammonia content*

Titrate the solutions with a standard solution of NaOH (about 0.1 M). Indicator: methylred, 0.1 % solution in ethanol.

Calculate the percentage of ammonia in the salt.

b) *Determination of the nickel content*

Add about 100 ml of water, 2 ml of ammonia solution (25 %) and 5 drops of murexide solution to the nickel solution, which now should have a yellow colour. Titrate the solution with a standard solution of EDTA (about 0.025 M) until a sharp colour change from yellow to violet is observed. Calculate the percentage of nickel in the salt.

c) *Determination of the chlorine content*

Execute the titration as quickly as possible after the addition of the reagent!

Add to each solution 25 ml of 0.1 M silver nitrate solution. Add about 5 ml of toluene, shake vigorously, add indicator and titrate with the standard solution of ammonium thiocyanate (-rhodanide, about 0.05 M) until a permanent colour change to red is observed. At the end of the titration, shake vigorously again. The red coloration should persist.

Indicator: 1 ml of a saturated solution of iron(III) sulphate.

Calculate the percentage of chlorine in the salt.

Data: Relative atomic masses: H = 1, Cl = 35.5, Ni = 58.7, N = 14.

Questions:

Calculate from the results obtained the molar ratio of the components to two decimal points and enter this on the report form in the format: Ni : Cl : NH₃ = 1.00 : x : y.

19th



5 theoretical problems
3 practical problems

THE NINETEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 6–15 JULY 1987, VESZPRÉM – BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

Treating waste water in a sewage plant, 45 % of its carbohydrate $(\text{CH}_2\text{O})_n$ is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is 16 m^3 per day ($25 \text{ }^\circ\text{C}$, 100 kPa).

- 1.1 What is the amount of carbohydrate remaining in the sludge measured in kg per day?
- 1.2 Using the heat of combustion of methane (-882 kJ mol^{-1}), calculate the amount of energy that can be produced by combustion of the methane formed per day.
- 1.3 Knowing that the concentration of the carbohydrate in the waste water is 250 mg dm^{-3} , calculate the daily amount of waste water processed in the plant in m^3 of water per day.

SOLUTION



For 16 m^3 of gases: $n(\text{gas}) = \frac{pV}{RT} = 646 \text{ mol}$ (55 %) with the rest (45 %) therefore

being in the sludge.

The amount in the sludge is $\frac{45}{55} \times 646 = 528 \text{ mol}$, that is 15.85 kg/day.

$$1.2 \quad n(\text{CH}_4) = \frac{5}{55} \times 646 = 58.71 \text{ mol}$$

$$\Delta H = -882 \times 58.71 = -5.178 \times 10^4 \text{ kJ/day}$$

1.3 The sum of CH₂O is $\frac{646}{0.55} = 1174$ mol. Since $250 \text{ mg dm}^{-3} = 0.25 \text{ kg m}^{-3}$, the daily

amount of water is: $V = \frac{1174 \times 30}{0.25 \times 10^3} = \underline{140.9 \text{ m}^3/\text{day}}$

PROBLEM 2

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 cm³ of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 cm³ and 20.0 cm³ of it are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 cm³. The pH at the end-point is 10.00.

Problems:

- 2.1 Calculate the percentage distribution by moles of all protonated H_nPO₄ⁿ⁻³ species at the end-point.
- 2.2 What is the stoichiometric formula of the salt?

The cumulative protonation constants are given by

$$\beta_n = \frac{[\text{H}_n\text{PO}_4^{n-3}]}{[\text{PO}_4^{3-}][\text{H}^+]^n}$$

where $\log\beta_1 = 11.70$; $\log\beta_2 = 18.6$; $\log\beta_3 = 20.6$.

The relative atomic masses are: Na = 23.0; P = 31.0; H = 1.0; O = 16.0.

SOLUTION

2.1 $[\text{H}_3\text{PO}_4] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{PO}_4^{3-}] = T_{\text{konst}}$; $[\text{H}^+] = 10^{-10} \text{ mol dm}^{-3}$

$$[\text{H}_3\text{PO}_4] = 1 \text{ mol dm}^{-3}$$

$$[\text{HPO}_4^{2-}] = \beta_1[\text{PO}_4^{3-}][\text{H}^+] = 1.25 \times 10^{10} \text{ mol dm}^{-3} = 97.97 \%$$

$$[\text{H}_2\text{PO}_4^-] = \beta_2[\text{PO}_4^{3-}][\text{H}^+]^2 = 1 \times 10^8 \text{ mol dm}^{-3} = 0.078 \%$$

$$[\text{PO}_4^{3-}] = (\beta_3[\text{H}^+]^3)^{-1} = 2.5 \times 10^9 \text{ mol dm}^{-3} = 1.955 \%$$

2.2 A general formula of the salt: $\text{Na}_{3-n}(\text{H}_n\text{PO}_4) \times m \text{ H}_2\text{O}$ ($n = 0, 1, 2$)

The titrated solution contains 100 mg (y mol) of the salt and 1.00 mmol of sulphuric acid. The reacted protons (in mmol) can be calculated using the results of a):

$$2 + (n - 0.9797 - 2 \times 0.00078) y = 2.653$$

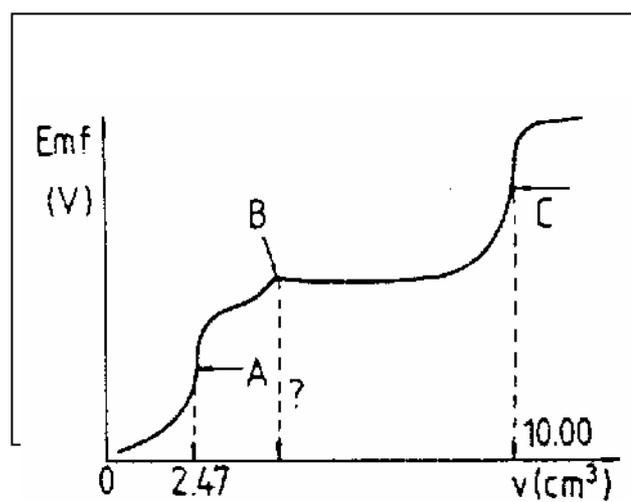
Since $y = 100/M$ (in mmol) but $M \geq 120 \text{ g mol}^{-1}$, the only real solution is $n = 2$.

Therefore $M = 156 \text{ g mol}^{-1}$, m is $(156-120)/18 = 2 \Rightarrow \underline{\text{NaH}_2\text{PO}_4 \cdot 2 \text{ H}_2\text{O}}$

PROBLEM 3

25.00 cm³ of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 °C using a silver electrode and a normal calomel half-cell with KNO₃ - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in cm³) is shown in Fig. 1.

Fig. 1



- 3.1 The end points of the reactions taking place during the titration, are marked with A, B and C. Write the balanced ionic equation for each reaction.
- 3.2 What volume of the titrant is required to reach point B?
- 3.3 Calculate the concentrations of KCl and KCN (in mol dm⁻³) in the sample solution.
- 3.4 Calculate the emf readings at the points A and C in volts.
- 3.5 What is the molar ratio Cl⁻/CN⁻ in the solution and in the precipitate at point C?

Data:

$$E^{\circ}(\text{Ag}^+/\text{Ag}) = 0.800 \text{ V}$$

$$E^{\circ}(\text{Calomel}) = 0.285 \text{ V}$$

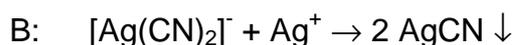
$$K_{sp}(\text{AgCN}) = 10^{-15.8}$$

$$K_{sp}(\text{AgCl}) = 10^{-9.75}$$

$$\beta_2 = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21.1}$$

SOLUTION

3.1 β_2 indicates that the complexation of Ag^+ with CN^- occurs easily. Thus A denotes the point where all Ag^+ is present in the complex form, having a higher potential than Ag^+ , B shows the point where the precipitation of AgCN starts, thus leading to a constant Ag^+ concentration until all CN^- is precipitated. Now at point C the precipitation of the more soluble AgCl begins:



3.2 $2 \times 2.47 \text{ cm}^3 = \underline{4.94 \text{ cm}^3}$

3.3 $[\text{CN}^-] = (4.94 \times 0.1 \times 40)/1000 \text{ mol dm}^{-3} = 1.98 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{Cl}^-] = ((10 - 4.94) \times 0.1 \times 40)/1000 \text{ mol dm}^{-3} = 2.02 \times 10^{-2} \text{ mol dm}^{-3}$

3.4 For the system Ag/Ag^+ at point A: $E = E_o + 0.059 \log[\text{Ag}^+]$.

The following equations are derived from the equilibrium conditions:

$$[\text{Ag}^+] = \frac{[\text{Ag}(\text{CN}^-)_2]}{[\text{CN}^-]^2 \beta_2}$$

$$[\text{Ag}^+] + [\text{Ag}(\text{CN}^-)_2] = \frac{2.47 \times 0.1}{25 + 2.47}$$

$$[\text{CN}^-] = 2 [\text{Ag}^+]$$

It yields an equation of third degree in $[\text{Ag}^+]$:

$$4\beta_2[\text{Ag}^+]^3 + [\text{Ag}(\text{CN}^-)_2] = 0$$

$[\text{Ag}(\text{CN}^-)_2]$ can be assumed to be $(2.47 \times 0.1) / 27.47 \text{ mol dm}^{-3}$, and therefore $[\text{Ag}^+]$ equals $1.213 \times 10^{-8} \text{ mol dm}^{-3}$.

The emf will be: $E = 0.8 + 0.059 \log[\text{Ag}^+] - 0.285 = \underline{0.048 \text{ V}}$

At point C: $[\text{Ag}^+] = \sqrt{K_{sp}(\text{AgCl})} = 1.333 \times 10^{-5}$ and

$$E = 0.8 + 0.059 \log[\text{Ag}^+] - 0.285 = \underline{0.227 \text{ V}}$$

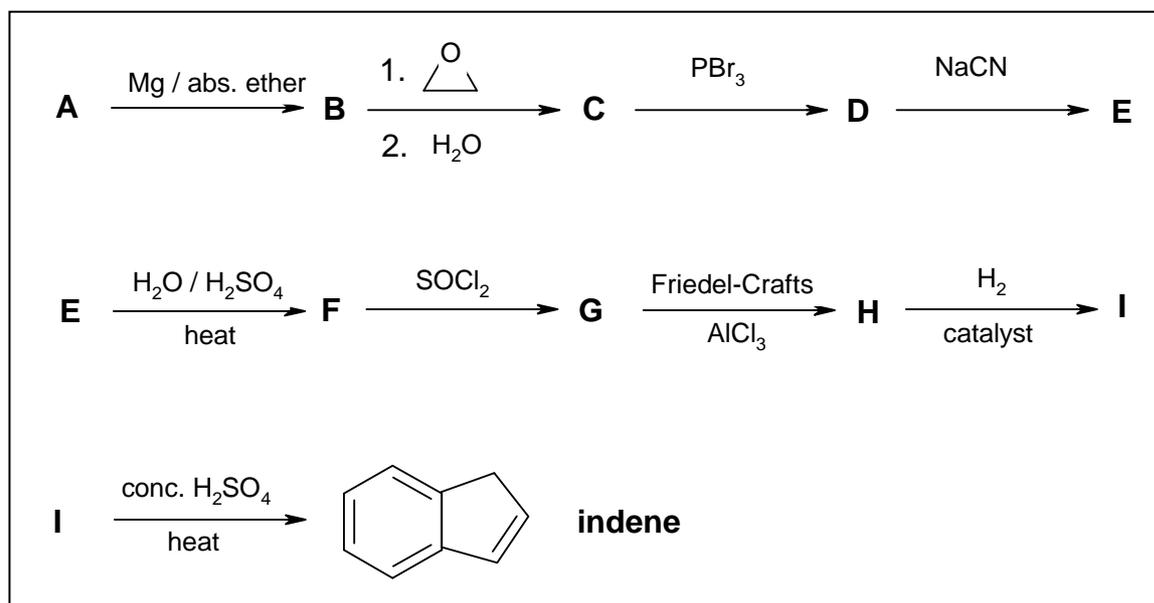
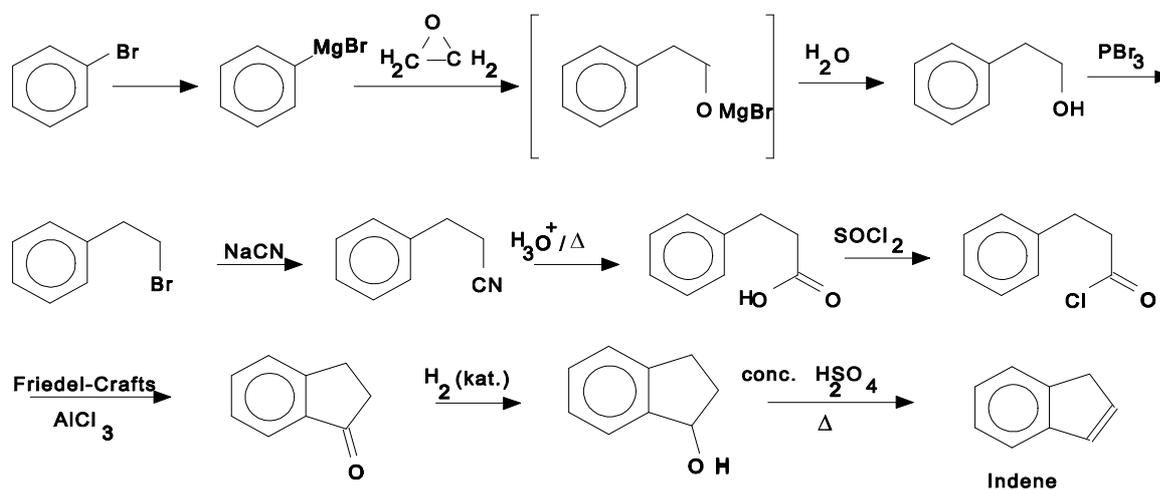
3.5 Since both AgCN and AgCl are present as the precipitate, the solution must be saturated:

$$\text{In the solution: } [\text{Cl}^-]/[\text{CN}^-] = K_{sp}(\text{AgCl})/K_{sp}(\text{AgCN}) = 10^{6.05} = \underline{1.222 \times 10^6}$$

$$\text{In the precipitate: } n(\text{AgCl}) / n(\text{AgCN}) = 2.02 / 1.98 = \underline{1.02}$$

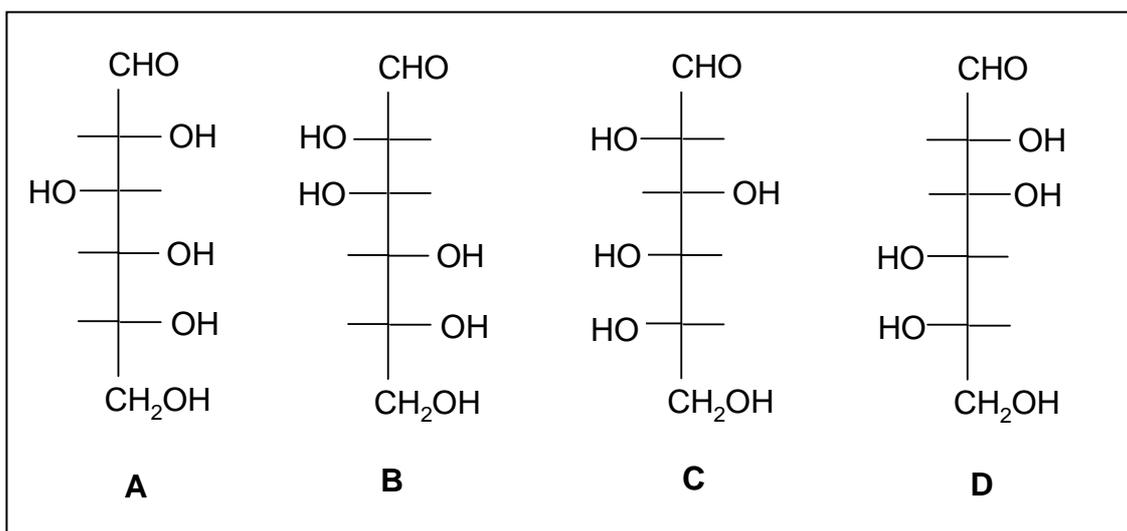
PROBLEM 4

Write the structural formulae of the compounds **A** to **I** in the following reaction sequence.

**SOLUTION**

PROBLEM 5

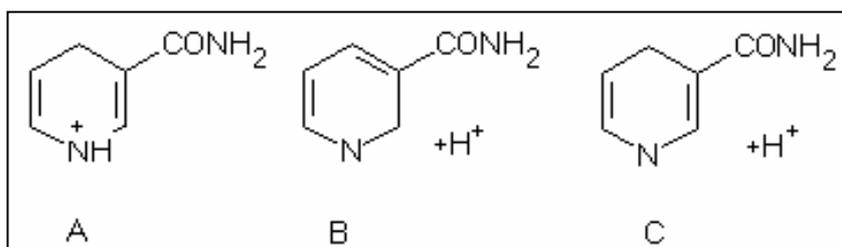
- 5.1** What ratio of primary / secondary / tertiary products can statistically be expected in the high temperature chlorination of methyl butane? Assume that the reaction rate of the substitution is equal for all C-H bonds.
- 5.2** Which of the following alcohols: pentan-1-ol, pentan-2-ol and 2-methyl-butan-2-ol react with the following reagents listed below?
1) cold, concentrated sulphuric acid; 2) $\text{CrO}_3 / \text{H}_2\text{SO}_4$; 3) $\text{ZnCl}_2 / \text{HCl}$; 4) I_2 / NaOH
- 5.3** Which of the following aldohexose structures are:
1) enantiomer pairs, 2) diastereomer pairs?



- 5.4** Two hydrocarbon compounds of the same molecular formula, C_4H_8 , easily react with hydrogen in the presence of a platinum catalyst. During ozonolysis only ethanal (acetaldehyde) is formed in both cases. The $^1\text{H-NMR}$ spectra of the two compounds show two types of protons in a ratio of 3 to 1. Draw the structures of the described compounds.
- 5.5** Select the components of the group listed below that can be obtained during complete hydrolysis of lecithin (a phospholipid): serine, phosphoric acid, sphingosine, choline, glycerol, myo-inositol, phosphatidic acid and fatty acids).
- 5.6** Which of the following carboxylic acid can be formed in the tricarboxylic acid cycle (Krebs' citric acid cycle):

maleic acid (cis-butenedioic acid), mandelic acid (α-hydroxy-phenylethanoic acid), malic acid (2-hydroxy-butanedioic acid), tricarb-allylic acid (propane-1,2,3-tricarboxylic acid), oxalacetic acid (2-oxo-butanedioic acid), keto-glutaric acid (2-oxo-pentanedioic acid), fumaric acid (trans-butenedioic acid) and acetoacetic acid (3-oxo-butanonic acid).

- 5.7 To which structures is the nicotinamide moiety (part) of NAD⁺ converted during the uptake of hydrogen to form NADH (A, B or C)?



SOLUTION

5.1 The ratio of primary, secondary and tertiary products will be 9 : 2 : 1.

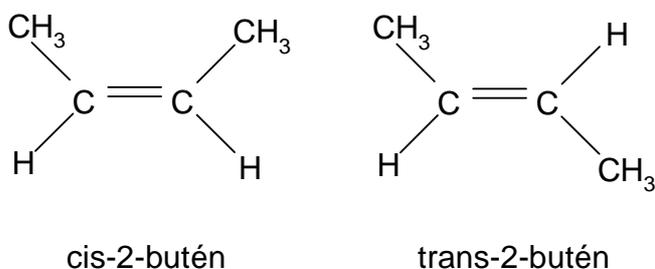
5.2 1-Pentanol reacts with 1) cold conc. sulphuric acid (elimination) and with 2) CrO₃/H₂SO₄ (oxidation).

2-Pentanol reacts with 1) under elimination, with 2) under oxidation, with 3) under reduction and with 4) (haloform oxidation).

2-Methyl-2-butanol reacts with 1) under elimination and with 3) under reduction.

5.3 a/c and b/d are enantiomers, a/b, a/d, b/c and c/d are diastereomers.

5.4



- 5.5** Glycerol, choline, phosphoric acid and fatty acids can be found during complete hydrolysis of lecithin.
- 5.6** maleic acid, oxalacetic acid, ketoglutaric acid, fumaric acid
- 5.7** c) is correct since the NAD^+ is converted into NADH/H^+
-
-

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

You are required to investigate seven inorganic compounds.

Your test-tube rack is numbered 1 to 9. Two of the positions are empty. Each of the seven test-tubes provided contains only one compound in aqueous solution. Using only these solutions, pH indicator paper, and test-tubes, you are to identify as many of the ions present as you are able.

For your information, record in the table the observations you make on mixing the solutions. Use the following symbols:

elimination reactions: ↓ precipitate; ↑ gaseous product;

↓_s precipitate soluble in the excess of a precipitating agent.

colours: w - white or colourless, b - blue, g - green, y - yellow, p - pink, r - red, br - brown.

pH: a - acidic, b - alkaline, n - neutral.

Equipment:

A home-made rack contained 9 test-tubes with the unknown solutions, 30 empty Wassermann-tubes and one small beaker containing the pH indicator paper. Into each solution a dropper was inserted, and thus, the test-tubes need not to be removed from the rack while handling them. According to the original plan the following nine unknown solutions were expected to be given to the participants: CoCl_2 , $\text{Fe}(\text{SCN})_3$, NH_4OH , KI , AgNO_3 , Na_2HAsO_4 , HgCl_2 , NiCl_2 , CuCl_2 .

During the discussion of the International Jury it became known that in some countries the corresponding laws forbid the pupils in secondary schools to handle mercury and arsenic compounds. For this reason these two compounds were removed from the rack and consequently the number of ions to be detected - and the marks available - were reduced to 12 (from the original 15). (Under these conditions the alkali and nitrate ions cannot be detected.)

The order of the test-tubes varied individually, but the first two contained invariably red solutions (CoCl_2 and $\text{Fe}(\text{SCN})_3$), while the last two were the green NiCl_2 and CuCl_2 symbolizing the Hungarian national colours, red-white-green.

SOLUTION

The ions of the remaining seven solutions can easily be identified by mutual reactions. Out of the 21 possible reactions, 12 are common positive reactions. Additional information is available from the colour of 4, and the smell of one solution.

AgNO₃: reacts with all the six compounds;

NH₃: with the exception of iodide it gives a characteristic reaction with all the others salts;

Fe(SCN)₃: its colour and reaction with NH₃, I⁻, Ag⁺ are characteristic;

CoCl₂: can be detected from its colour and by adding NH₃ or Ag⁺;

KI: can be identified by its reaction with Ag⁺ and from the evolution of I₂ due to an addition of Fe³⁺ or Cu²⁺;

CuCl₂: can be detected from its colour and reaction with NH₃, I⁻ and Ag⁺;

NiCl₂: has a characteristic colour and reacts with NH₃ and Ag⁺.

PROBLEM 2 (practical)

You are required to estimate the heat (enthalpy) change on mixing a series of 5 liquids to produce equimolar mixtures and to explain the temperature changes.

Procedure:

1. A mixture of trichloromethane (chloroform) and propanone (acetone)

Measure 0.5 mol of trichloromethane in the measuring cylinder labelled A₁ and measure its temperature. Dry the thermometer with a piece of tissue paper. Measure 0.5 mol of propanone using measuring cylinder B₁, pour it into a beaker and measure its temperature. Record the average of the two temperatures as temperature t_1 (to 0.1 °C). Leave the thermometer in the beaker. Add the trichloromethane to the propanone, stir the mixture carefully and follow the temperature changes until a maximum or minimum is reached. Record this extreme temperature as temperature t_2 . Dispose the mixture into a special bottle labelled "waste solution", dry the reaction beaker and the thermometer and proceed to the next part of the experiment.

2. A mixture of methanol and propanone (acetone)

Measure 0.5 mol of propanone in measuring cylinder B₁ and 0.5 mol of methanol in measuring cylinder A₂, and continue as in part 1.

3. A mixture of methanol and n-hexane

Measure 0.5 mol of methanol into measuring cylinder A₂ and 0.5 mol of hexane into measuring cylinder B₂, and continue as in part 1.

4. A mixture of methanol and water

Measure 0.5 mol of methanol into measuring cylinder A₂, measure its temperature and pour it into the beaker. Rinse the cylinder thoroughly with distilled water and then measure 0.5 mole of water using this measuring cylinder. Continue as instructed in the above part 1.

Tasks:

Calculate the enthalpy (heat) changes involved in the mixings on the basis of the temperature changes observed. In your calculations you should neglect heat exchanges with the surroundings as well as the heat capacity of the beaker and thermometer. Briefly explain your results in terms of the molecular interactions in the pure liquids and in the mixture, preferably using sketches.

Data:

Substance	Relative molecular mass	Density (g cm ⁻³)	Molar heat capacity (J K ⁻¹ mol ⁻¹)
methanol	32.04	0.79	80.61
chloroform	119.38	1.49	114.94
acetone	58.08	0.79	124.96
n-hexane	86.18	0.66	190.10
water	18.02	1.00	75.35

PROBLEM 3 (practical)

You are required to determine the concentrations of hydrochloric acid and potassium iodate in the diluted solution containing both.

Procedure:

A solution containing potassium iodate and hydrochloric acid has already been measured into the volumetric flask provided. Fill the flask to the mark with distilled water using the wash bottle, close it with a stopper and shake it thoroughly. Fill the burette with the standard sodium thiosulphate solution using one of the beakers provided. (The exact concentration of the thiosulphate is given on the label of the bottle.)

a) First titration

Pipette a 10.00 cm³ aliquot (portion) of the solution from the volumetric flask into a glass stoppered conical flask. Dilute it with 10 cm³ of distilled water, add 1 g (a small spatula end-full) of potassium iodide and acidify with 10 cm³ of 10 % sulphuric acid using a measuring cylinder. Titrate immediately the iodine formed with the standard sodium thiosulphate solution until the solution in the flask is pale yellow. Add with a pipette 1 cm³ of starch indicator solution and continue the titration to completion. Repeat the titration twice more and record your readings on the result sheet.

b) Second titration

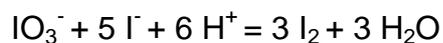
Pipette a 10.00 cm³ aliquot of the solution into another glass stoppered conical flask, dilute with 10 cm³ of distilled water, add 1 g of solid potassium iodide, and leave to stand for 10 minutes. Then titrate the iodine formed using the standard sodium thiosulphate solution, adding 1 cm³ of starch indicator solution when the mixture is pale yellow. Repeat the titration twice more, recording your readings on the result sheet.

Task:

Calculate the concentration of the HCl and the KIO₃ in the solution that you prepared by dilution (in mol dm⁻³).

SOLUTION

The reaction:



occurs to be quantitative both with respect to IO_3^- and H^+ . Consequently the first titration (in the presence of sulphuric acid) is suitable for the determination of iodate, while the second one for the determination of the hydrochloric acid content.

20th



6 theoretical problems
2 practical problems

THE TWENTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 2–9 JULY 1988, ESPOO, FINLAND

THEORETICAL PROBLEMS

PROBLEM 1

The periodic system of the elements in our three-dimensional world is based on the four electron quantum numbers $n = 1, 2, 3, \dots$; $l = 0, 1, \dots, n - 1$, $m = 0, \pm 1, \pm 2, \dots, \pm l$; and $s = \pm 1/2$. In Flatlandia, a two-dimensional world, the periodic system is thus based on three electron quantum numbers: $n = 1, 2, 3, \dots$; $m_l = 0, \pm 1, \pm 2, \dots, \pm (n-1)$; and $s = \pm 1/2$ where m_l plays the combined role of l and m_l of the three dimensional world. The following tasks relate to this two-dimensional world, where the chemical and physical experience obtained from our world is supposed to be still applicable.

- 1.1 Draw the first four periods of the Flatlandian periodic table of the elements. Number them according to their nuclear charge. Use the atomic numbers (Z) as symbols of the specific element. Write the electron configuration for each element.
- 1.2 Draw the hybrid orbitals of the elements with $n = 2$. Which element is the basis for the organic chemistry in Flatlandia? Find the Flatlandian analogous for ethane, ethene and cyclohexane. What kind of aromatic ring compounds are possible?
- 1.3 Which rules in Flatlandia correspond to the octet and the 18-electron rules in the three dimensional world?
- 1.4 Predict graphically the trends in the first ionization energies of the Flatlandian elements with $n = 2$. Show graphically how the electronegativities of the elements increase in the Flatlandian periodic table.
- 1.5 Draw the molecular orbital energy diagrams of the neutral homonuclear diatomic molecules of the elements with $n = 2$. Which of these molecules are stable in Flatlandia?
- 1.6 Consider simple binary compounds of the elements ($n = 2$) with $Z = 1$. Draw their Lewis structure, predict their geometries and propose analogues for them in the three dimensional world.

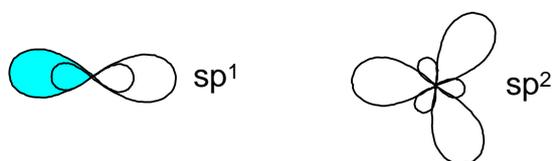
1.7 Consider elements with $n \leq 3$. Propose an analogue and write the chemical symbol from our world for each of these Flatlandian elements. On the basis of this chemical and physical analogue predict which two-dimensional elements are solid, liquid or gaseous at normal pressure and temperature.

SOLUTION

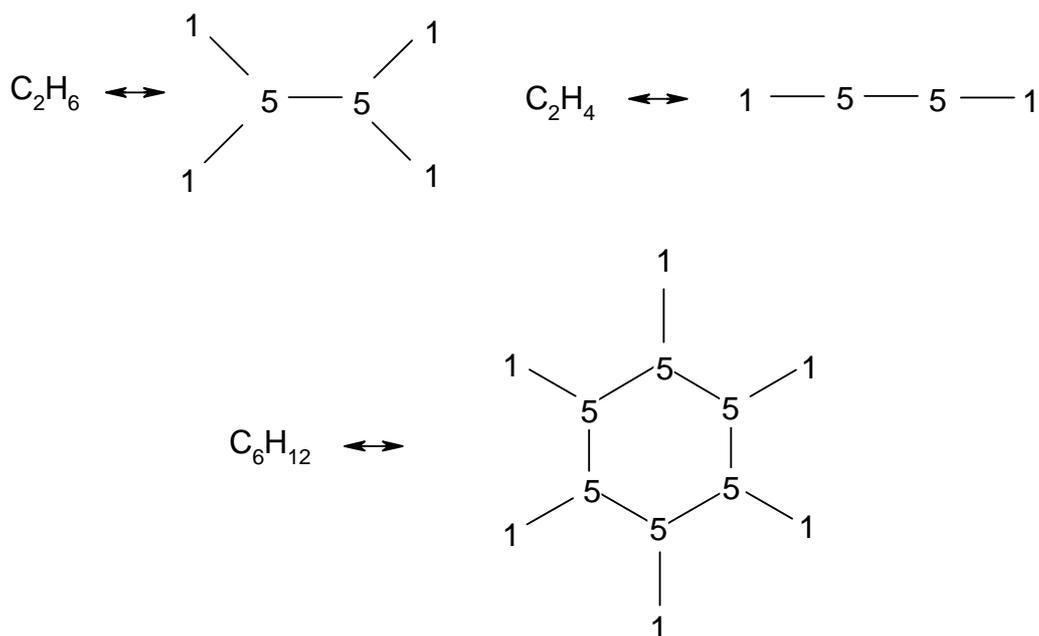
1.1 In the two dimensional world and the electron quantum numbers given, we obtain the following Flatlandian periodic table:

1 1s ¹								2 1s ²	
3 []2s ¹	4 []2s ²					5 []2s ² 2p ¹	6 []2s ² 2p ²	7 []2s ² 2p ³	8 []2s ² 2p ⁴
9 []3s ¹	10 []3s ²					11 []3s ² 3p ¹	12 []3s ² 3p ²	13 []3s ² 3p ³	14 []3s ² 3p ⁴
15 []4s ¹	16 []4s ²	17 []4s ² 3d ¹	18 []4s ² 3d ²	19 []4s ² 3d ³	20 []4s ² 3d ⁴	21 []4s ² 3d ⁴ 4p ¹	22 []4s ² 3d ⁴ 4p ²	23 []4s ² 3d ⁴ 4p ³	24 []4s ² 3d ⁴ 4p ⁴

1.2 sp^1 and sp^2 hybrid orbitals are possible:



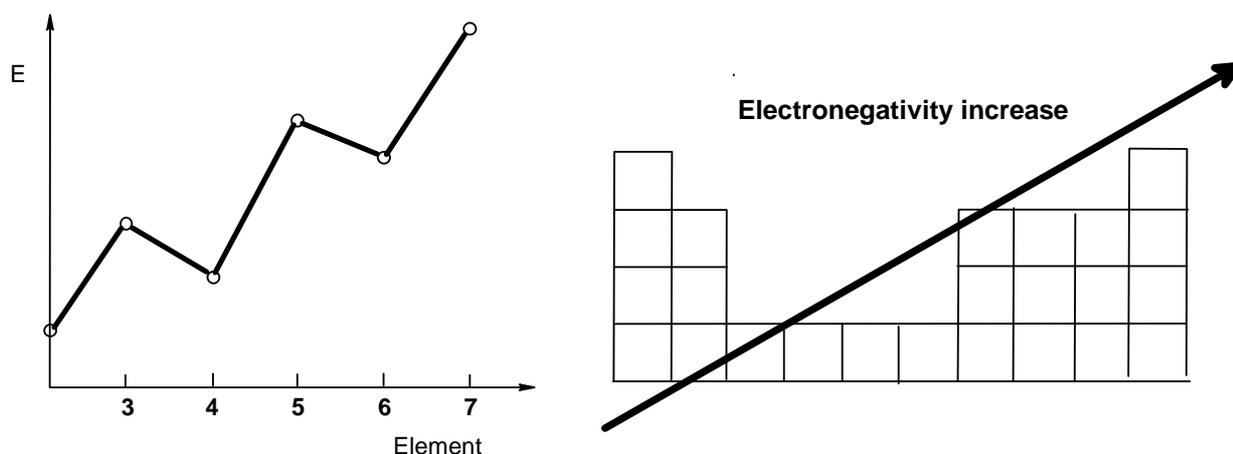
The element of life is the element with $Z = 5$. The corresponding compounds of ethane, ethene and cyclohexane are:



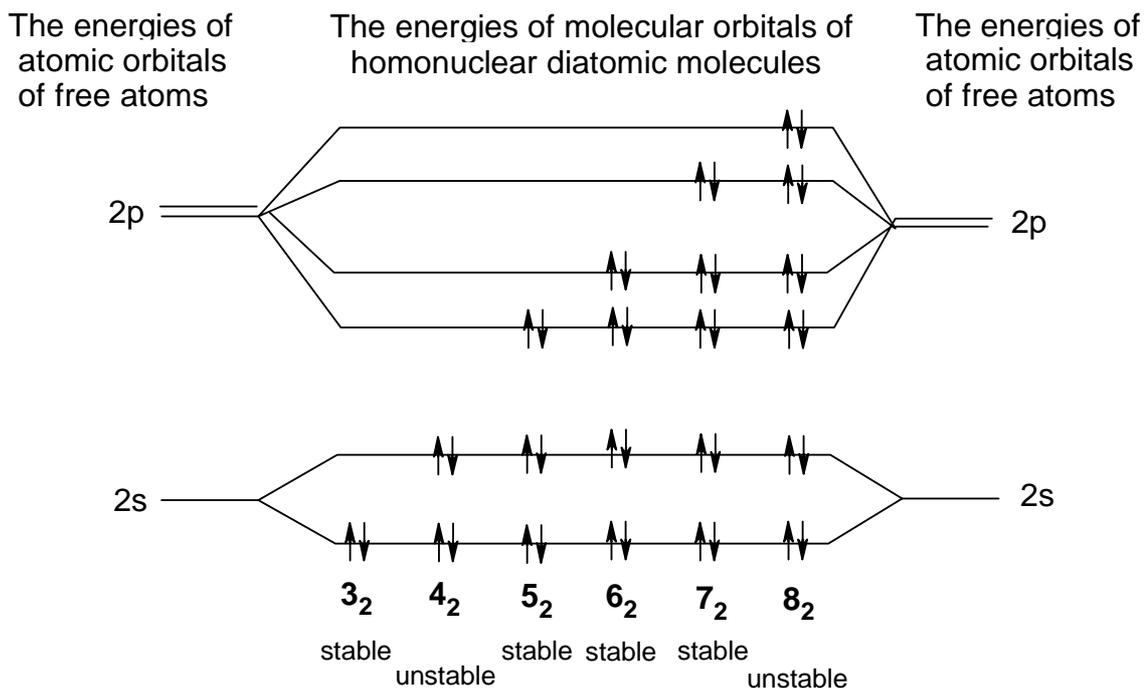
Aromatic ring compounds are not possible since there are no electron orbitals left that may overlap in the case of sp^2 .

1.3 The Octet rule is changed to a Sextet rule, the 18-electron rule corresponds to a 10-electron rule.

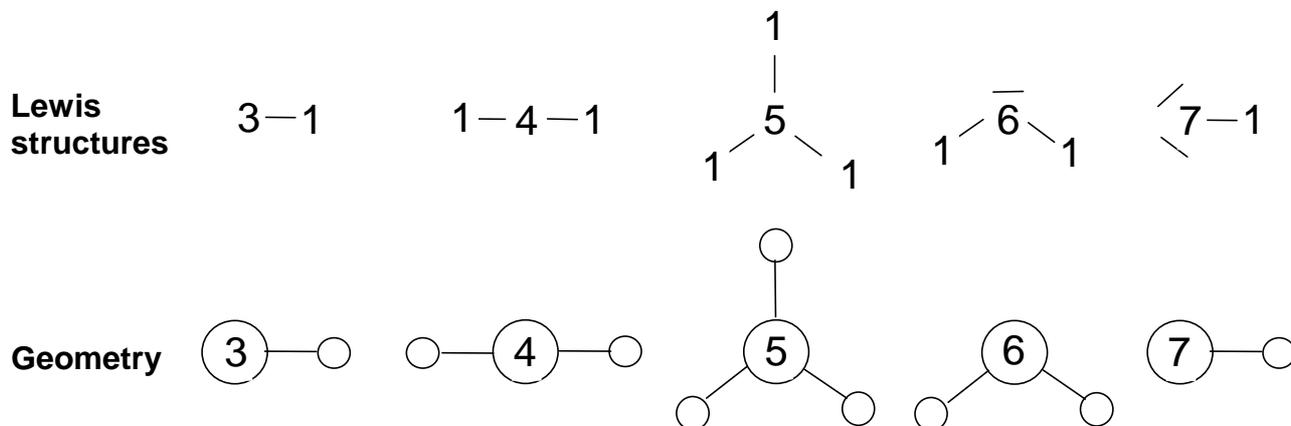
1.4 The ionization energies and the trends in electronegativity



1.5 The molecular orbital diagram of the homonuclear X_2 molecules:



1.6 The Lewis structures and geometries:

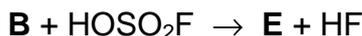


1.7 The three-dimensional analogues of Flatlandian elements are:

- | | | | |
|--------------|------------------|---------------------|-------------|
| 1: H, gas | 5: B or C, solid | 9: Na, solid | 13: Cl, gas |
| 2: He, gas | 6: N or O, gas | 10: Mg, solid | 14: Ar, gas |
| 3: Li, solid | 7: F, gas | 11: Al or Si, solid | |
| 4: Be, solid | 8: Ne, gas | 12: P or S, solid | |

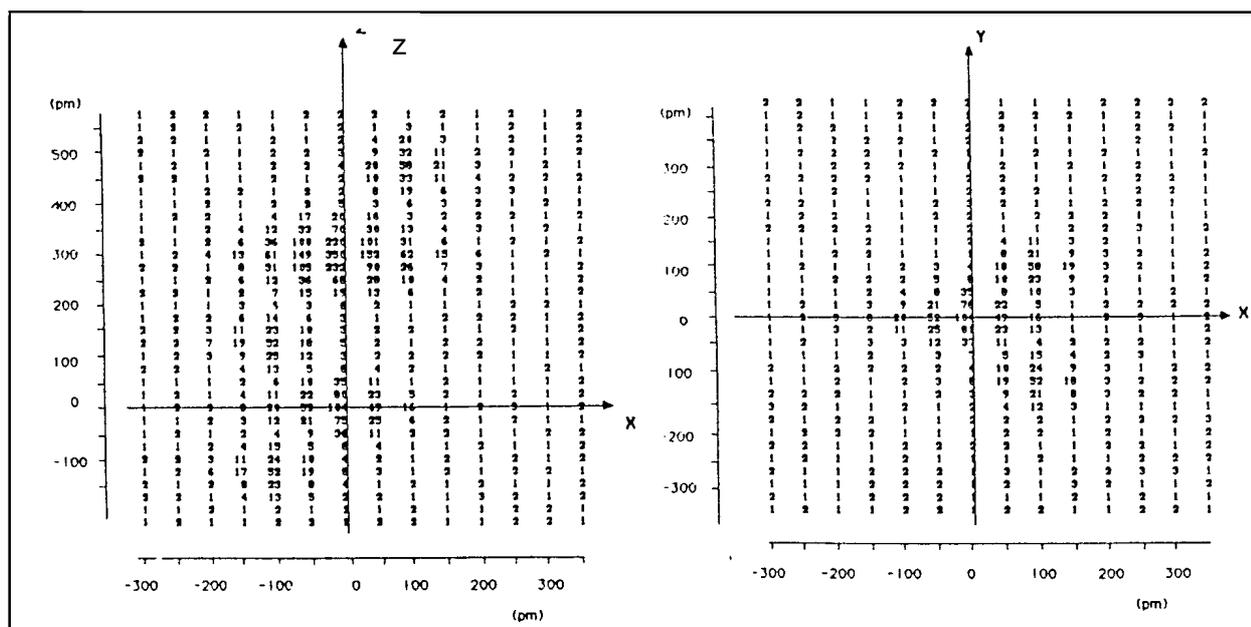
PROBLEM 2

Upon heating of a mixture of **A** and fluorine (molar ratio 1 : 9, pressure approximately 1 MPa) to 900 °C three compounds (**B**, **C** and **D**) are formed. All three products are crystalline solids at ambient temperature with melting points below 150 °C. The fluorine content of **C** is found to be 36.7 % and that of **D** 46.5 % (by weight). When **B** is treated with anhydrous HOSO₂F at -75 °C a compound **E** is formed:



E is a solid which is stable for weeks at 0 °C, but decomposes in days at room temperature. The electron density distribution of **E** obtained through X-ray diffraction studies is shown on two intersecting, mutually perpendicular planes (see Fig. 1).

Fig. 1



The numbers indicated on the maps relate to the electron density in the neighbourhood of the atoms of **E** as a function of the spatial coordinates. The maxima found in these maps coincide with the locations of the atoms and the values are approximately proportional to the number of electrons in the atom in question.

2.1 Show where the maxima lie by drawing the contour curves around the maxima, connecting points of equal electron densities. Label each maximum to show the identities of the atoms in **E**.

- 2.2** When 450.0 mg of **C** was treated with an excess of mercury, 53.25 ml of **A** was liberated at a pressure of 101.0 kPa and a temperature of 25 °C. Calculate the relative atomic mass of **A**.
- 2.3** Identify **A**, **B**, **C**, **D** and **E**.
- 2.4** Use the valence-shell electron-pair repulsion theory (VSEPR) to propose electron-pair geometries for **B** and **C**. Using the two electron density maps, sketch the molecular geometry of **E**.

The original mixture was hydrolysed in water. **B** reacts to **A** while liberating oxygen and producing aqueous hydrogen fluoride. Hydrolysis of **C** leads to **A** and oxygen (in molar ratio of 4 : 3) and yields an aqueous solution of AO_3 and hydrogen fluoride. **D** hydrolyses to an aqueous solution of AO_3 and hydrogen fluoride.

- 2.5** Write the equations for the three hydrolysis reactions.
- 2.6** Quantitative hydrolysis of a mixture of **B**, **C** and **D** gives 60.2 ml of gas (measured at 290 K and 100 kPa). The oxygen content of this gas is 40.0% (by volume). The amount of AO_3 dissolved in water is titrated with an aqueous 0.1 molar FeSO_4 solution and 36.0 ml used thereby. During the titration Fe^{2+} is oxidized to Fe^{3+} and AO_3 is reduced to **A**. Calculate the composition (% by moles) of the original mixture of **B**, **C** and **D**.

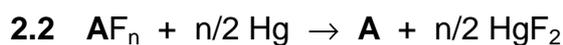
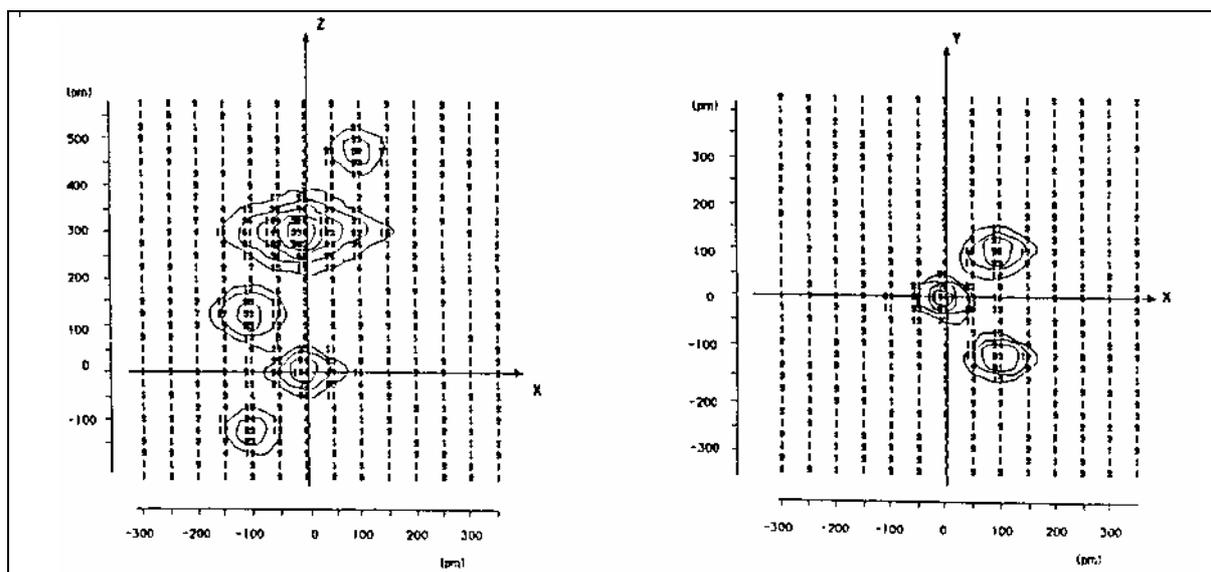
SOLUTION

- 2.1** Fig. 2 shows the electron densities with maxima 52, 58, 104, and 350. Since compound **E** is supposed to contain the atoms of fluorine, oxygen, sulphur, and **A**, the above maxima can be assign to particular atoms as follows:

Maximum	Element	Atomic number
52	O	8
58	F	9
104	S	16
350	A	?

The atomic number of **A** is 54. Thus, the element **A** is xenon.

Fig. 2



$$n_{\text{gas}} = \frac{pV}{RT} = \frac{101\,000 \text{ Pa} \times 53.25 \times 10^{-6} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 2.17 \times 10^{-3} \text{ mol} = n(\text{A}) = n(\text{AF}_n)$$

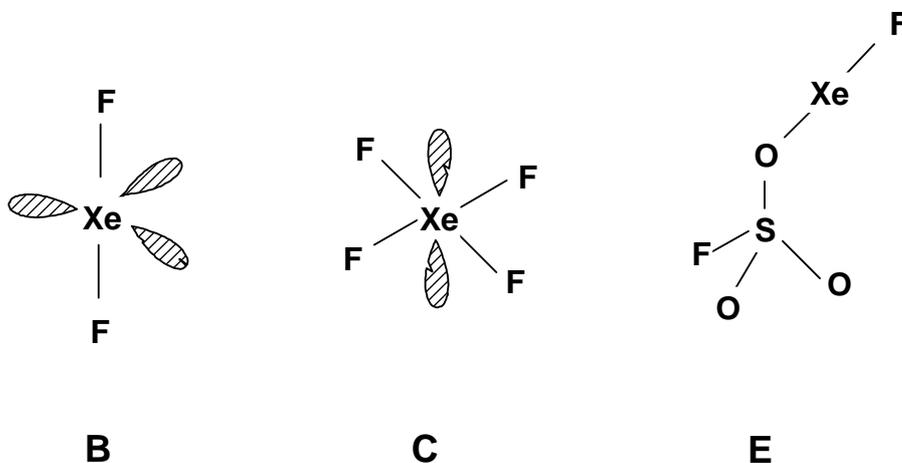
$$\underline{M(\text{AF}_n)} = \frac{0.45}{2.17 \times 10^{-3}} = \underline{207.4 \text{ g mol}^{-1}} = M(\text{A}) + n M(\text{F})$$

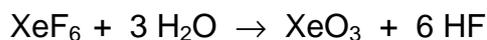
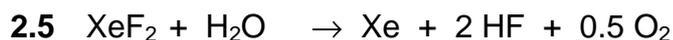
$$n M(\text{F}) = 0.367 M(\text{AF}_n) \Rightarrow n = \frac{207 \times 0.367}{19} = 4.0055 \Rightarrow \underline{\text{AF}_4};$$

$$\underline{M(\text{A})} = M(\text{AF}_n) - n M(\text{F}) = 207.4 - 76.1 = \underline{131.3 \text{ g mol}^{-1}}$$



2.4





2.6
$$n_{\text{gas}} = \frac{pV}{RT} = \frac{100\,000 \text{ Pa} \times 60.2 \times 10^{-6} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 290 \text{ K}} = 2.50 \times 10^{-3} \text{ mol}$$

$n(\text{O}_2) = 0.4 \times n_{\text{gas}} = 1.00 \times 10^{-3} \text{ mol}$

$n(\text{Xe}) = 1.50 \times 10^{-3} \text{ mol}$

Assume $n(\text{XeF}_2) = a$; $n(\text{XeF}_4) = b$; $n(\text{XeF}_6) = c$

$n(\text{Xe}) = a + 2/3 b$;

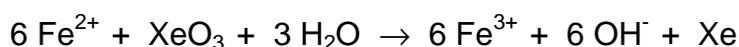
$n(\text{O}_2) = 1/2 a + 1/2 b$;

$n_{\text{gas}} = n(\text{Xe}) + n(\text{O}_2) = 3/2 a + 7/6 b = 2.50 \times 10^{-3} \text{ mol}$

$n(\text{O}_2) = 1/2 a + 1/2 b = 1.00 \times 10^{-3} \text{ mol}$

Solution of the equations:

$a = 0.5 \times 10^{-3} \text{ mol}$; $b = 1.5 \times 10^{-3} \text{ mol}$



$$n(\text{XeO}_3) = 1/6 n(\text{Fe}^{2+}) = 1/6 [c(\text{Fe}^{2+}) V(\text{Fe}^{2+})] = 1/6 \times 0.100 \times 36.0 \times 10^{-3} \text{ mol} =$$

$$= 6.00 \times 10^{-4} \text{ mol} = 1/3 b + c$$

$c = 0.6 \times 10^{-3} - 0.5 \times 10^{-3} = 1 \times 10^{-4}$

<u>molar composition:</u>	XeF_2 :	$0.5 \times 10^{-3} \text{ mol}$	(23.8 %)
	XeF_4 :	$1.5 \times 10^{-3} \text{ mol}$	(71.4 %)
	XeF_6 :	$1 \times 10^{-4} \text{ mol}$	(4.8 %)

PROBLEM 3

A typical family car has four cylinders with a total cylinder volume of 1600 cm³ and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4-trimethylpentane, C₈H₁₈. The compression ratio of the cylinder is 1:8.

- 3.1** Calculate the air intake of the engine (m³/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. Temperature of both incoming air and fuel are 100 °C. Air contains 21.0 % (by volume) of O₂ and 79.0 % of N₂. It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.
- 3.2** The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	ΔH_f (kJ/mol)	C_p (J/mol K)
O ₂ (g)	0.0	29.36
N ₂ (g)	0.0	29.13
CO(g)	-110.53	29.14
CO ₂ (g)	-395.51	37.11
H ₂ O(g)	-241.82	33.58
2,2,4-trimethylpentane	-187.82	

- 3.3** Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.
- 3.4** To convert CO(g) into CO₂(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4} k \left[\frac{n(\text{CO})}{n(\text{CO}_2)} \right]_1 v e^{-\frac{T}{T_0}}$$

where $[n(\text{CO}) / n(\text{CO}_2)]_1$ is the molar ratio before the catalyst, v is the flow rate in

mol/s and T the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases). T_0 is a reference temperature (373 K) and k is equal to 3.141 s/mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

SOLUTION

3.1 $M_r(\text{C}_8\text{H}_{18}) = 114.0$,

Cylinder volume (V_0) = $4.00 \times 10^{-4} \text{ m}^3$, $p_0 = 101\,000 \text{ Nm}^{-2}$, $T_0 = 373 \text{ K}$

Considering one cylinder during one burn cycle one obtains (f = fuel):

$$m_f = 0.400 / 25 \text{ g} = 0.0160 \text{ g}, \quad n_f = 1.4004 \times 10^{-4} \text{ mol}$$

(m_f = mass of fuel, n_f = amount of substance of fuel)

$$n_G = n_f + n_A = p_0 V_0 / (RT_0) = 0.0130 \text{ mol}$$

(n_G = number of moles of gases, n_A = moles of air)

$$\Rightarrow n_A = 0.0129 \text{ mol}$$

\Rightarrow Air intake of one cylinder during 25 burn cycles:

$$V_A = 25 n_A R T_0 / p_0 = 9.902 \times 10^{-3} \text{ m}^3/\text{s}$$

\Rightarrow The air intake of the whole engine is therefore: $V_{\text{total}} = 4 V_A = 0.0396 \text{ m}^3/\text{s}$

3.2 The composition of the exhaust gases of one cylinder during one burn cycle is considered:

before: $n_{\text{O}_2} = 0.21 n_A = 2.709 \text{ mmol}$

$$n_{\text{N}_2} = 0.79 n_A = 10.191 \text{ mmol}$$



Amounts of substances (in mol) before and after combustion:

	C_8H_{18}	O_2	CO	CO_2	H_2O
before	1.404×10^{-4}	2.709×10^{-3}	0	0	0
after	0	10.10×10^{-4}	1.123×10^{-4}	10.11×10^{-4}	12.63×10^{-4}

The composition of the gas after combustion is therefore:

Component	N ₂	O ₂	CO	CO ₂	H ₂ O	Total
mol × 10 ⁴	101.91	10.10	1.12	10.11	12.63	135.87
%	75.0	7.4	0.8	7.5	9.3	100

From thermodynamics the relation between the enthalpy and temperature change is given by

$$\Delta H = \int_{T_1}^{T_2} \sum_{i=1}^{i=k} c_{pi} n_i dT = \sum_{i=1}^{i=k} c_{pi} n_i (T_2 - T_1)$$

$$\Delta H = n_f [0.8 \Delta H_f(\text{CO}) + 7.2 \Delta H_f(\text{CO}_2) + 9 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_8\text{H}_{18})] = -0.6914 \text{ kJ}$$

This yields to: $691.4 = 0.4097 (T_2 - 373)$ and $T_2 = \underline{2060 \text{ }^\circ\text{C}}$

3.3 The final temperature of the leaving gases from one cylinder:

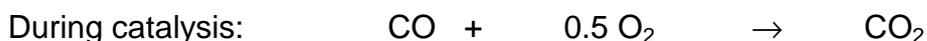
$$p_2 = 200\,000 \text{ Pa}, V_0 = 4.00 \times 10^{-4} \text{ m}^3,$$

$$n_G = \text{moles of exhaust gases in one cylinder} = 0.01359 \text{ mol}$$

$$T_2 = \frac{p_2 V_0}{n_G R} = \underline{708 \text{ K}}$$

3.4 The flow from all four cylinders is given: $v = 4 \times 25 \times n_G = 1.359 \text{ mol/s}$, so that

$$\frac{n(\text{CO})}{n(\text{CO}_2)_2} = 0.25 \times 3.141 \times \frac{1.12 \times 10^4}{10.11 \times 10^4} \times 1.359 \times e^{\frac{708}{373}} = 0.01772$$



moles × 10⁴ (4 cylinders):

initial	4.48	40.40	40.44
final	4.48 - x	40.40 - 0.5 x	40.44 + x

$$0.01772 (40.44 + x) = 4.48 + x \Rightarrow x = 3.70$$

Thus, the composition of the gas after the catalyst is:

Component	N ₂	O ₂	CO	CO ₂	H ₂ O	Total
mol × 10 ⁴	407.64	40.40 - 0.5x	4.48 - x	40.44 + x	50.52	541.63
		38.55	0.78	44.14		
%	75.26	7.12	0.15	8.14	9.33	100

PROBLEM 4

Chloride ions are analytically determined by precipitating them with silver nitrate. The precipitate is undergoing decomposition in presence of light and forms elemental silver and chlorine. In aqueous solution the latter disproportionates to chlorate(V) and chloride. With excess of silver ions, the chloride ions formed are precipitated whereas chlorate(V) ions are not.

- 4.1** Write the balanced equations of the reactions mentioned above.
- 4.2** The gravimetric determination yielded a precipitate of which 12 % by mass was decomposed by light. Determine the size and direction of the error caused by this decomposition.
- 4.3** Consider a solution containing two weak acids HA and HL, 0.020 molar and 0.010 molar solutions, respectively. The acid constants are 1×10^{-4} for HA and 1×10^{-7} for HL. Calculate the pH of the solution.
- 4.4** M forms a complex ML with the acid H₂L with the formation constant K_1 . The solution contains another metal ion N that forms a complex NHL with the acid H₂L. Determine the conditional equilibrium constant, K'_1 for the complex ML in terms of $[H^+]$ and K values.

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K'_1 = \frac{[ML]}{[M'] [L']}$$

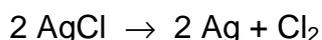
$[M']$ = total concentration of M not bound in ML

$[L']$ = the sum of the concentrations of all species containing L except ML

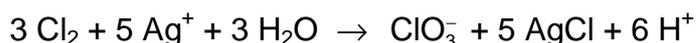
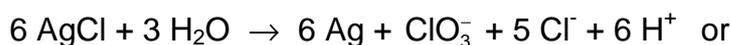
In addition to K_1 , the acid constants K_{a1} and K_{a2} of H₂L as well as the formation constant K_{NHL} of NHL are known.

$$K_{NHL} = \frac{[NHL]}{[N][L][H^+]}$$

You may assume that the equilibrium concentration $[H^+]$ and $[N]$ are known, too.

SOLUTION

Total:



4.2 From 100 g AgCl 12 g decompose and 88 g remain. 12 g equals 0.0837 mol and therefore, 0.04185 mol Cl₂ are liberated. Out of that $(12 \times 107.9) / 143.3 = 9.03$ g Ag remain in the precipitate. $5/6 \times 0.837$ mol AgCl are newly formed (= 10.0 g), so that the total mass of precipitate (A) yields:

$$A = 88 \text{ g} + 9.03 \text{ g} + 10.0 \text{ g} = \underline{107.03 \text{ g}}; \text{ relative error} = \underline{7.03 \%}$$



$$[\text{HA}] + [\text{A}^-] = 0.02 \text{ mol dm}^{-3} \quad \text{p}K(\text{HA}) = \text{pH} + \text{p}[\text{A}^-] - \text{p}[\text{HA}] = 4$$

$$[\text{HL}] + [\text{L}^-] = 0.01 \text{ mol dm}^{-3} \quad \text{p}K(\text{HL}) = \text{pH} + \text{p}[\text{L}^-] - \text{p}[\text{HL}] = 7$$

For problems like these, where no formal algebraic solution is found, only simplifications lead to a good approximation of the desired result, e.g.

1. $[\text{H}^+] = [\text{A}^-]$ (since HA is a much stronger acid than HL then $[\text{A}^-] \gg [\text{L}^-] + [\text{OH}^-]$)

$$[\text{H}^+]^2 + K_{(\text{HA})}[\text{H}^+] - K_{(\text{HA})}0.02 = 0$$

$$[\text{H}^+] = 1.365 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = \underline{2.865}$$

2. Linear combination of the equations

$$[\text{H}^+] = K_{(\text{HA})} \frac{[\text{HA}]}{[\text{A}^-]} = K_{(\text{HL})} \frac{[\text{HL}]}{[\text{L}^-]};$$

$$[\text{HA}] = 0.02 - [\text{A}^-];$$

$$[\text{HL}] = 0.01 - [\text{L}^-];$$

$$[\text{H}^+] = [\text{A}^-] + [\text{L}^-] + [\text{OH}^-]$$

yields:

$$[A] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}}$$

$$[L] = \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}}$$

$$[H^+] = \frac{0.02 \times K_{(HA)}}{[H^+] + K_{(HA)}} + \frac{0.01 \times K_{(HL)}}{[H^+] + K_{(HL)}} + \frac{K_w}{[H^+]}$$

The equation above can only be solved by numerical approximation methods. The result is $\text{pH} = 2.865$. We see that it is not necessary to consider all equations. Simplifications can be made here without loss of accuracy. Obviously it is quite difficult to see the effects of a simplification - but being aware of the fact that already the so-called exact solution is not really an exact one (e.g. activities are not being considered), simple assumption often lead to a very accurate result.

4.4

$$K_1 = \frac{[ML]}{[M]([L] + [HL] + [NHL] + [H_2L])} = \frac{K_1 [L]}{([L] + [HL] + [NHL] + [H_2L])}$$

$$[HL] = \frac{K_{a1} [H_2L]}{[H]}$$

$$[HL] = \frac{[L] [H]}{K_{a2}}$$

$$[L] = \frac{K_{a2} [HL]}{[H]} = \frac{K_{a1} K_{a2} [H_2L]}{[H]^2}$$

$$[NHL] = K_{NHL} [N] [L] [H]$$

$$K_1 = \frac{K_1}{\left[1 + \frac{[H]}{K_{a1}} + \frac{[H]^2}{K_{a1} K_{a2}} + K_{NHL} [N] [H] \right]}$$

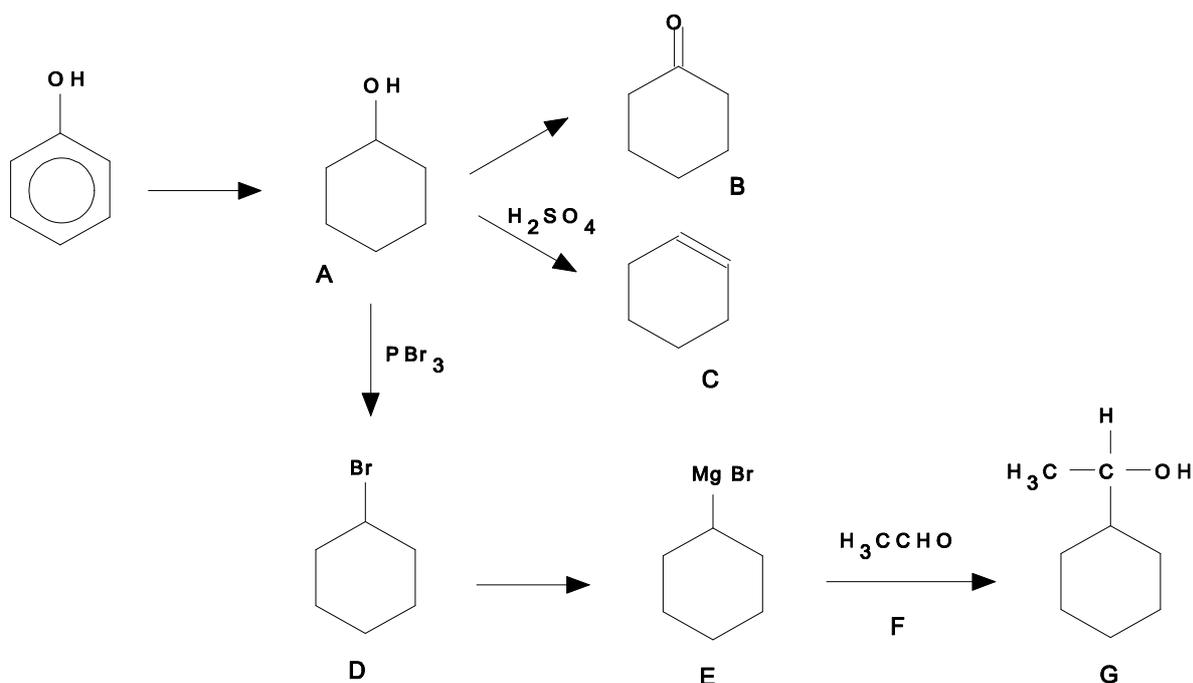
PROBLEM 5

A common compound **A** is prepared from phenol and oxidized to compound **B**. Dehydration of **A** with H_2SO_4 leads to compound **C** and treatment of **A** with PBr_3 gives **D**. In the mass spectrum of **D** there is a very strong peak at $m/e = 83$ (base peak) and two molecular ion peaks at $m/e = 162$ and 164 . The ratio of intensities of the peaks 162 and 164 is 1.02. Compound **D** can be converted to an organomagnesium compound **E** that reacts with a carbonyl compound **F** in dry ether to give **G** after hydrolysis. **G** is a secondary alcohol with the molecular formula $\text{C}_8\text{H}_{16}\text{O}$.

- 5.1 Outline all steps in the synthesis of **G** and draw the structural formulae of the compounds **A – G**.
- 5.2 Which of the products **A – G** consist of configurational stereoisomeric pairs?
- 5.3 Identify the three ions in the mass spectrum considering isotopic abundances given in the text.

SOLUTION

5.1

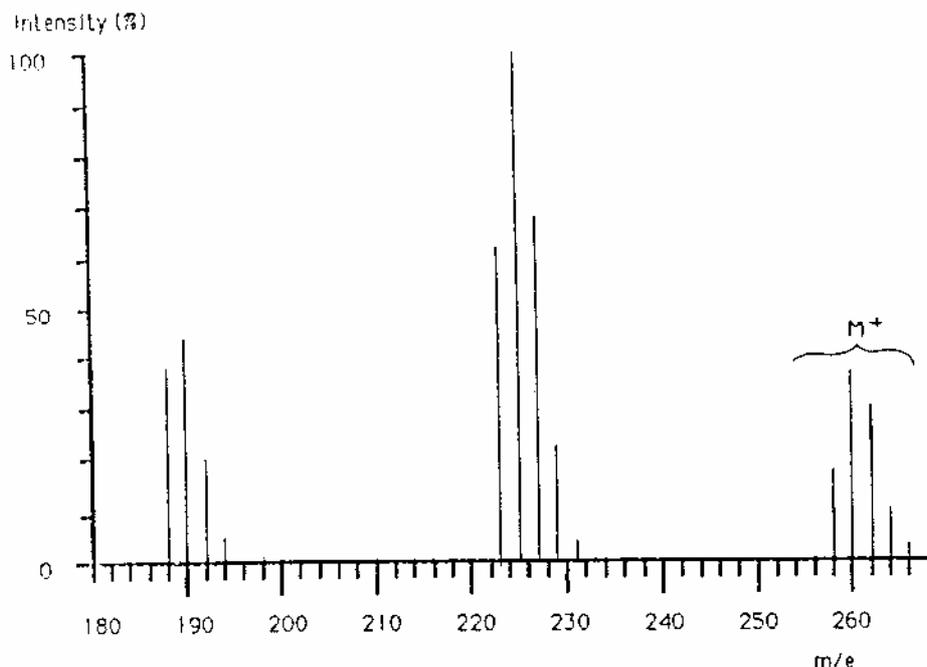


5.2 **G** has two stereoisomeric pairs since it has a chiral carbon.

5.3 The base peak at $m/e = 83$ is due to the cyclohexyl-cation, $C_6H_{11}^+$, the peaks at $m/e = 162$ and 164 show the same ratio as the abundance of the two bromine isotopes. Therefore, they are the molecular peaks of bromocyclohexane.

PROBLEM 6

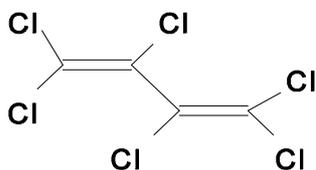
Upon analyzing sea mussels a new bio-accumulated pollutant **X** was found as determined by mass spectroscopy coupled to a gas chromatograph. The mass spectrum is illustrated in figure. Determine the structural formula of **X** assuming that it is produced out of synthetic rubber used as insulation in electrolysis cells that are used for the production of chlorine. Give the name of the compound **X**. The isotopic abundances of the pertinent elements are shown in the figure and table below. Intensities of the ions $m/e = 196, 233, 268$ and 270 are very low and thus omitted. Peaks of the ^{13}C containing ions are omitted for simplicity.



Element	Mass	Norm.abundanc	Mass	Norm.abundanc	Mass	Norm.abundanc
H	1	100.0	2	0.015		
C	12	100.0	13	1.1		
N	14	100.0	15	0.37		
O	16	100.0	17	0.04	18	0.20
P	31	100.0				
S	32	100.0	33	0.80	34	4.4
Cl	35	100.0			37	32.5
Br	79	100.0			81	98.0

SOLUTION

The molecule **X** is hexachlorobutadiene. Butadiene is the monomer of synthetic rubber and freed by decomposition:



PRACTICAL PROBLEMS**PROBLEM 1 (practical)**Synthesis of a derivative (NaHX) of the sodium salt of an organic acid*Apparatus:*

1 beaker (250 cm³), 2 beakers (50 cm³), 1 pipette (10 cm³; graduated at intervals of 0.1 cm³), 1 measuring cylinder (50 cm³), 1 capillary pipette (Pasteur pipette), 1 thermometer, 1 filter crucible (G4), apparatus for suction filtering, 1 glass rod.

Reagents:

Sodium salt of 1-naphtol-4-sulfonic acid (S), (sodium 1-naphtol-4-sulfonate), ($M = 246.22 \text{ g mol}^{-1}$), sodium nitrite ($M = 69.00 \text{ g mol}^{-1}$), aqueous solution of HCl (2 mol dm⁻³), deionised water, absolute ethanol.

Procedure:

Mix the given lot of technical grade starting material, labelled I, (contains 1.50 g of sodium 1-naphtol-4-sulfonate, S) and 0.6 g of NaNO₂ with about 10 cm³ of water in 50 cm³ beaker. Cool in ice bath (a 250 cm³ beaker) to the temperature 0 – 5 °C. Keeping the temperature in the 0 – 5 °C range, add dropwise 5 cm³ of 2 M HCl (aq) to the reaction mixture. Stir for ten more minutes in an ice bath to effect the complete precipitation of the yellow-orange salt NaHX · n H₂O. Weigh the filter crucible accurately (± 0.5 mg). Filter the product with suction in the crucible and wash with a small amount (ca. 5 cm³) of cold water and then twice (about 10 cm³) with ethanol. Dry the product in the filter crucible at 110 °C for 30 minutes. Weigh the air-cooled anhydrous material together with the crucible and present it to the supervisor.

Calculate the percentage yield of NaHX ($M = 275.20 \text{ g mol}^{-1}$).

The purity of the product NaHX influences your results in Problem 2!

Question:

Write the reaction equation using structural formulae.

PROBLEM 2 (practical)

The spectrophotometric determination of the concentration, acid constant K_{a2} and pK_{a2} of H_2X

Apparatus:

7 volumetric flasks (100 cm³), 2 beakers (50 cm³), 1 capillary pipette (Pasteur), 1 pipette (10 cm³; graduated in intervals of 0.1 cm³), 1 washing bottle, 1 glass rod, 1 container for waste materials, funnel.

Reagents:

Compound NaHX, aqueous stock solution of Na₂X (0.00100 mol dm⁻³), aqueous solution of sodium perchlorate (1.00 mol dm⁻³), aqueous solution of HCl (0.1 mol dm⁻³), aqueous solution of NaOH (0.1 mol dm⁻³).

Procedure:

- a) Weigh accurately 183.5 ± 0.5 mg of NaHX and dissolve it in water in a volumetric flask and dilute up to the 100 cm³ mark. Pipette 15.0 cm³ of this solution into another 100 cm³ volumetric flask and fill up to the mark with water to obtain the stock solution of NaHX. If you do not use your own material, you will get the NaHX from the service desk.
- b) Prepare 5 solutions, numbered 1-5, in the remaining five 100 cm³ volumetric flasks. These solutions have to fulfil the following requirements:
 - The total concentration of ($[X^{2-}] + [HX^-]$) in each solution must be exactly 0.000100 mol dm⁻³.
 - The concentration of sodium perchlorate in each solution must be 0.100 mol dm⁻³ to maintain constant ionic strength. The solutions are prepared by pipetting into each volumetric flask 1-5 the accurate volumes of the NaHX and Na₂X stock solutions, adding a required volume of sodium perchlorate solution and filling up to the mark with water.
 - Solution 1 is prepared by pipetting the required amount of the stock solution of NaHX. Add ca. 3 cm³ of HCl (aq) with the pipette to ensure that the anion is completely in the form HX^- , before adding the sodium perchlorate solution.

- Solution 5 is prepared by pipetting the required amount of the stock solution of Na₂X which is provided for you. Add ca. 3 cm³ of the NaOH(aq) to ensure that the anion is completely in the form X²⁻, before adding the sodium perchlorate solution.
- The three remaining solutions 2-4 are prepared by pipetting the stock solutions of NaHX and Na₂X in the following ratios before adding the sodium perchlorate solution:

Solution No.	Ratio NaHX(aq) : Na ₂ X(aq)
2	7 : 3
3	1 : 1
4	3 : 7

- c) Take the five volumetric flasks to the service centre where their UV-vis spectra will be recorded in the region 300-500 nm for you. In another service centre the accurate pH of each solution will be recorded. You may observe the measurements.
- d) From the plot of absorbance vs. wavelength, select the wavelength most appropriate for the determination of pK_{a2} of H₂X, and measure the corresponding absorbance of each solution.
- e) Calculate the pK_{a2} of H₂X from the pH-absorbance data when the ionic strength $I = 0.1$ and the temperature is assumed to be ambient (25 °C). Note that:

$$K_{a2} = \frac{[H^+][X^-]}{[HX^-]} = \frac{c_{H^+} \times c_{X^{2-}}}{c_{HX^-}}$$

$$K_{a2} = \frac{(A - A_{HX^-})[H^+]}{(A_{X^{2-}} - A)} \quad \text{or} \quad A = A_{X^{2-}} - (A - A_{HX^-}) \frac{[H^+]}{K_{a2}}$$

$$pf_{H^+} = \frac{0.509 \times \sqrt{I}}{1 + \sqrt{I}}$$

- f) Which of your prepared solutions shows the largest buffer capacity? Calculate this buffer capacity, P , by any suitable method. You may use the equations given:

$$P = 2.3 \times \left([OH^-] + [H^+] + \frac{K_a [H^+] C}{(K_a + [H^+])^2} \right)$$

$$P = 2.3 \times \left(\frac{K_w}{[H^+]} + [H^+] + \frac{[X^{2-}][HX^-]}{C} \right)$$

C is the total concentration of the acid.

$K_w = 2.0 \times 10^{-14}$ at $I = 0.1$ and $25\text{ }^\circ\text{C}$.

21st



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE TWENTY-FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 2–10 JULY 1989, HALLE, GERMAN DEMOCRATIC REPUBLIC

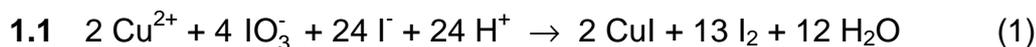
THEORETICAL PROBLEMS

PROBLEM 1

To determine the solubility product of copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, by iodometric titration in an acidic solution (25 °C) 30.00 cm³ of a 0.100 molar sodium thiosulphate solution are needed to titrate 20.00 cm³ of a saturated aqueous solution $\text{Cu}(\text{IO}_3)_2$.

- 1.1 Write the sequence of balanced equations for the above described reactions.
- 1.2 Calculate the initial concentration of Cu^{2+} and the solubility product of copper(II) iodate. Activity coefficients can be neglected.

SOLUTION



- 1.2 From (2):

$$n(\text{S}_2\text{O}_3^{2-}) = c V = 0,100 \text{ mol dm}^{-3} \times 0,03000 \text{ dm}^3 = 3,00 \times 10^{-3} \text{ mol}$$

From (2) and (1):

$$n(\text{I}_2) = 1,50 \times 10^{-3} \text{ mol}$$

$$n(\text{Cu}^{2+}) = \frac{1,50 \times 10^{-3} \text{ mol}}{13} \times 2 = 2,31 \times 10^{-4} \text{ mol}$$

$$c(\text{Cu}^{2+}) = \frac{2,31 \times 10^{-4} \text{ mol}}{0,02000 \text{ dm}^3} = 1,15 \times 10^{-2} \text{ mol}$$

$$[\text{Cu}^{2+}] = 1,15 \times 10^{-2}$$

$$[\text{IO}_3^-] = 2 [\text{Cu}^{2+}]$$

$$K_{sp} = [\text{Cu}^{2+}] [\text{IO}_3^-]^2 = 4 [\text{Cu}^{2+}]^3 = 4 \times (1.15 \times 10^{-2})^3 = 6.08 \times 10^{-6}$$

PROBLEM 2

A mixture of gases containing mainly carbon monoxide and hydrogen is produced by the reaction of alkanes with steam:



2.1 Using equations (1) and (2) write down an overall reaction (3) so that the net enthalpy change is zero.

2.2 The synthesis of methanol from carbon monoxide and hydrogen is carried out either

a) in two steps, where the starting mixture corresponding to equation (3) is compressed from 0.1×10^6 Pa to 3×10^6 Pa, and the mixture of products thereof compressed again from 3×10^6 Pa to 6×10^6 Pa

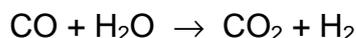
or

b) in one step, where the mixture of products corresponding to equation (3) is compressed from 0.1×10^6 Pa to 6×10^6 Pa.

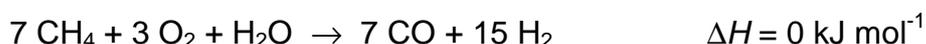
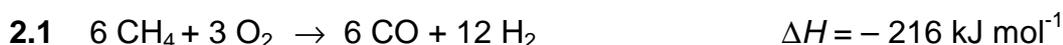
Calculate the work of compression, W_a , according to the two step reaction for 100 cm^3 of starting mixture and calculate the difference in the work of compression between the reactions 1 and 2.

Assume for calculations a complete reaction at constant pressure. Temperature remains constant at 500 K, ideal gas behaviour is assumed.

To produce hydrogen for the synthesis of ammonia, a mixture of 40.0 mol CO and 40.0 mol of hydrogen, 18.0 mol of carbon dioxide and 2.0 mol of nitrogen are in contact with 200.0 mol of steam in a reactor where the conversion equilibrium is established.



2.3 Calculate the number of moles of each gas leaving the reactor.

SOLUTION

- a) For a pressure increase in two steps under the conditions given, the work of compression is:

$$W_2 = n_1 RT \ln \frac{p_1}{p_2} + n_2 RT \ln \frac{p_2}{p_1} = n_1 RT \left(\ln \frac{p_1}{p_0} + 2 \ln \frac{p_2}{p_1} \right)$$

$$= 100 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K} \times \left(\ln \frac{3.0 \text{ MPa}}{0.1 \text{ MPa}} + 2 \ln \frac{6.0 \text{ MPa}}{3.0 \text{ MPa}} \right) = 1.99 \text{ MJ}$$

- b) For a pressure increase in one step the work of compression only depends on n_2 , p_2 and p_0 :

$$W_1 = n_2 RT \ln \frac{p_2}{p_0} = 100 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K} \times \ln \frac{6.0 \text{ MPa}}{0.1 \text{ MPa}} = 3.40 \text{ MJ}$$

It means

$$\Delta W = W_1 - W_2 = \underline{1.41 \text{ MJ}}$$

2.3 With $K = 3.3$, the following equilibrium is valid:

$$K = \frac{n_{\text{CO}_2} \times n_{\text{H}_2}}{n_{\text{CO}} \times n_{\text{H}_2\text{O}}} = \frac{(18 + x)(40 + x)}{(40 - x)(200 - x)}$$

$$x_{1/2} = 184 \pm 151.6; \quad x_1 = 33.2; \quad x_2 = 336.4$$

The composition of the leaving gas is:

6.8 mol CO, 51.2 mol CO₂, 2.0 mol CH₄ and N₂, 73.2 mol H₂ and 166.8 mol H₂O.

PROBLEM 3

Sulphur dioxide is removed from waste gases of coal power stations by washing with aqueous suspensions of calcium carbonate or calcium hydroxide. The residue formed is recovered.

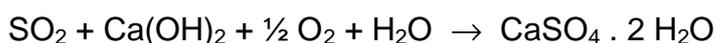
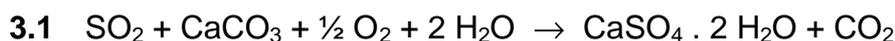
- 3.1** Write all reactions as balanced equations.
- 3.2** How many kilograms of calcium carbonate are daily consumed to remove 95 % of the sulphur dioxide if 10000 m³/h of waste gas (corrected to 0 °C and standard pressure) containing 0.15 % sulphur dioxide by volume are processed? How many kilograms of gypsum are recovered thereby?
- 3.3** Assuming that the sulphur dioxide is not being removed and equally spread in an atmospheric liquid water pool of 5000 m³ and fully returned on earth as rain, what is the expected pH of the condensed water?
- 3.4** If a sodium sulphite solution is used for absorption, sulphur dioxide and the sulphite solution can be recovered. Write down the balanced equations and point out possible pathways to increase the recovery of sulphur dioxide from an aqueous solution.

Note:

Protolysis of sulphur dioxide in aqueous solutions can be described by the first step dissociation of sulphurous acid. The dissociation constant $K_{a,1}(\text{H}_2\text{SO}_3) = 10^{-2.25}$.

Assume ideal gases and a constant temperature of 0 °C at standard pressure.

$M(\text{CaCO}_3) = 100 \text{ g mol}^{-1}$; $M(\text{CaSO}_4) = 172 \text{ g mol}^{-1}$.

SOLUTION

3.2 Under given conditions:

$$n(\text{SO}_2)/\text{h} = v(\text{SO}_2/\text{h}) / V = 669.34 \text{ mol h}^{-1}$$

$$m(\text{CaCO}_3/\text{d}) = n(\text{SO}_2/\text{h}) \times M(\text{CaCO}_3) \times 24 \text{ h} \cdot \text{d}^{-1} \times 0.95 = 1.53 \times 10^3 \text{ kg/d}$$

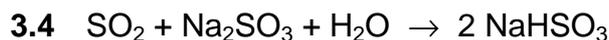
$$m(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}) = \frac{M(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O})}{M(\text{CaCO}_3)} \times m(\text{CaCO}_3) / d = 2.63 \times 10^3 \text{ kg/d}$$

$$3.3 \quad pH = -\log[\text{H}_3\text{O}^+]; \quad K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{SO}_2] - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+]_{1/2} = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_a [\text{SO}_2]}$$

Solving for $[\text{H}_3\text{O}^+]$:

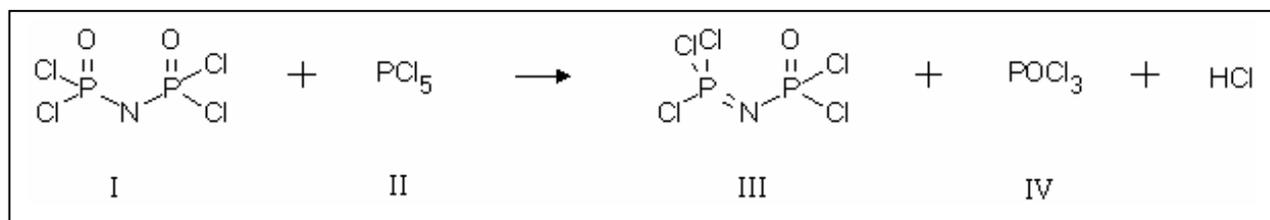
If $[\text{SO}_2] = n(\text{SO}_2) / V = 1.34 \times 10^{-4}$ and $K_a = 1 \times 10^{-2.25}$, then $[\text{H}_3\text{O}^+] = 1.32 \times 10^{-4}$ and $pH = 3.88$



Possibilities to increase the recovery of SO_2 are: temperature rise, reduced pressure, lower pH -value.

PROBLEM 4

³²P labelled phosphorus pentachloride (half-life $t_{1/2} = 14.3$ days) is used to study the electrophilic attack of a PCl_4^+ cation on nitrogen or on oxygen.



The reaction is carried out in CCl_4 and the solvent and product **IV** distilled off. Samples of **III** (remaining in the distillation flask), of **IV** (in the distillate) and samples of the starting material **II** are hydrolyzed by heating with a strong sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. Purified samples of the three precipitates are then dissolved by known volumes of water and the radioactivity measured.

- 4.1 Write the balanced equations for the reaction of red phosphorus forming PCl_5
- 4.2 Write the reaction equations for complete hydrolysis of the compounds **II** and **III** using sodium hydroxide.
- 4.3 How long does it take in order to lower the initial radioactivity to 10^{-3} of the initial value?
- 4.4 Write two alternative mechanisms for the reaction of labelled PCl_4^- with the anion of **I**.
- 4.5 After hydrolysis the precipitated ammonium magnesium phosphates show the following values for radioactivity:
 - II. 2380 Bq for 128 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - III. 28 Bq for 153 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - IV. 2627 Bq for 142 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

Using these data, what can you say about the nucleophilic centre attacked by PCl_4^- ?

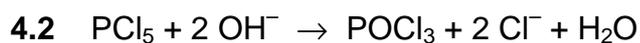
Data: For H_3PO_4 : $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$

Solubility product of $\text{Mg}(\text{NH}_4)\text{PO}_4$: $pK_s = 12.6$

Equilibrium concentration of $\text{NH}_4^+ = 0.1 \text{ mol dm}^{-3}$

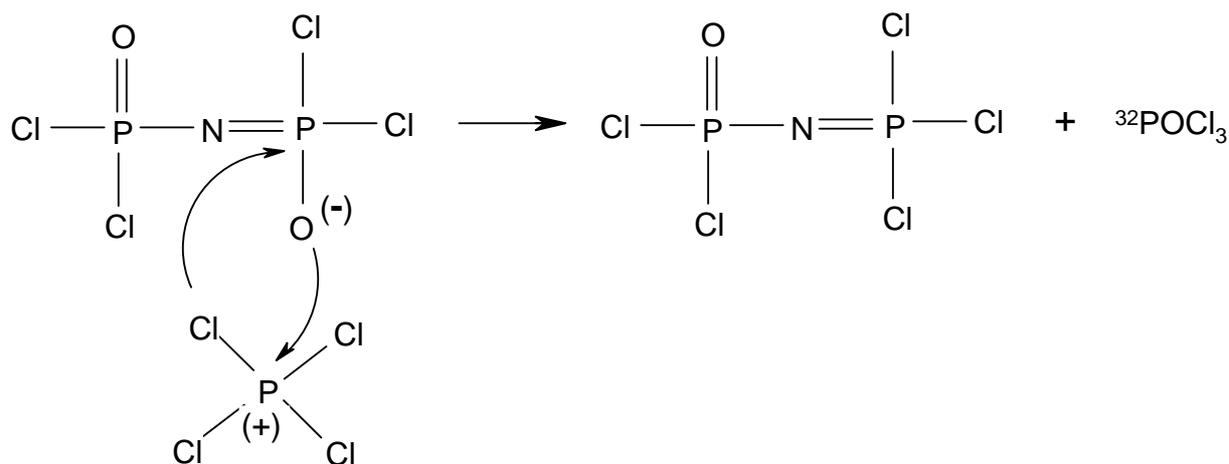
4.6 Calculate the solubility for $\text{Mg}(\text{NH}_4)\text{PO}_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

SOLUTION

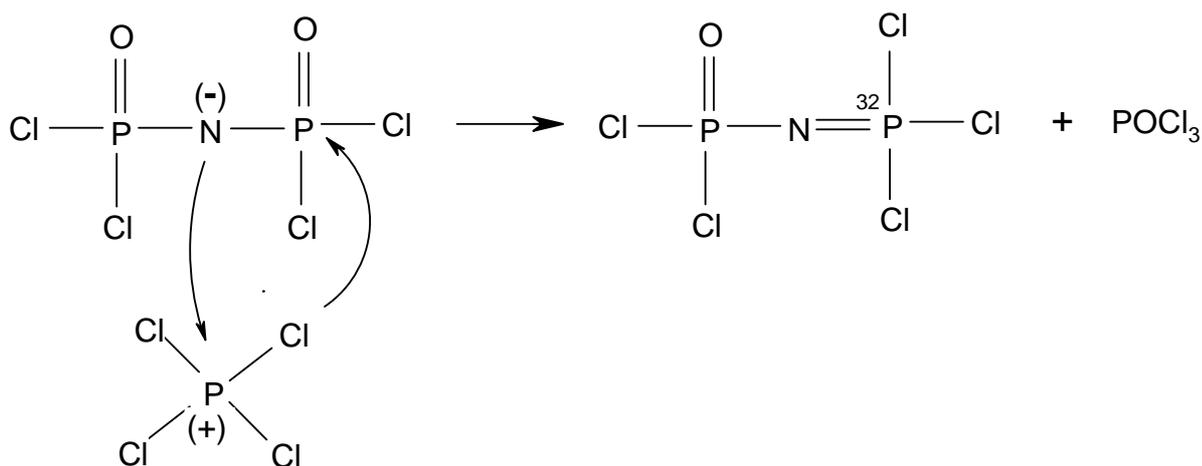


$$t = \frac{\ln A \ln A_0}{\lambda} = \frac{\ln 10^3}{\frac{\ln 2}{14.3}} \text{ d} = 142.5 \text{ d}$$

4.4



1st mechanism



2nd mechanism

- 4.5 Specific activities $A_{\text{sp}}(\text{II}) = 18.6 \text{ Bq/mg}$,
 $A_{\text{sp}}(\text{III}) = 0.18 \text{ Bq/mg}$,
 $A_{\text{sp}}(\text{IV}) = 18.5 \text{ Bq/mg}$.

Because of $A_{\text{sp}}(\text{II}) \approx A_{\text{sp}}(\text{IV})$ the first mechanism, proposed in d), is probable and therefore it is PCl_4^+ that attacks the O-atom.

- 4.6 Given data: $K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}] = 10^{-12.6}$; $[\text{NH}_4^+] = 0.1$; $\text{pH} = 10$; $\text{p}K_1 = 2.2$;
 $\text{p}K_2 = 7.2$; $\text{p}K_3 = 12.4$.

Exact solution:

$$2 [\text{Mg}^{2+}] + [\text{NH}_4^+] + [\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-] + 2 [\text{HPO}_4^{2-}] + 3 [\text{PO}_4^{3-}] + [\text{OH}^-]$$

$$[\text{HPO}_4^{2-}] = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{K_3}$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{K_2} = \frac{[\text{PO}_4^{3-}][\text{H}^+]^2}{K_2 K_3}$$

$$[\text{PO}_4^{3-}] = \frac{K_{\text{sp}}}{[\text{NH}_4^+][\text{Mg}^{2+}]}$$

$$\Rightarrow 2 [\text{Mg}^{2+}] = \left(\frac{[\text{H}^+]^2}{K_1 K_3} + \frac{2 [\text{H}^+]}{K_3} + 3 \right) \frac{K_{\text{sp}}}{[\text{NH}_4^+]} - [\text{Mg}^{2+}] ([\text{NH}_4^+] + [\text{H}^+] - [\text{OH}^-])$$

etc.

A simpler solution:

At pH = 10 the main component is HPO_4^{2-} :

$$[\text{HPO}_4^{2-}] = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{K_3} = 10^{2.4} [\text{PO}_4^{3-}]$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{K_2} = 10^{-2.8} [\text{HPO}_4^{2-}]$$

$$S = [\text{Mg}^{2+}] [\text{HPO}_4^{2-}] \text{ and } K_{sp} = [\text{NH}_4^+] \times S \times K_3 \times \frac{S}{[\text{H}^+]}$$

$$pS = 0.5 (pK_{sp} + pH - pK_3 - p[\text{NH}_4^+]) = 0.5 (12.6 + 10.0 - 12.4 - 1.0) = 4.6;$$

$$S = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

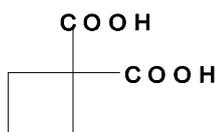
PROBLEM 5

Carboxylic acids are a chemically and biologically important class of organic compounds.

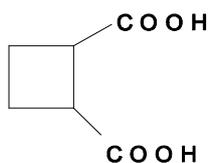
- 5.1 Draw the constitutional (structural) formulae of all isomeric cyclobutanedicarboxylic acids and give the systematic names for these compounds.
- 5.2 There are three stereoisomers, I, II and III, of cyclobutane-1,2-dicarboxylic acid. Draw perspective or stereo formulas of I, II and III indicating the relative configuration of each molecule.
- 5.3 Which pairs of stereoisomers I, II and III are diastereoisomers and which are enantiomers of each other?
- 5.4 Which reaction can be used to determine the relative configuration of diastereoisomers?
- 5.5 How may the enantiomers of cyclobutane-1,2-dicarboxylic acid be separated?
- 5.6 Indicate the absolute configurations of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (*R,S* system).

SOLUTION

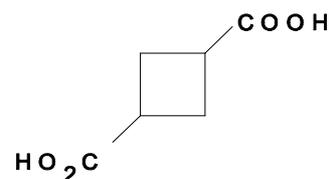
- 5.1 Constitutional isomers:



1,1 - cyclobutane -
dicarboxylic acid

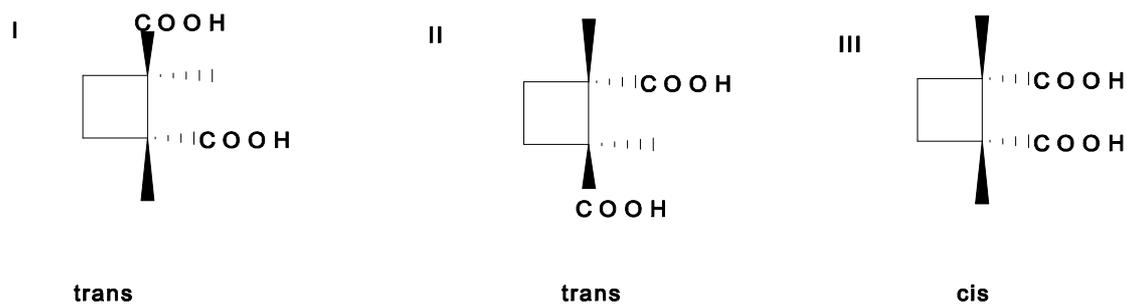


1,2 - cyclobutane -
dicarboxylic acid



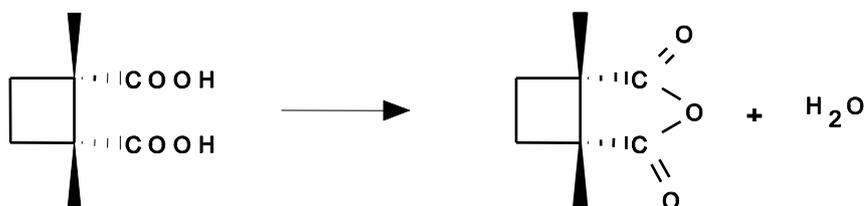
1,3 - cyclobutane -
dicarboxylic acid

- 5.2 Stereoisomers:



5.3 Diastereomers are I, III and II, III. Enantiomeric pairs are I and II.

5.4 On losing water the *cis*-diastereomer forms the corresponding anhydride according to:



5.5 The *trans*-diastereomer can be precipitated with an optically active base.

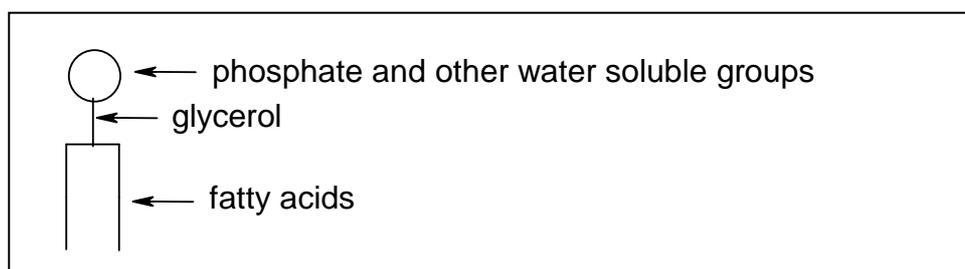
5.6 Stereoisomers absolute configuration:

I: *R,R*; II: *S,S*; III: *R,S*

PROBLEM 6

Fats (lipids) contain a non-polar (hydrophobic) and a polar (hydrophilic) group. The lipids insoluble in water, have important biological functions.

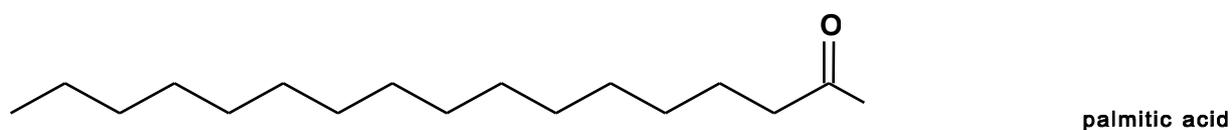
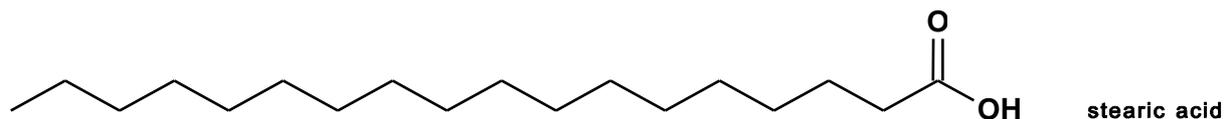
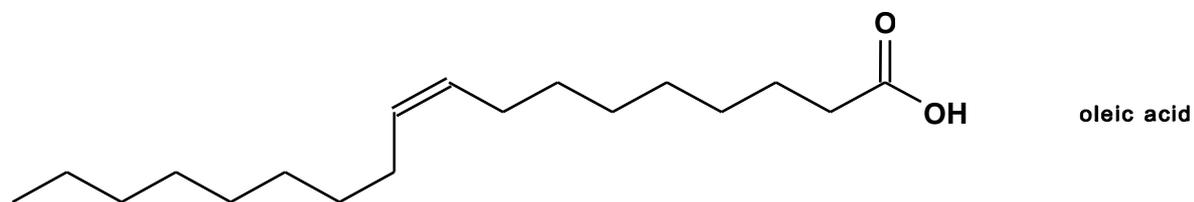
- 6.1 Draw the structures of *Z*-octadec-9-enoic acid (oleic acid), octadecanoic acid (stearic acid), and hexadecanoic acid (palmitic acid).
- 6.2 Using these three fatty acids in part 6.1 draw one possible structure of a triacyl glyceride.
- 6.3 Write the equation for the hydrolysis reaction of your triacyl glyceride in part 6.2 in aqueous NaOH solution. Give the mechanism of the hydrolysis of one of the fatty acids from your glyceride.
- 6.4 Which of the following fatty acids, $C_{21}H_{43}COOH$, $C_{17}H_{35}COOH$ or $C_5H_{11}COOH$, is the least soluble in water?
- 6.5 Phospholipids are an important class of bioorganic compounds. Draw the structure of the phosphatidic acid derived from your triacyl glyceride in part 6.2.
- 6.6 Phospholipids are frequently characterized by the diagram:



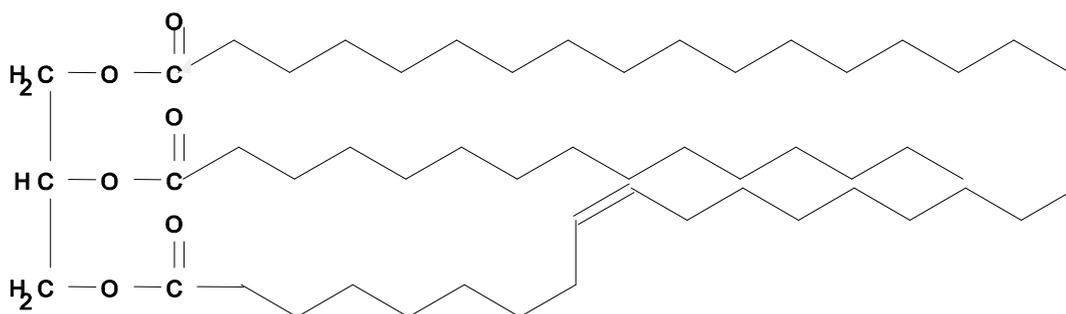
- Mark the hydrophilic and hydrophobic groups on a copy of the above diagram.
- Draw two possibilities for the association of six identical molecules of a phospholipid in water using the above diagram.
- Biomembranes consist of a phospholipid bi-layer. Draw such a model for a membrane using the above diagram.
- Such a model (iii) is incomplete. What other bio-macromolecules are contained in such biomembranes?

SOLUTION

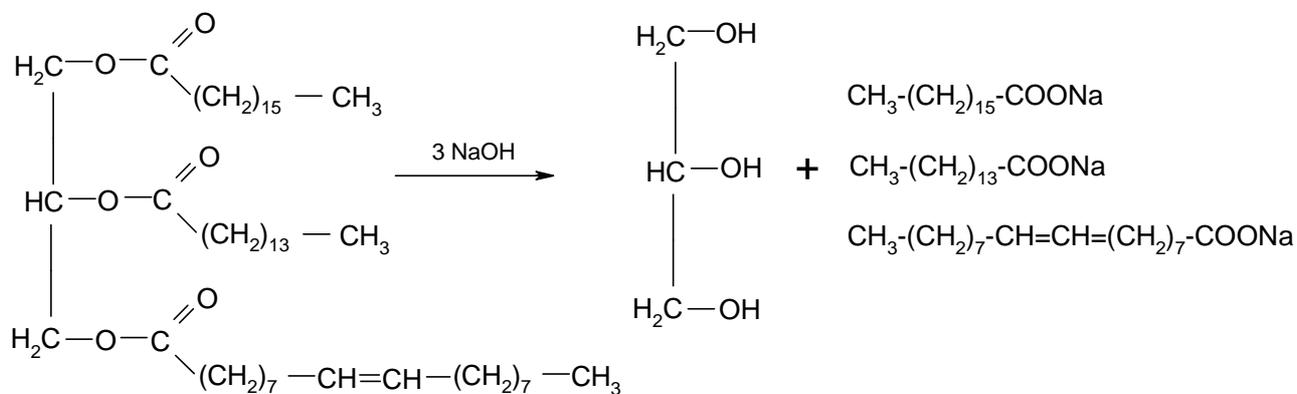
6.1

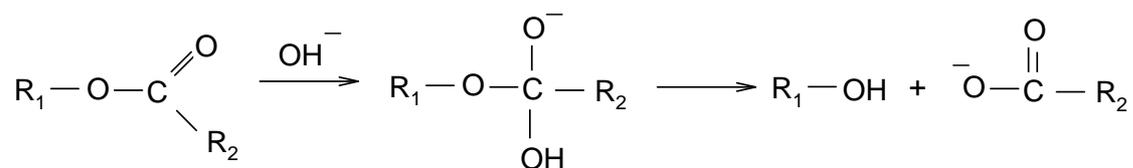


6.2 A possible structure of a triacyl glyceride with the fatty acids mentioned is:



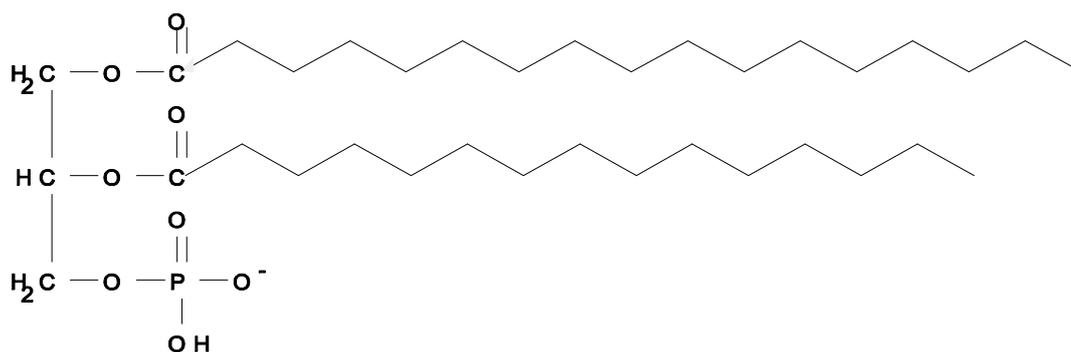
6.3



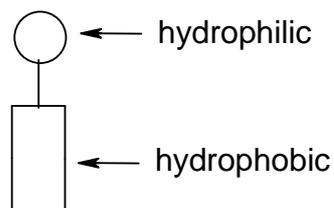


6.4 It is C₂₁H₄₃COOH.

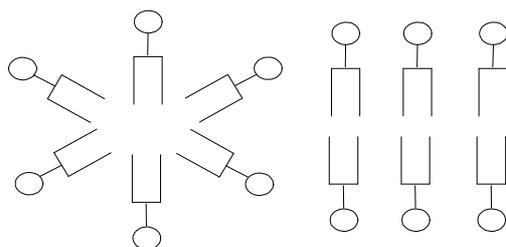
6.5 An example for a phospholipid is:



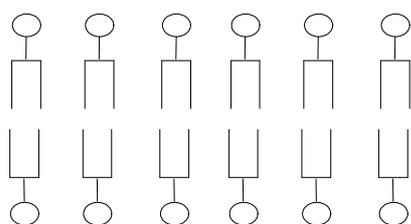
6.6 i)



ii)



iii)



phospholipid bilayer

iv) For example, proteins (enzymes)

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Synthesis**

Preparation of 2-Ethanoxybenzoic Acid (Acetylsalicylic Acid, also known as Aspirin) by Ethanoylation (Acetylation) of 2-Hydroxybenzoic Acid (Salicylic Acid) with Ethanoic Anhydride (acetic anhydride).

Relative atomic masses: C: 12.011; O: 15.999; H: 1.008

Reagents

2-hydroxybenzoic acid (melting point 158 °C)

Ethanoic anhydride (boiling point 140 °C)

Phosphoric acid (85 % H₃PO₄)

Ethanol

Deionised/distilled water

Procedure

In a 100 cm³ Erlenmeyer flask mix 2.760 g of 2-hydroxybenzoic acid (from weighing bottle A) with 5.100 g of ethanoic anhydride (from flask B), and with cautious swirling add 5 – 7 drops of 85 % phosphoric acid. Heat the flask to 70 – 80 °C in a beaker of near boiling water and maintain the mixture at this temperature for 15 minutes. Remove the flask from the water bath and, with gentle swirling, add dropwise 1 cm³ of deionised water to the still hot flask; then immediately add 20 cm³ of the cold deionised water all at once to the reaction flask. Place the flask in an ice bath. If no crystals are deposited, or if oil appears, gently scratch the inner surface of the flask with a glass rod while the flask remains in the ice bath.

Using a Büchner funnel, filter the product under suction. Rinse the flask twice with a small amount of cold deionised water. Recrystallize the crude product in the 100 cm³ Erlenmeyer flask using suitable amounts of water and ethanol. If no crystals form or if oil appears, scratch gently the inner surface of the flask with a glass rod. Filter the crystals under suction and wash with a small amount of cold deionised water. Place the

crystals on the porous plate to draw water from them. When the crystals have been air dried, transfer the product to the small glass dish labeled C. This dish has previously been weighed. The dish containing the product should be given to a technician who will dry it in an oven for 30 minutes at 80 °C.

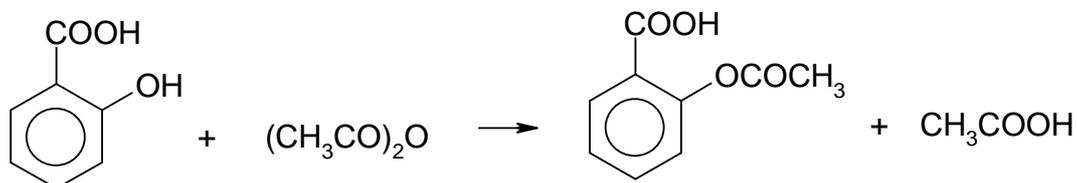
A technician should then weigh the cooled dish containing your product in your presence. Record the mass. The melting point will subsequently be taken by a technician to check the purity of your product.

Questions:

1. Write the balanced chemical equation for the reaction using structural formulae.
2. What is the percentage yield?

SOLUTION

1.



PROBLEM 2 (Practical)**Analysis**

Determination of Mass of a given Sample of 2-Ethanoyl-oxybenzoic Acid (Acetylsalicylic Acid, or Aspirin) by Volumetric Back Titration after Hydrolysis with Excess of Sodium Hydroxide.

Reagents

Aqueous solution of sodium hydroxide (about 0.5 mol dm^{-3})

Standard aqueous solution of hydrochloric acid ($0.4975 \text{ mol dm}^{-3}$)

Ethanolic phenolphthalein solution (indicator dropping bottle II)

Deionised/distilled water

Part 1:

Determine accurately the concentration of the about 0.5 mol dm^{-3} sodium hydroxide solution using the standard hydrochloric acid solution. (Record the answer as mol dm^{-3} with four places after decimal point.)

Procedure:

Pipette 20.00 cm^3 of the sodium hydroxide solution into a 300 cm^3 Erlenmeyer flask and dilute it to about 100 cm^3 with deionized water. Titrate the obtained solution with the standard $0.4975 \text{ mol dm}^{-3}$ hydrochloric acid solution using the phenolphthalein indicator. Repeat the procedure to produce three acceptable values and calculate the mean volume.

Part 2:

Determine accurately the mass of aspirin in Erlenmeyer flask I. Record your answer in g with three places after the decimal point.

Procedure:

Pipette 50.00 cm^3 of your standardized sodium hydroxide solution into the Erlenmeyer flask I (with a ground glass joint) which contains your unknown mass of aspirin. Add 3 – 5 boiling stones to the flask and boil the reaction mixture for 15 minutes using a reflux condenser and the electrical hot plate. After cooling, remove the reflux

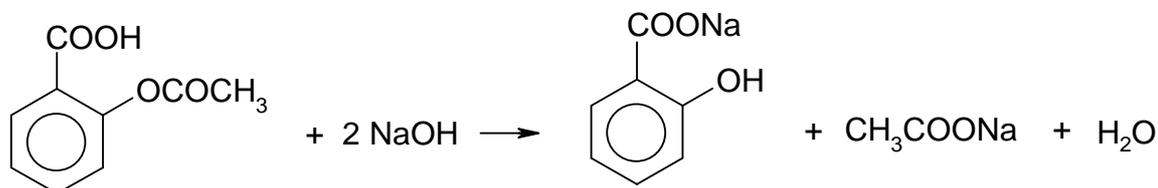
condenser and rinse it with a small quantity of deionised water into Erlenmeyer flask I. Pour the whole solution into a 100.0 cm³ volumetric flask and fill it exactly to the mark with deionised water. Pipette 20.00 cm³ of this solution into a 300 cm³ Erlenmeyer flask and dilute to about 100 cm³ with deionised water. Back titrate the residual sodium hydroxide with the standard hydrochloric acid solution (0.4975 mol dm⁻³) using a 10 cm³ burette and phenolphthalein indicator. Repeat the volumetric procedure to produce three acceptable values and calculate the mean volume.

Questions:

- 1) Write the balanced chemical equation for the ester hydrolysis of aspirin by sodium hydroxide using structural formulae. Note that 1000 cm³ aqueous solution of 0.5000 mol dm⁻³ sodium hydroxide is equivalent to 0.0450 g of aspirin.
- 2) Calculate the mass of aspirin that you were given.

SOLUTION

1.



22nd



International Chemistry Olympiad

**7 theoretical problems
4 practical problems**

THE TWENTY-SECOND INTERNATIONAL CHEMISTRY OLYMPIAD 8-17 JULY 1990, PARIS, FRANCE

THEORETICAL PROBLEMS

PROBLEM 1

PHOSPHORIC ACID

The elemental phosphorus is present in the nature as phosphate in a complex mineral apatite. This mineral contains, in addition to phosphate, silica and the following ions: Ca^{2+} , CO_3^{2-} , SO_4^{2-} , SiO_3^{2-} , and F^- .

Let us assume that this mineral is a mixture of tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, calcium sulphate, calcium fluoride, calcium carbonate and silica.

For uses as fertilizer the calcium bis(dihydrogenphosphate), $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which is soluble in water, has been prepared. For this purpose, apatite is treated with a mixture of phosphoric and sulphuric acid. At the same time this operation eliminates the majority of impurities.

The elemental analysis of an apatite gave the following results in which, except of fluorine, the elemental composition is expressed as if the elements were in the form of oxides:

	CaO	P ₂ O ₅	SiO ₂	F	SO ₃	CO ₂
% by mass	47.3	28.4	3.4	3.4	3.5	6.1

Operation 1 - A sample of m_0 of this mineral is treated with 50.0 cm³ of a solution containing 0.500 mol dm⁻³ phosphoric and 0.100 mol dm⁻³ sulphuric acids. The mixture is completely dehydrated by heating up to about 70 °C avoiding temperature rising above 90 °C. This operation is carried out under the hood since toxic gaseous substances are emitted. The dry residue is ground and weighed; m_1 is the mass of the residue obtained.

In these conditions only dihydrogenphosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, is formed while silica and silicate do not react.

Operation 2 - 1.00 g of this residue is treated with 50.0 cm^3 of water at $40 \text{ }^\circ\text{C}$, then filtered, dried and weighed. The mass of the residue obtained is m_2 . This new residue is mainly containing gypsum, $\text{CaSO}_4 \cdot 2 \text{ H}_2\text{O}$, whose solubility can be considered as constant between $20 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$ and is equal to 2.3 g dm^{-3} .

- 1.1 Write the balanced equations for the reactions that are involved.
 1.2 From what mass of apatite should one start if all the reactions are stoichiometric?

Starting with m_0 of obtained apatite, $m_1 = 5.49 \text{ g}$ of residue are obtained.

- 1.3 What mass should theoretically be obtained?
 1.4 This result is due to the presence of products that are not expected to be found in the residue. Give two of them that under these experimental conditions can plausibly account for the data.

Traditionally, in industry the analysis and the yield are expressed as percentage of oxide. The phosphorous content is expressed as if it were P_2O_5 .

If n_2 is the amount of a soluble product obtained, n_1 the amount of a substance added as acid, n_0 the amount of apatite added, the yield is:

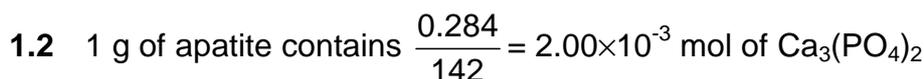
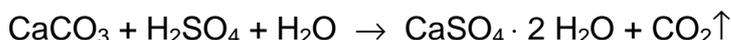
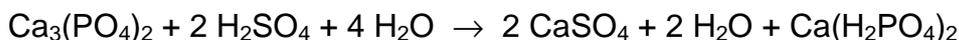
$$r_{\text{exp}} = \frac{n_2}{n_1 + n_0} 100$$

$m_2 = 0.144 \text{ g}$ of residue is obtained on the filter.

- 1.5 Calculate r_{exp} .
 1.6 The experimental yield is over 100 %. Calculate a value of r nearer to the real yield.

Relative atomic masses of P: 31; Ca: 40; O: 16; H: 1; F: 19; C: 12; Si: 28;
 S: 32.

Values of pK : $\frac{\text{HSO}_4^-}{\text{SO}_4^{2-}} = 2$ $\frac{\text{HF}}{\text{F}^-} = 3$ $\frac{\text{H}_3\text{PO}_4}{\text{H}_2\text{PO}_4^-} = 2$ $\frac{\text{H}_2\text{PO}_4^-}{\text{HPO}_4^{2-}} = 7$ $\frac{\text{HPO}_4^{2-}}{\text{PO}_4^{3-}} = 12$

SOLUTION

$$\frac{0.034}{2 + 19} = 0.89 \times 10^{-3} \text{ mol of } \text{CaF}_2$$

$$\frac{0.061}{44} = 1.39 \times 10^{-3} \text{ mol of } \text{CaCO}_3$$

$$\frac{0.035}{80} = 0.44 \times 10^{-3} \text{ mol of } \text{CaSO}_4$$

$$\frac{0.473}{56} - \frac{3 \times 0.284}{142} - \frac{0.034}{38} - \frac{0.061}{44} - \frac{0.035}{80} = 2.72 \times 10^{-4} \text{ mol CaO that remain.}$$

The amount of H_3PO_4 needed to react with 1 g of apatite is equal to $n(\text{H}_3\text{PO}_4) = 4 n(\text{Ca}_3(\text{PO}_4)_2) + 2 n(\text{CaF}_2) + 2 n(\text{CaCO}_3) = 12.56 \times 10^{-3} \text{ mol}$.

50 cm^3 of the acid contains $25 \times 10^{-3} \text{ mol}$ of H_3PO_4 , therefore $25 / 12.56 = \underline{1.99 \text{ g}}$ apatite is needed to neutralize the H_3PO_4 present.

The amount of H_2SO_4 needed to react with 1 g of apatite can be calculated in the same way:

$n(\text{H}_2\text{SO}_4) = 2 n(\text{Ca}_3(\text{PO}_4)_2) + n(\text{CaF}_2) + n(\text{CaCO}_3) = 6.28 \times 10^{-3} \text{ mol}$. 50 cm^3 of the acid contains $5.00 \times 10^{-3} \text{ mol}$ of sulphuric acid. Therefore $5 / 6.28 = 0.80 \text{ g}$ of apatite is needed to neutralize the H_2SO_4 .

The total amount of apatite is $m_0 = 1.99 + 0.80 = \underline{2.79 \text{ g}}$

1.3 Formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$:

1.99 g of apatite needed to neutralize the H_3PO_4 contains $1.9 \times 2.00 \times 10^{-3} \text{ mol}$ of $\text{Ca}_3(\text{PO}_4)_2$, thus $3 \times 2 \times 2 \times 10^{-3} = 1.2 \times 10^{-2} \text{ mol}$ of dihydrogen phosphate is being formed.

From CaF_2 , $1.99 \times 0.89 = 1.80$ mol and from CaCO_3 , $1.99 \times 1.39 = 2.77$ mol of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ are formed.

0.8 g of apatite that reacts with 50 cm^3 of the sulphuric acid yields $2 \times 0.8 \times 10^{-3} = 1.6 \times 10^{-3}$ mol of $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

$$m(\text{Ca}(\text{H}_2\text{PO}_4)_2) = 18.07 \times 10^{-3} \text{ mol} = 4.230 \text{ g}$$

Formation of gypsum: $n(\text{CaSO}_4) = n(\text{H}_2\text{SO}_4) = 5.00 \times 10^{-3} \text{ mol} \hat{=} 0.86 \text{ g}$

The amount of CaSO_4 that was already present in 1 g of apatite and yielded gypsum is $0.434 \times 10^{-3} \times 172 = 0.075 \text{ g}$. There remain also 0.034 g of silica, and thus the theoretical mass of the residue should be:

$$m_{\text{th}} = 4.230 + 0.86 + (0.0753 + 0.034) \times 2.79 = \underline{5.39 \text{ g}}$$

1.4 The difference of 0.1 g may be due to water and unreacted CaF_2 in the residue.

1.5 The second reaction is intended to dissolve $\text{Ca}(\text{H}_2\text{PO}_4)_2$, while all the other products remain on the filter.

According to the yielded residue of 0.144 g, 1 g of residue contains $1 - 0.144 = 0.856$ g of soluble product. If it were all $\text{Ca}(\text{H}_2\text{PO}_4)_2$ it would correspond to $0.856 / 234 = 3.66 \times 10^{-3}$ mol. For 5.49 g of residue it is 0.0201×10^{-3} mol of soluble product (n_2). The amount of acid used is $0.500 / 20 = 0.025$ mol H_3PO_4 (equals 0.0125 mol P_2O_5) and 0.005 mol H_2SO_4 . The amount of $\text{Ca}_3(\text{PO}_4)_2$ in 2.79 g apatite is 0.00558 mol (equals 0.00558 mol P_2O_5). So, $r_{\text{exp}} = 100 \times [0.0201 / (0.0125 + 0.00558)] = \underline{111 \%}$

Since 50 cm^3 water dissolve 0.115 g of gypsum, the real quantity of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is $0.856 - 0.115 = 0.741$ mol, so that the real yield gives: $r_{\text{exp}} = 100 \times [0.0174 / (0.0125 + 0.00558)] = \underline{96 \%}$.

1.6 The theoretical value for r_{exp} is: $r_{\text{exp}} = 100 \times [4.23 / 234 / (0.0125 + 0.00558)] = 100 \%$, so this calculation makes sense.

PROBLEM 2**IONIC SOLUTIONS – AQUEOUS SOLUTIONS OF COPPER SALTS**

This part is about the acidity of the hydrated Cu^{2+} ion and the precipitation of the hydroxide.

Consider a $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ solution of copper(II) nitrate. The pH of this solution is 4.65.

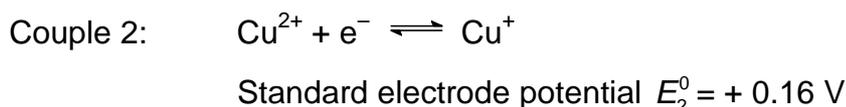
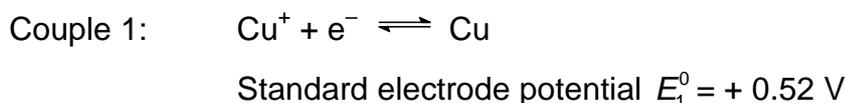
- 2.1** Give the equation for the formation of the conjugate base of the hydrated Cu^{2+} ion.
2.2 Calculate the pK_a of the corresponding acid-base pair.

The solubility product of copper(II) hydroxide is $K_{sp} = 1 \times 10^{-20}$.

- 2.3** At what pH value hydroxide $\text{Cu}(\text{OH})_2$ precipitates from the solution under consideration? Justify your calculation showing that the conjugate base of this hydrated Cu^{2+} ion is present in negligible quantity.

Disproportionation of copper(I) ions

The Cu^+ ion is involved in two redox couples:



- 2.4** Write down the equation for the disproportionation of copper(I) ions and calculate the corresponding equilibrium constant.
2.5 Calculate the composition of the solution (in mol dm^{-3}) obtained on dissolving $1.00 \times 10^{-2} \text{ mol}$ of copper(I) in 1.0 dm^3 of water.
2.6 Apart from Cu^+ ions, name two chemical species which also disproportionate in aqueous solution; write down the equations and describe the experimental conditions under which disproportionation is observed.

Consider the stability of copper(I) oxide, Cu_2O , in contact with a $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ solution of Cu^{2+} ions. The solubility product of copper(I) oxide is $K_{sp} = [\text{Cu}^+][\text{OH}^-] = 1 \times 10^{-15}$

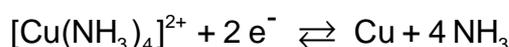
2.7 Calculate the pH value at which Cu_2O becomes stable. Quote a simple experiment allowing the observation of the precipitation of Cu_2O .

Complex formation involving Cu^+ and Cu^{2+} ions

2.8 The dissociation constant of the complex ion $[\text{Cu}(\text{NH}_3)_2]^+$ is $K_D = 1 \times 10^{-11}$. Calculate the standard electrode potential of the couple:



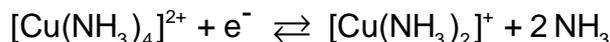
2.9 The standard electrode potential of the couple



$$E_3^0 = -0,02 \text{ V.}$$

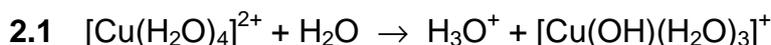
Calculate the dissociation constant for the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

2.10 Deduce from it the standard electrode potential of the couple:



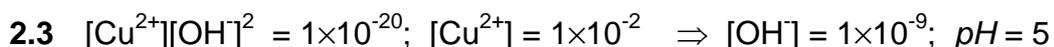
Does the disproportionation of the cation $[\text{Cu}(\text{NH}_3)_2]^+$ take place?

SOLUTION

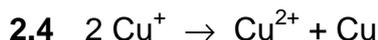


$$2.2 \quad K_a = \frac{[\text{H}_3\text{O}^+][[\text{Cu}(\text{OH})(\text{H}_2\text{O})_3]^+]}{[[\text{Cu}(\text{H}_2\text{O})_4]^{2+}]} = \frac{[\text{H}_3\text{O}^+]^2}{[[\text{Cu}(\text{H}_2\text{O})_4]^{2+}]} = \frac{(2.24 \times 10^{-5})^2}{1 \times 10^{-2}} = 5.01 \times 10^{-8}$$

$$pK_a = 7.30$$



$$[[\text{Cu}(\text{OH})(\text{H}_2\text{O})_3]^+] : [[\text{Cu}(\text{H}_2\text{O})_4]^{2+}] = K_a : 10^{-pH} = 1 \times 10^{-7.3} : 1 \times 10^{-5} = 1 : 200$$



$$K = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$$

$$0.52 - 0.16 = 0.059 \log K \text{ (Nernst equation)} \Rightarrow K = 1 \times 10^6$$

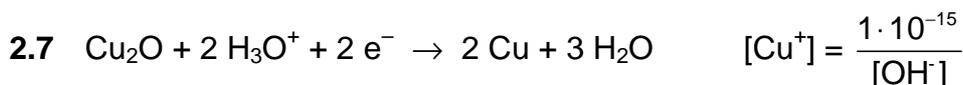
2.5 At equilibrium: $[\text{Cu}^+] + 2 [\text{Cu}^{2+}] = 1 \times 10^{-2}$ and $[\text{Cu}^{2+}] = 1 \times 10^6 [\text{Cu}^+]$ so that the following equation is obtained:

$$2 \times 10^6 [\text{Cu}^+]^2 + [\text{Cu}^+] - 1 \times 10^{-2} = 0$$

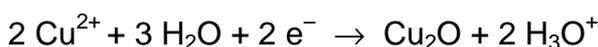
with the solution

$$[\text{Cu}^+] = \underline{7.07 \times 10^{-5}} \text{ and } [\text{Cu}^{2+}] = \underline{4.96 \times 10^{-3}} .$$

2.6 Other disproportionation reactions:



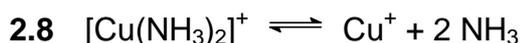
$$E_1 = 0.52 + \frac{0.059}{2} \log ([\text{Cu}^+][\text{H}_3\text{O}^+]^2) = 0.49 - 0.0885 \text{ pH}$$



$$E_2 = 0.16 + \frac{0.059}{2} \log \frac{1 \times 10^{-4}}{[\text{Cu}^+][\text{H}_3\text{O}^+]^2} = 0.07 + 0.0885 \text{ pH}$$

Cu_2O is stable when $E_2 > E_1$ i.e. $0.42 < 0.177 \text{ pH}$, or $\text{pH} > 2.4$

Cu_2O can be obtained by the reduction of Cu^{2+} in acid or basic media, e.g. by Fehling's solution or reducing sugars.



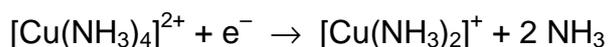
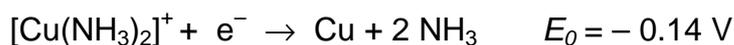
$$K_D = \frac{[\text{Cu}^+][\text{NH}_3]^2}{[\text{Cu}(\text{NH}_3)_2^+]} = 1 \times 10^{-11}$$

Knowing $E_0(\text{Cu}^+/\text{Cu}) = 0.52 \text{ V}$, the $E^0([\text{Cu}(\text{NH}_3)_2]^+ / \text{Cu}^+)$ becomes:

$$E_{f1} = 0.52 - 0.06 \text{ p}K_D = \underline{-0.14 \text{ V}}$$

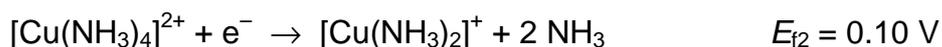
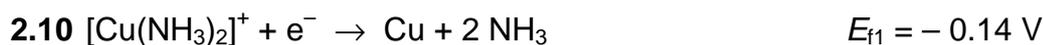
2.9 The standard *emf* of a Cu^{2+}/Cu cell is thus: $E^0 = (0.5 + 0.16)/2 = 0.33 \text{ V}$ and $E_3^0 = 0.33 - 0.03 \text{ p}K_2$.

$$\text{Thereout: } \text{p}K_2 = (0.33 - E_3^0) / 0.03 = (0.33 - (-0.02)) / 0.03 = \underline{12}$$



Since only ΔG^0 is additive and from $\Delta G^0 = -n F E^0$ it follows:

$$E_{f2} = 2 \times (-0.02) - (-0.14) = 0.10 \text{ V}$$



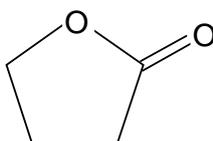
Since $E_{f1} < E_{f2}$ the $[\text{Cu}(\text{NH}_3)_2]^+$ ion doesn't disproportionate (the *emf* would be $-0.14 - 0.10 = -0.24 \text{ V}$)

PROBLEM 3**ORGANIC SYNTHESIS – SYNTHESIS OF HALOPERIDOL**

Haloperidol is a powerful neuroleptic prescribed in cases of psychomotoric disorder and for the treatment of various psychoses. A synthesis of this compound is proposed.

3.1 Give a scheme for the preparation of methyl 4-chlorobenzoate starting from benzene and all necessary inorganic substances. Diazomethane (H_2CN_2) must be used in your synthesis.

γ -Butyrolactone (**J**) is a cyclic ester represented below.

**J**

3.2 How can γ -butyrolactone **J** be converted into 4-hydroxybutanoic acid (**K**)?

3.3 Convert **K** into 4-chlorobutanoyl chloride (**L**).

The reactions described below do not correspond to those used in the industrial synthesis of haloperidol for which the route is quite complex.

Methyl 4-chlorobenzoate is treated with an excess of vinylmagnesium bromide in anhydrous ether. **M** is obtained after hydrolysis. When **M** is treated with an excess of hydrogen bromide in anhydrous conditions in the presence of benzoyl peroxide, **N** is obtained. **N** reacts with ammonia to form 4-(4-chlorophenyl)-4-hydroxypiperidine (**O**).

3.4 Write down the structure of **M**, **N** and **O** and indicate the mechanism of the reaction leading to **M**.

In the presence of a moderate amount of aluminium chloride, **L** reacts with fluorobenzene to yield mainly a ketone **P** ($\text{C}_{10}\text{H}_{10}\text{OFCl}$).

3.5 Sketch the structure of **P** and indicate the mechanism.

3.6 Give a chemical and physical test method for the determination of the carbonyl group. How can you make sure that the carbonyl group does not belong to an aldehyde group?

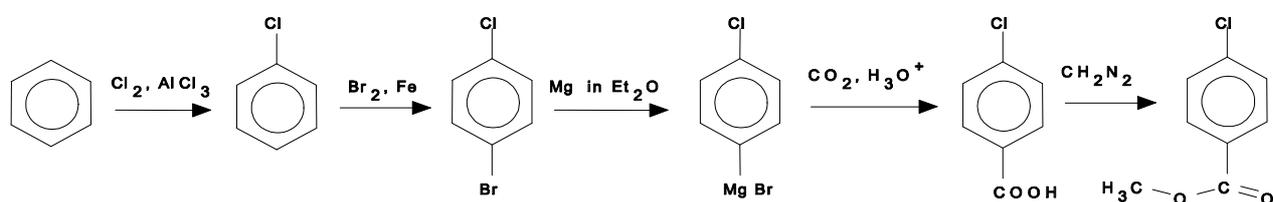
P reacts with **O** in basic media in a 1 : 1 molar ratio to give **H** that contains only one chlorine atom on the aromatic ring.

3.7 Give the structure of **H** which is haloperidol.

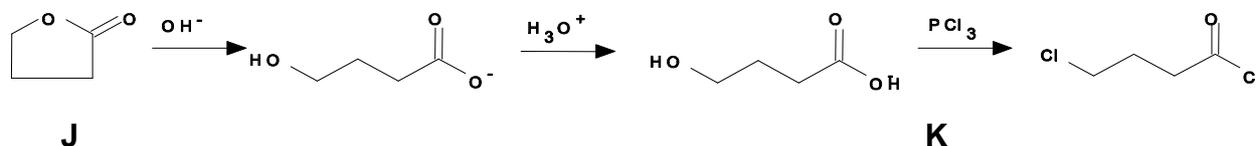
3.8 State the multiplicity of each resonance in the ¹H NMR spectrum of **K**. Assume that all coupling constants between protons and adjacent carbons are identical.

SOLUTION

3.1

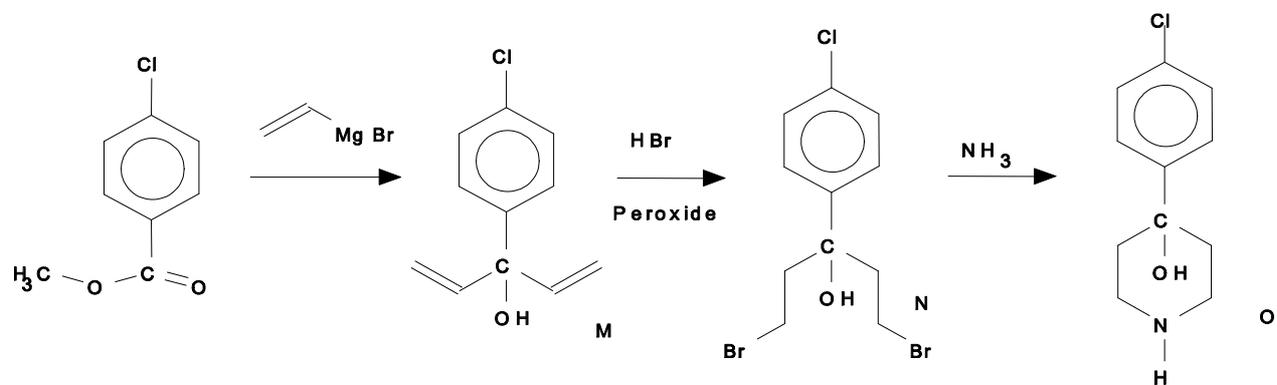


3.2 and 3.3

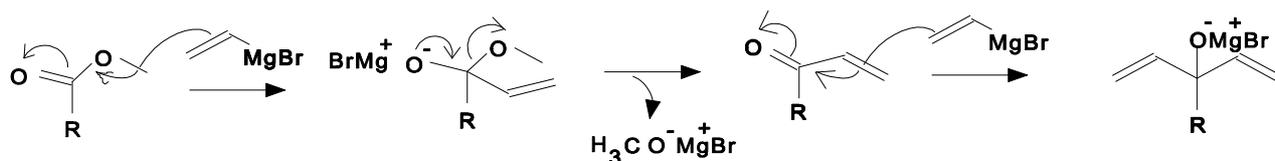


L

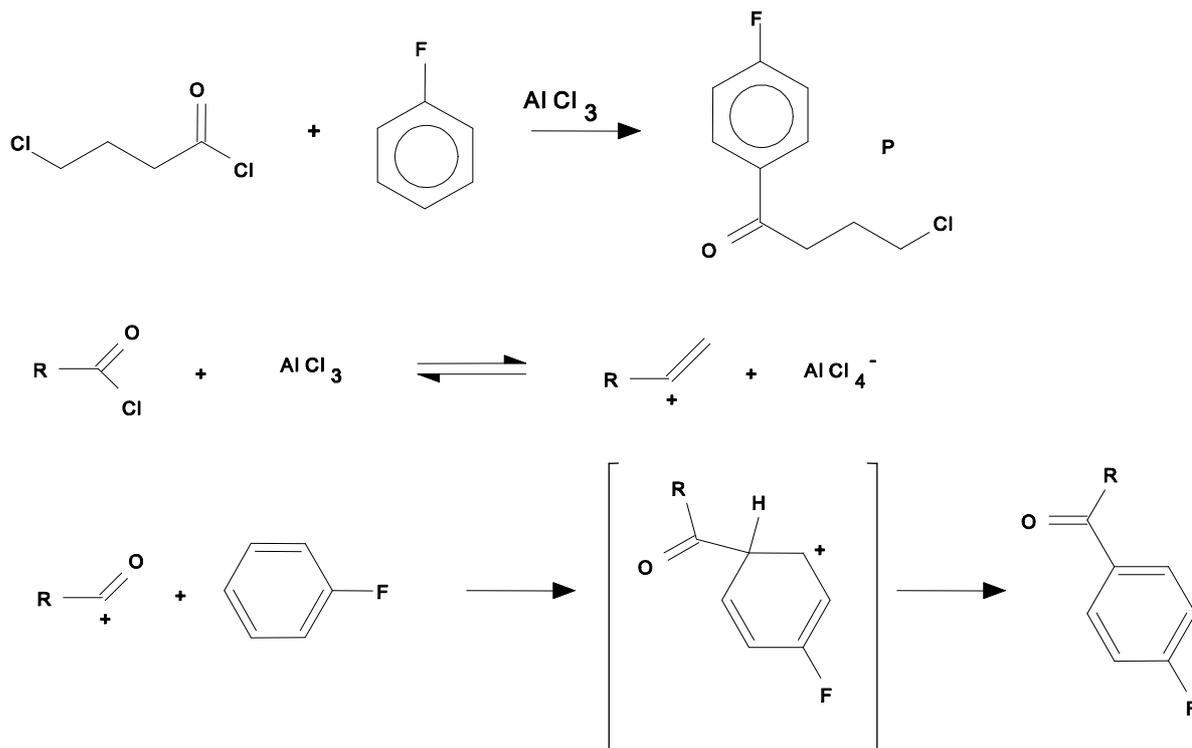
3.4



Mechanism of the Grignard reaction:



3.5

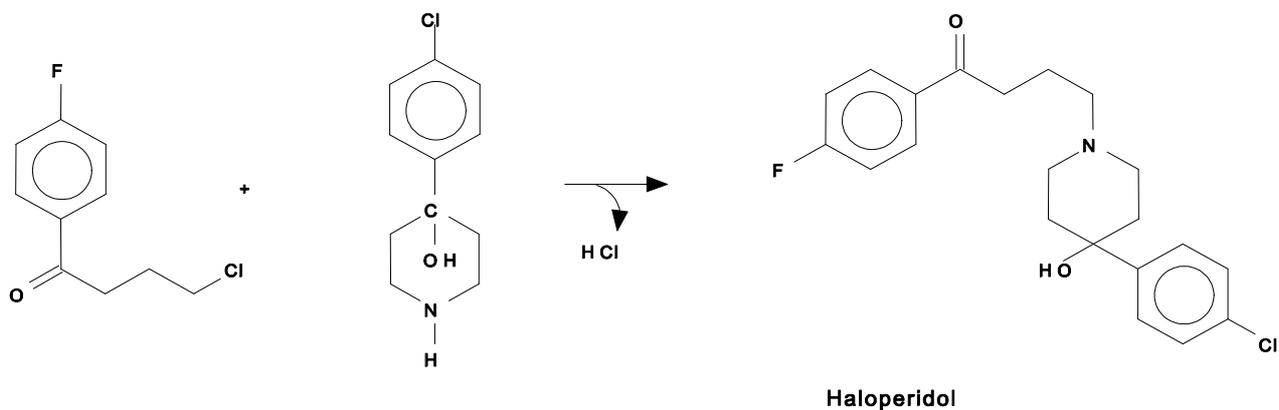


3.6 Chemical test: carbonyl groups react with phenylhydrazines to phenylhydrazones with a sharp, specific melting point.

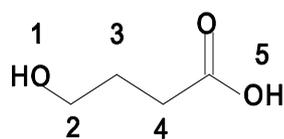
Physical test: IR-absorption at 1740 cm^{-1}

A possibility to distinguish between ketones and aldehydes is the Tollens-test (silver mirror). Ketones cannot be reduced whereas aldehydes easily reduce the silver ions to elementary silver.

3.7



3.8

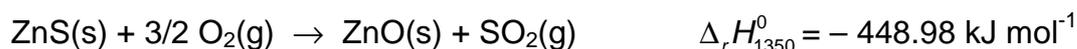


proton1:singulet
 proton2:triplet
 proton3:quintuplet
 proton4:triplet
 proton5:singulet

PROBLEM 4**CHEMICAL THERMODYNAMICS**

The production of zinc from zinc sulphide proceeds in two stages: the roasting of zinc sulphide in the air and the reduction of the zinc oxide formed by carbon monoxide. In this problem we will consider the roasting of zinc sulphide.

This operation consists in burning zinc sulphide in the air. The equation of the reaction taking place is as follows:



Industrially this reaction is carried out at 1350 K.

4.1 Show that the reaction can be self-sustaining, i.e. that the heat produced is sufficient to bring the reactants from ambient temperature to the reaction temperature.

Suppose that the zinc containing mineral contains only zinc sulphide, ZnS.

4.2 Starting with a stoichiometric mixture of one mole zinc blend only and a necessary quantity of the air at 298 K, calculate the temperature to which the mixture will raise by the heat evolved during the roasting of the mineral at 1350 K under standard pressure. Is the reaction self-sustaining? Air is considered to be a mixture of oxygen and nitrogen in a volume ratio equal to 1 : 4.

In fact, zinc blend is never pure and is always mixed with a gangue that can be assumed to be entirely silica SiO₂.

4.3 Assuming that the gangue does not react during the roasting, calculate the minimum ZnS content of the mineral for which the reaction would be self-sustaining at 1350 K despite the presence of silica. Give the answer in grams of ZnS per hundred grams of zinc blend.

Data:

Standard molar heat capacities averaged over the temperature range considered (in J K⁻¹ mol⁻¹):

ZnS (solid):	58.05	ZnO (solid):	51.64
SO ₂ (gas):	51.10	O ₂ (gas):	34.24
N ₂ (gas):	30.65	SiO ₂ (solid):	72.50
Molar masses (in g mol ⁻¹):		ZnS: 97.5	SiO ₂ : 60.1

SOLUTION

4.1 The heat given off heats 1 mol of ZnS, 1.5 mol of O₂ and 6 mol of N₂. Therefore:

$$\Delta_r H_{1350}^0 = \int_{298}^T [c_p(\text{ZnS}) + 1.5 c_p(\text{O}_2) + 6 c_p(\text{N}_2)] dT = 293.3(T - 298) = 448\,980 \text{ J mol}^{-1}$$

Thus $T \approx 1830 \text{ K}$, which indicates that the reaction is self-sustaining.

4.2 If n denotes the quantity (in moles) of SiO₂ per mol of ZnS, the heat given off heats 1 mol of ZnS, n mol of SiO₂, 1.5 mol of O₂ and 6 mol of N₂ from 298 to 1350 K:

$$\Delta_r H^0 = \int_{298}^{1350} \sum (n_i \times c_{p(i)}) dT = \int_{298}^{1350} (293.3 + 72.5n) dT$$

Wherefrom: $448\,980 = (293.3 + 72.5n)(1350 - 298)$, so $n = 1.84 \text{ mol}$

4.3 By mass, we have 110.6 g of SiO₂ per 97.5 g of ZnS, or 46.9 g of ZnS per 100 g of mineral. Thus, the minimum tolerated ZnS content in the mineral is 46.9 %.

PROBLEM 5**CHEMICAL KINETICS**

Nitramide NO_2NH_2 decomposes slowly in aqueous solution according to the reaction:



The experimental kinetic law is as follows:

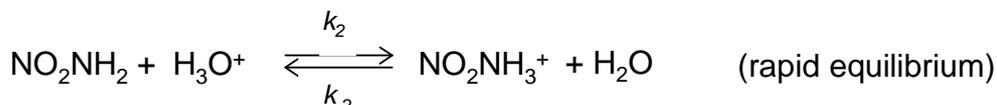
$$\frac{d[\text{N}_2\text{O}]}{dt} = k \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

- 5.1** What is the apparent order of this reaction in a buffered solution?
- 5.2** Which of the following mechanisms is the most appropriate for the interpretation of this kinetic law? Justify your answer.

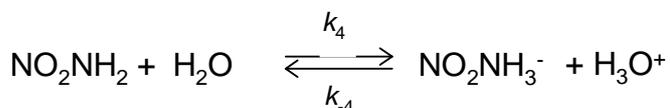
Mechanism 1:



Mechanism 2:



Mechanism 3:



- 5.3** Show the relationship between the experimentally observed rate constant and the rate constants of the selected mechanism.
- 5.4** Show that hydroxyl ions catalyze the decomposition of nitramide.

The decomposition is studied in a buffered solution of a constant volume V at a constant temperature by measuring the partial pressure of the gas N_2O , considered to be insoluble in water, in a constant volume of the same value V above the solution. The following results are obtained:

$t(\text{min})$	0	5	10	15	20	25
$p(\text{Pa})$	0	6800	12400	17200	20800	24000

After a sufficiently long time, the pressure stabilises at 40000 Pa.

5.5 Express the pressure p as a function of time and the constant k' such that

$$k' = \frac{k}{[\text{H}_3\text{O}^+]}$$

5.6 Verify graphically that the kinetic law is confirmed by these experimental results.

5.7 Calculate k' giving its units.

SOLUTION

5.1 In a buffer solution $[\text{H}_3\text{O}^+]$ is constant and the reaction is of the first order:

$$v = k' [\text{NO}_2\text{NH}_2]$$

5.2 The rate laws of the three mechanisms proposed are:

$$v_1 = k_1 [\text{NO}_2\text{NH}_2]$$

$$v_2 = k_3 [\text{NO}_2\text{NH}_3^+] = \frac{k_3 k_2}{k_{-2}} [\text{NO}_2\text{NH}_2] [\text{H}_3\text{O}^+]$$

$$v_3 = k_5 [\text{NO}_2\text{NH}^-] = \frac{k_5 k_4}{k_{-4}} \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

Thus, it is the third mechanism that is correct.

5.3
$$k = \frac{k_5 k_4}{k_{-4}}$$

5.4 Noting that $[\text{H}_3\text{O}^+] = K_e / [\text{OH}^-]$ it follows that $v = k / K_e [\text{NO}_2\text{NH}_2] [\text{OH}^-]$, which shows the catalytic role of OH^- .

5.5 $d[\text{N}_2\text{O}]$ can be expressed by the change of pressure $dp(\text{N}_2\text{O})/RT$ (according to $pV = nRT$). We obtain:

$$v = \frac{d[\text{N}_2\text{O}]}{dt} = \frac{1}{RT} \frac{dp(\text{N}_2\text{O})}{dt} = \frac{1}{RT} \frac{dp}{dt} = k \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

We also know that $V[\text{NO}_2\text{NH}_2] = n(\text{NO}_2\text{NH}_2)_{\text{init}} - n(\text{N}_2\text{O}) = n(\text{N}_2\text{O})_{\infty} - n(\text{N}_2\text{O})$ from which

$$\frac{dp}{dt} = \frac{k}{[\text{H}_3\text{O}^+]} \times \frac{RT}{V} \times (n(\text{N}_2\text{O})_{\infty} - n(\text{N}_2\text{O}))$$

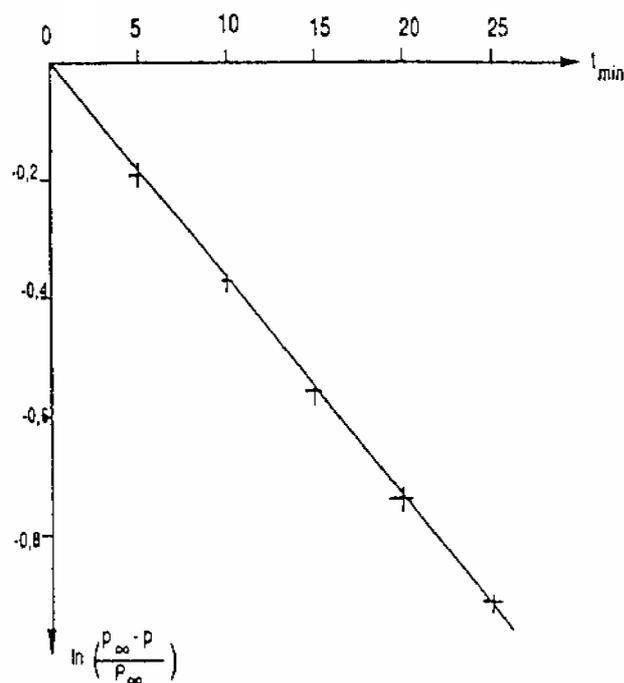
and thus

$$\frac{dp}{dt} = \frac{k}{[\text{H}_3\text{O}^+]} \times (p_{\infty} - p) = k'(p_{\infty} - p)$$

Integration gives $p = p_{\infty} (1 - e^{-k't})$

wherefrom: $e^{-k't} = 1 - p/p_{\infty}$

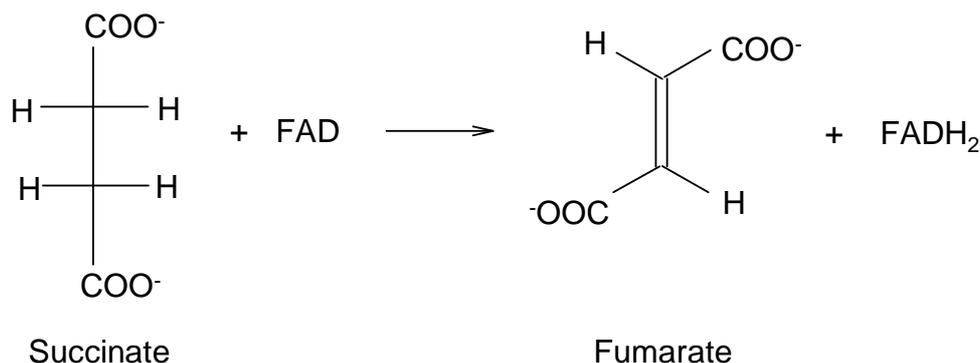
5.6



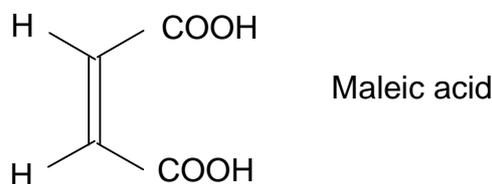
5.7 The graph of $f(x) = \ln(1 - p/p_{\infty}) = -k't$ is a straight line with the slope k' shown in Fig. k' was determined to be $3.7 \times 10^{-2} \text{ min}^{-1}$.

PROBLEM 6**BIO-ORGANIC CHEMISTRY**

The reaction of dehydrogenation of succinate to fumarate is a one step in the tricarboxylic Krebs cycle, catalysed by the enzyme succinic dehydrogenase. Flavine-adenine-dinucleotide, FAD, acts as a coenzyme. The equation of the process:



The stereochemistry of the dehydrogenation of succinate to fumarate has been studied. Consider the enzymatic reaction with the 2,3-dideuteriosuccinates related to the acids or obtained by catalytic deuteration (in the presence of palladium on coal) of fumaric and maleic acids.



6.1 Using Fischer formulae, write down structures for all the possible stereoisomers obtained by catalytic deuteration of maleic and fumaric acids. How many isomers are there? Indicate those that are optically active. Establish a stereochemical relationship between them (compare the isomers two by two). Using Newman projections show the most stable conformation of each isomer.

The proportion of dideuterated fumarate (obtained when each of the above 2-3 dideuterated succinates is submitted to the enzymatic reaction) is 4 % when using fumaric acid as starting molecule, but 48.5 % when using maleic acid.

It is assumed that at the active site, the enzymatic dehydrogenation occurs on the succinate, in the most stable conformation as proposed in 6.1. The dehydrogenation stereochemistry can be *syn* or *anti*.

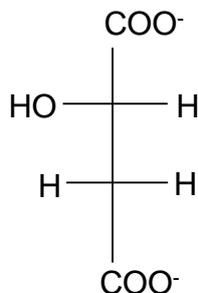
6.2 On the basis of the Newman projections of the most stable conformations of each isomer and the above facts, determine the percentage of dideuterated fumarate formed by *syn* and *anti* dehydrogenation.

(Assume that the percentages of dideuterated fumarate are 0 or 50 %, respectively.)

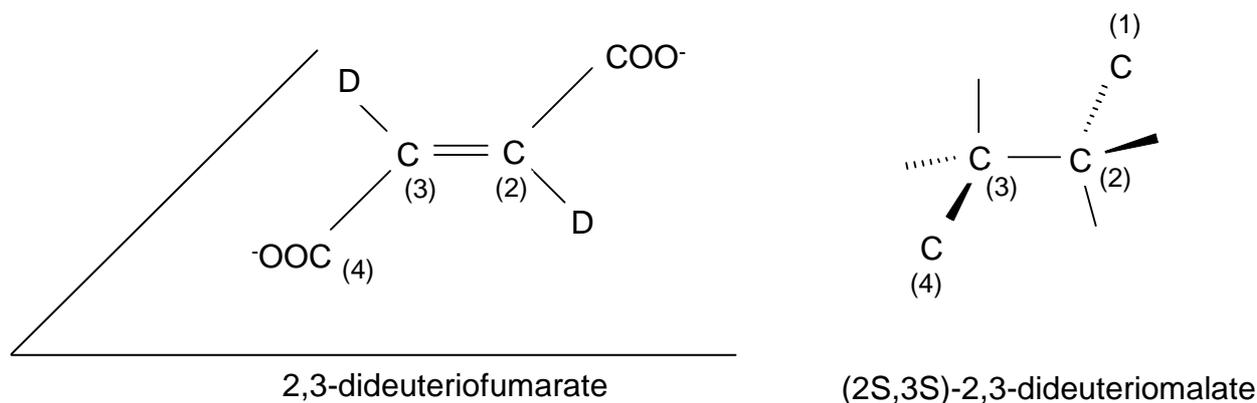
6.3 Show the stereochemistry of the enzymatic dehydrogenation.

In the following step of the Krebs cycle and in the presence of fumarase enzyme, fumarate adds on a water molecule to yield (*S*)-malate (also called as L-malate).

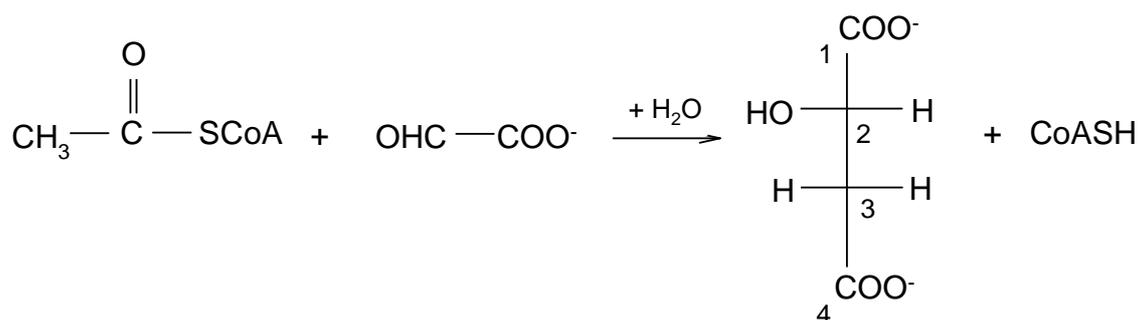
Fischer projection of (*S*)-malate:



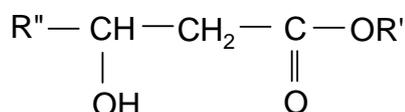
6.4 The 2,3-dideuterofumarate reacts with fumarase to (*2S,3S*)-2,3-dideuteromalate (through addition of water). Show the stereochemical pathway of the reaction. Use the schematic drawing below to answer this question.



The acetylcoenzyme A, CH_3COSCoA reacts with glyoxylate, OHC-CO_2^- , in the presence of malate synthetase enzyme to (*S*)-malate.



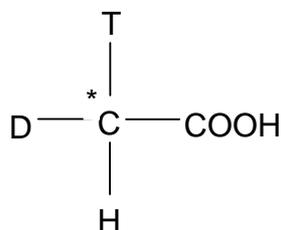
A similar reaction can proceed between an ester $\text{CH}_3\text{COOR}'$ (similar to the thioester CH_3COSCoA) and an aldehyde $\text{R}''\text{CHO}$ (similar to the glyoxylate) in the presence of $\text{R}'\text{-O}^-$ ions. It leads to a β -hydroxyester.



($\text{R}'\text{-O}^-$ enter the reaction as a base to produce an intermediate carbanion from the ester)

6.5 Write the steps of the mechanism.

The enzymatic reaction is carried out using acetylcoenzyme A which is obtained from acetic acid CH_3COOH having *R*-configuration.



(tritium $\text{T} = {}^3_1\text{H}$, deuterium $\text{D} = {}^2_1\text{H}$)

The formed (*S*)-malate is dehydrated (the reverse reaction of question 6.4) by an enzymatic reaction.

6.6 What enzyme can be used?

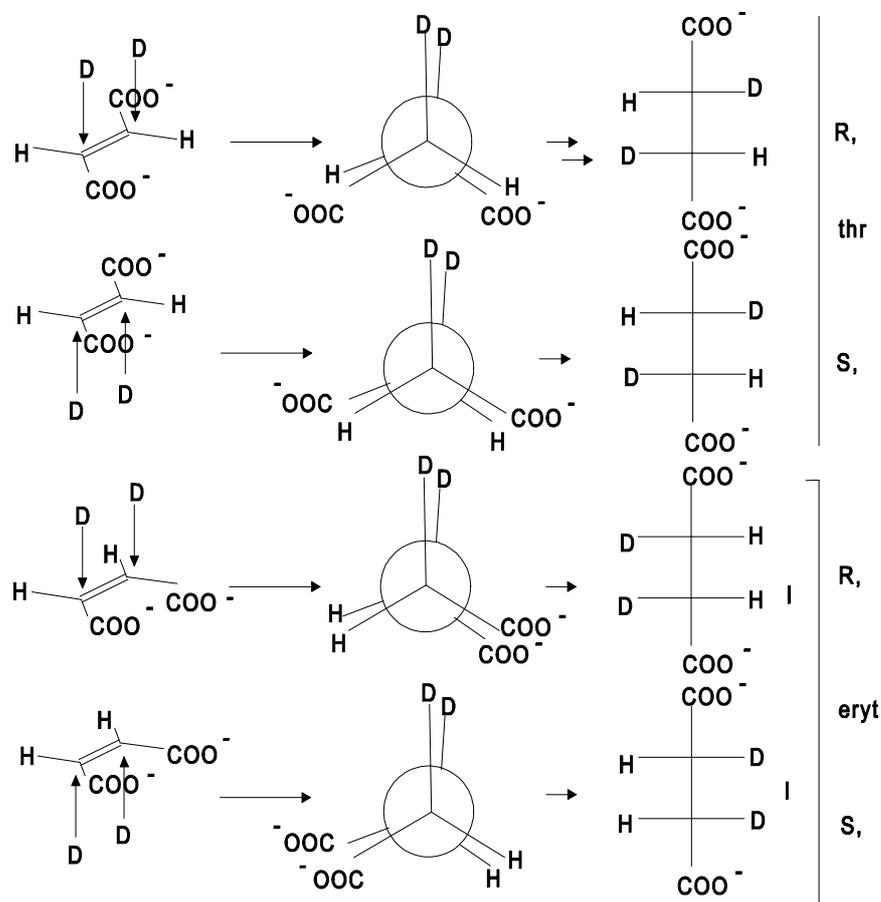
The major product is monotritiated fumarate (79%) with 21 % untritiated fumarate.

6.7 Write down the Fischer projections of the two possible structures of the major product (*S*)-malate arising from the acetylcoenzyme A which has a labelled acetyl group with *R*-configuration.

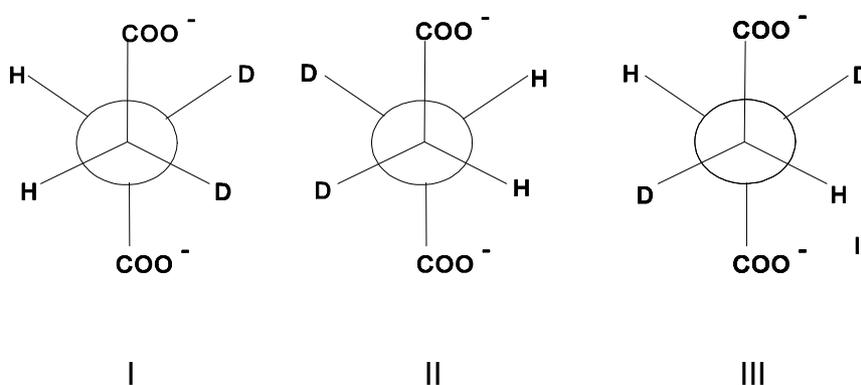
6.8 What would be the products if the starting material has a labelled acetyl group with *S*-configuration?

SOLUTION

6.1 There are three isomers. The catalytic deuteration is a syn deuteration.



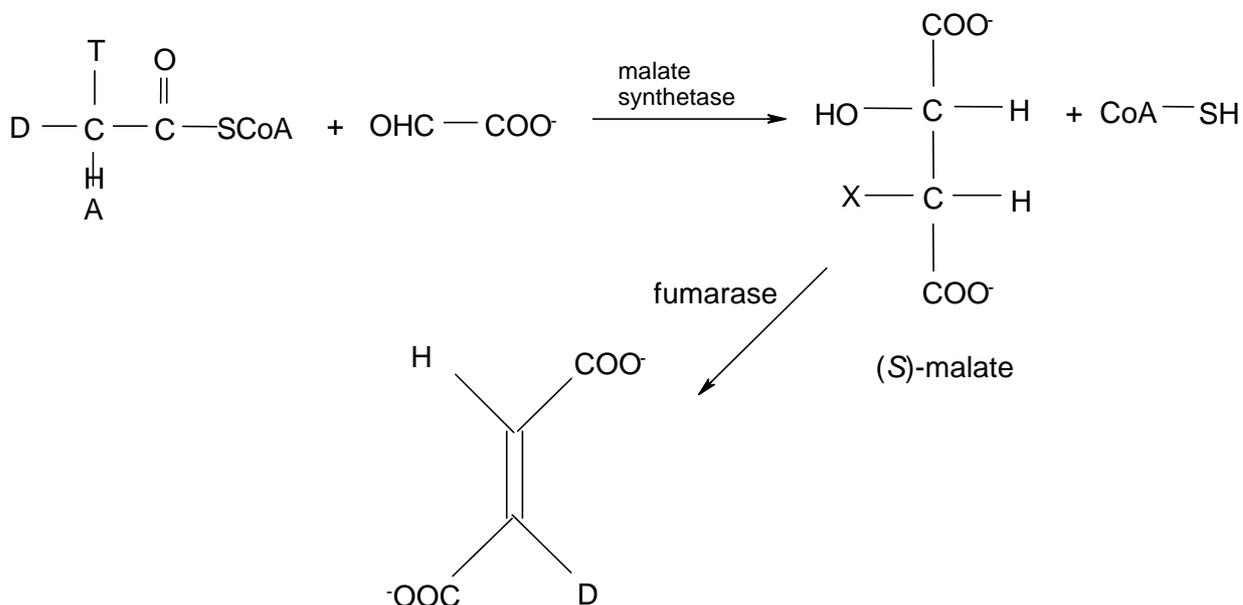
The most stable conformation for succinates is the anti form, since the distance between the bulky COO⁻ groups is maximal:



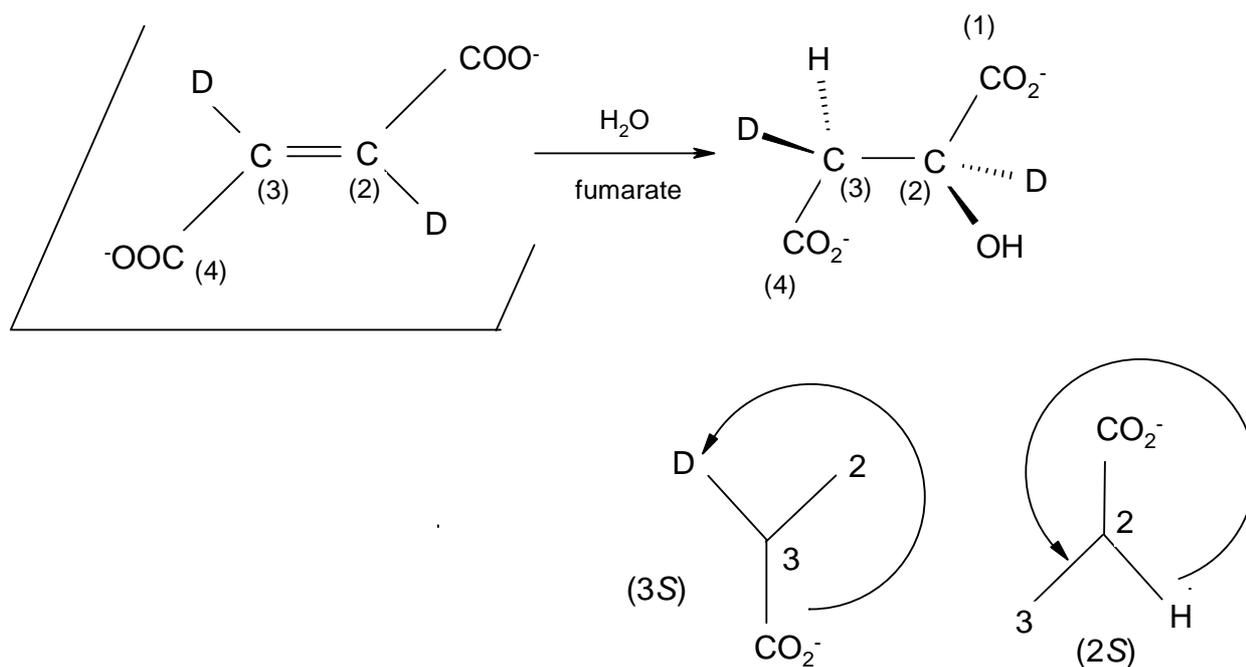
I and II are enantiomers, II and III are a meso isomer, thus there are in total three isomers (two enantiomers and one meso form). Each threo and the meso form are diastereomers.

6.2 Considering the Newman projections of the three isomers it is clear that *syn* elimination of I and II leads either to fumarate containing no D or to dideuterated fumarate (percentage of dideuterated fumarate is thus 50 %) whereas *anti* elimination leads to monodeuterated fumarate. Concerning the experiment 4 % of dideuterated fumarate indicates that *anti* elimination occurs. *Syn* - elimination of the meso-form only leads to monodeuterated fumarate, whereas *anti*-elimination gives 50 % normal and 50% dideuterated fumarate. This is in accordance with the experiment where 48.5% of dideuterated fumarate are obtained after enzymatic dehydrogenation of the meso isomer formed from maleic acid.

6.3 The enzymatic dehydrogenation is a anti elimination as shown above.

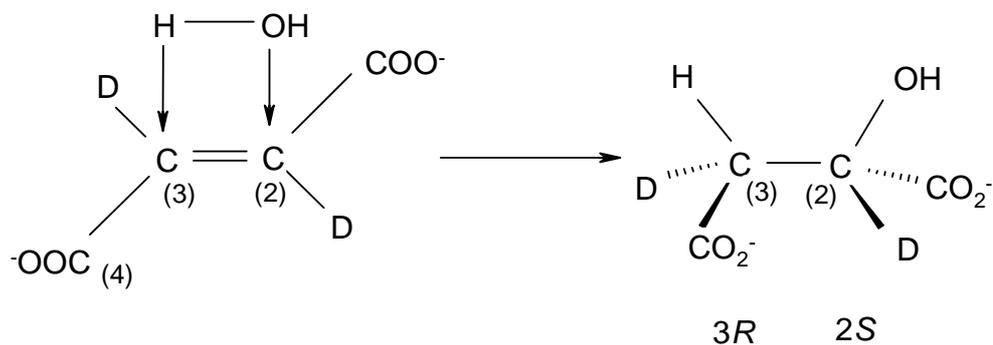


6.4



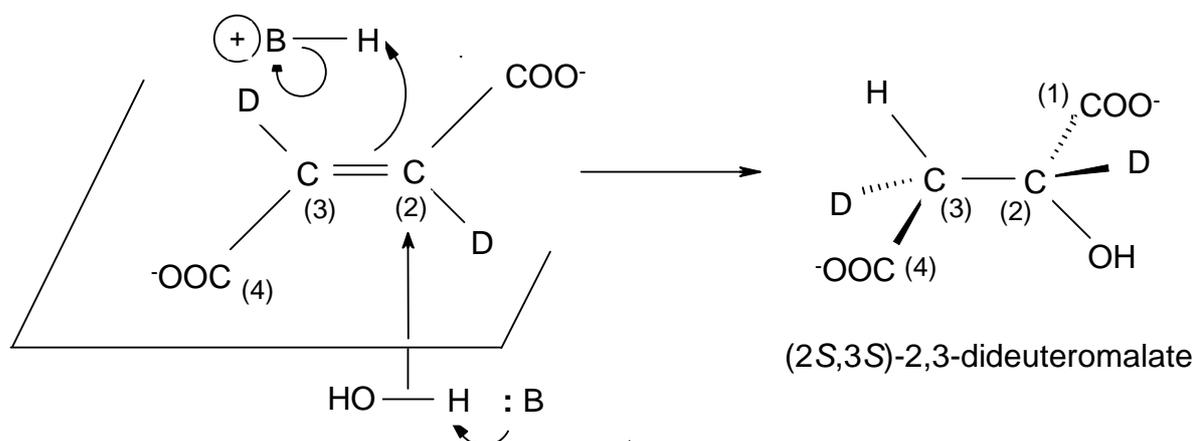
Stereospecific addition, *syn* or *anti*

Syn addition:

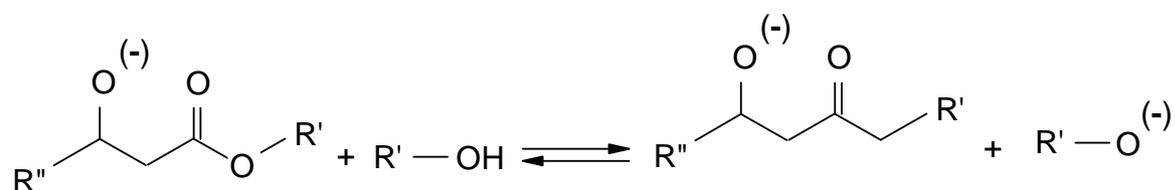
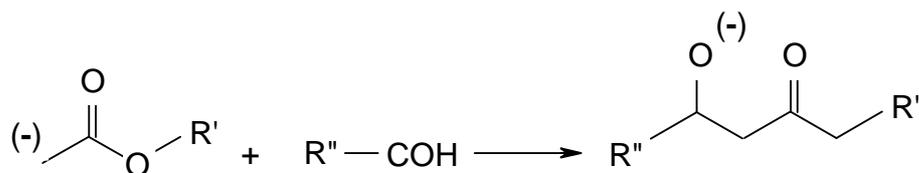
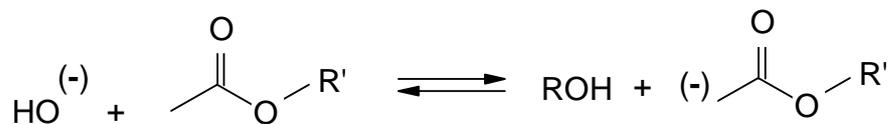


Syn addition would yield 2S, 3R or 2R, 3S

Anti addition:

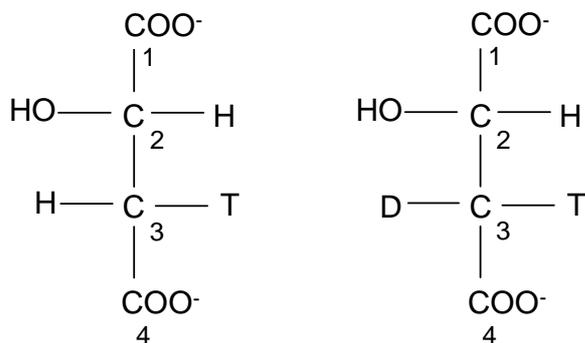


6.5

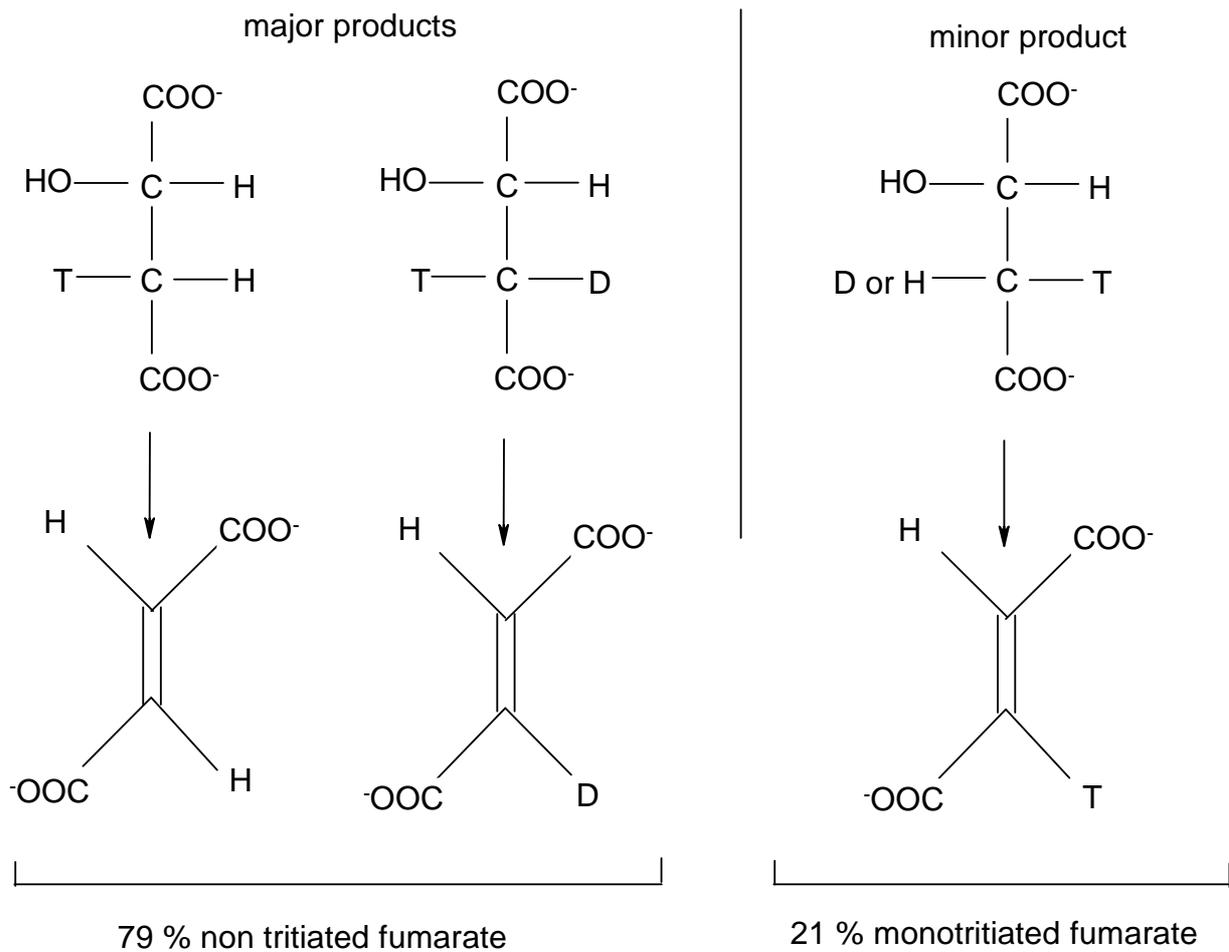


6.6 We would have (2*R*) (3*R*) if the enzyme did not produce enantiospecific addition.
Thus: enantiospecific addition *anti*.

6.7 Thus Y = T and X = H or D; then the two Fischer projections are:



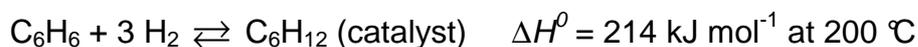
6.8 Starting from an acetyl group of *S* configuration one obtains a configuration inversion of carbon 3 for L-malate and two possible structures are:



PROBLEM 7

In this problem tick the appropriate box in the tables of the answer sheet.

Hydrogenation of benzene to cyclohexane is performed in continuous reactors. The reaction is as follows:



Two basic types of continuous reactors are examined: a continuous plug flow reactor and a continuous stirred reactor.

The continuous plug flow reactor (Fig. 1)

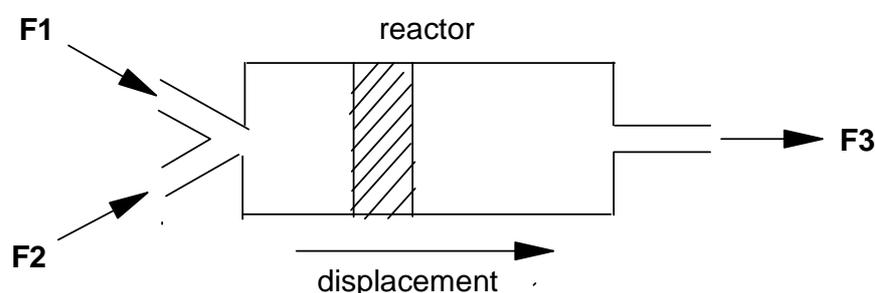


Fig. 1

The reagents are introduced and mixed at the inlet of the reactor (flow F1 and F2). Each slice of the reaction medium (marked zone in the diagram) moves along inside the plug flow reactor without mixing with the others and exits from the reactor (flow F3). When the flow has stabilized, concentrations and conditions are time-independent but dependent on the location in the reactor.

The continuous stirred reactor (Fig. 2)

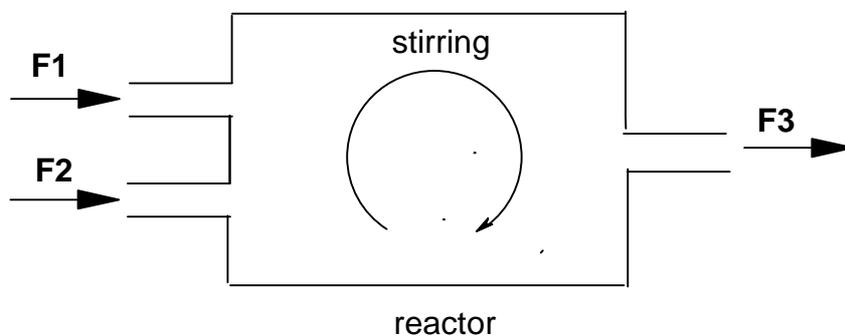


Fig. 2

The reagents are introduced into the reactor (flows F1 and F2). Inside the reactor they are stirred perfectly and instantaneously. When the flow is stabilized, concentrations and conditions are time-independent and identical at every point of the reactor.

The differential yield of hydrogenation (Y) is given by $Y = -\frac{d([C_6H_{12}])}{d([C_6H_6])}$.

The proportion of benzene already hydrogenated is given by $p = \frac{[C_6H_{12}]}{[C_6H_{12}] + [C_6H_6]}$.

The relationship between p and Y is shown in Fig. 3.

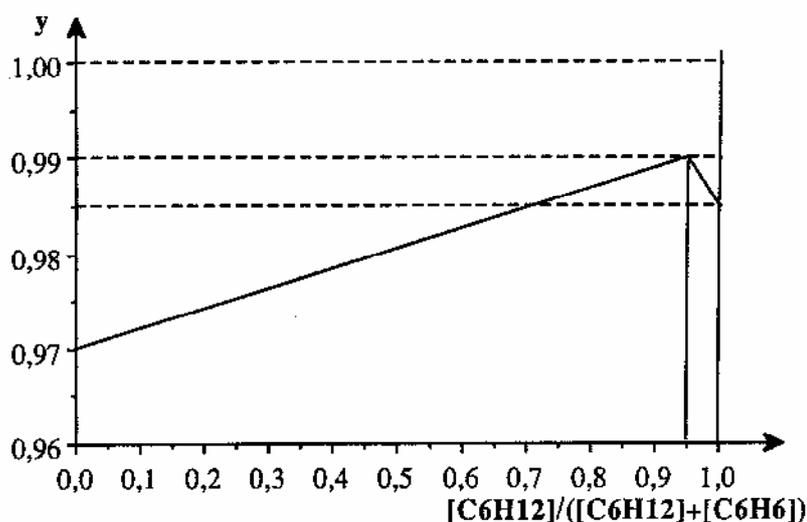


Fig. 3

The aim is to hydrogenate almost all the benzene, i.e. $0.9 \leq p \leq 1$ with the best mean yield

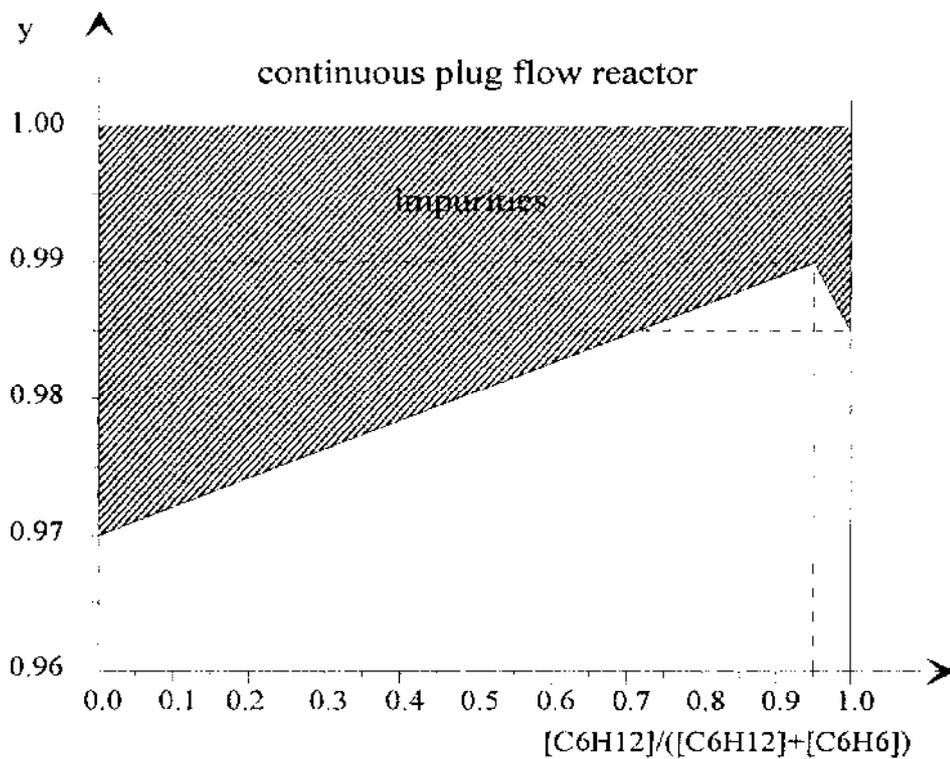
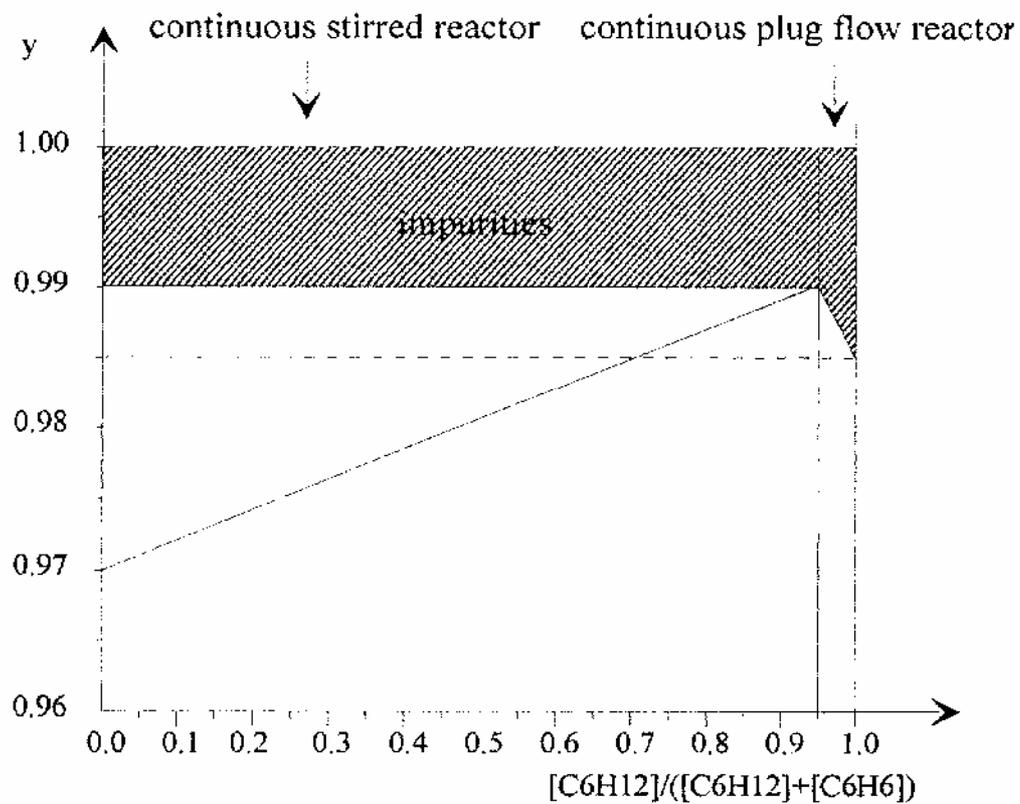
$$Y = -\frac{\Delta[C_6H_{12}]}{\Delta[C_6H_6]}$$

- 7.1** What is the value of p in a continuous stirred reactor leading to the maximal mean yield of hydrogenation? What is the maximal value of Y ?
- 7.2** For a continuous plug flow reactor, give a rough value of Y for $0.9 \leq p \leq 1$:
 $Y = 0.97, 0.98, 0.99$ or 1.00 ?
- 7.3** Represent by grey shading in the graph (Fig. 3) the quantities of benzene lost in installation P (plug flow reactor) and installation MP (stirred reactor + plug flow reactor).
- 7.4** Give the amount of annual benzene lost in installation P and MP assuming an annual consumption of 100 000 tons of benzene.

SOLUTION

- 7.1** In the continuous stirred reactor, concentrations are time independent and identical at every point. This means that the differential yield y for a given p is identical to the mean yield Y . A maximum mean yield is therefore obtained for y_{\max} . From the Fig. 1 it's seen that $y_{\max} = 0.99$ with $p = 0.95$.
- 7.2** In a continuous plug flow reactor concentrations are time-independent but dependent upon the location in the reactor. We shall consider a thin slice dx of the reactor at the entrance and at the end of the reactor. At the entrance $[C_6H_6] = 1$ and $[C_6H_{12}] = 0$, thus $p = 0$ and $y = 0.97$. At the outlet of the reactor we have: $[C_6H_6] = 0$ and $[C_6H_{12}] = 1$. So, $p = 1$ and $y = 0.985$. The mean yield is now the average of y over all p , which is 0.98, as one can easily see from the Fig. 1.
- 7.3** In the plug flow reactor, the quantity of benzene lost (not hydrogenated) is $1 - p$. Fig. 1 shows the area that represents the amount of benzene that is not hydrogenated and therefore lost. For the installation MP we first have the amount of benzene lost in the continuous stirred reactor which is always $1 - 0.99 = 0.01$ independent from p up to a point $p = 0.95$. At $p > 0.95$ to the continuous plug reactor has the same loss of benzene as already indicated in the Fig 1 below.
- 7.4** In the plug reactor the percentage of benzene lost is 2 % (the best mean yield is 0.98), therefore the amount of benzene annually lost is 2000 tons.
In a MP installation, the yield of hydrogenation is 0.99 (except for $0.95 < p < 1$ where it slightly decreases to 0.985, but this can be neglected) and therefore, the overall mean yield of hydrogenation is also 0.99.
The amount of benzene annually lost is therefore 1000 tons.

Figure 1

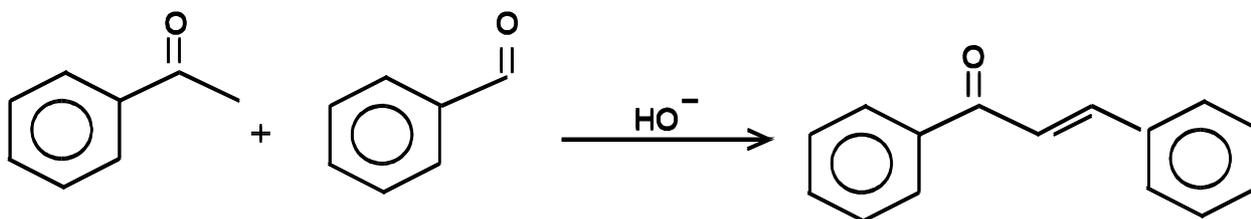


PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis involving Carbanions Chalcone

The aim of this experiment is to condense acetophenone and benzaldehyde in a mixed aldol condensation. After spontaneous dehydration, an α,β - unsaturated ketone is obtained: the chalcone, 1,3-diphenylprop-2-en-1-on.



a) *Starting the condensation reaction*

In a 250 cm³ ground neck Erlenmeyer (conical) flask, dissolve about 5 g of potassium hydroxide, KOH, (50 pellets) in 30 cm³ of water, then add slowly under stirring 20 cm³ of ethanol. From the automatic dispensers, add 9.6 g (0.08 mol = 9.5 cm³) of acetophenone and 8.5 g (0.08 mol = 8.5 cm³) of benzaldehyde. Set up a condenser in the vertical reflux position and reflux vigorously while stirring the mixture with the magnetic stirrer for an hour.

b) *Isolation of the crude chalcone*

After refluxing, cool the contents of the Erlenmeyer flask in an ice bath. The chalcone should crystallize. If crystals do not appear, scratch the inside wall of the flask with a glass rod. Collect the crystals in a Büchner funnel, wash them with a little ice cold ethanol, then air dry and weigh the crystals.

c) *Recrystallization of the chalcone*

Recrystallize this crude chalcone from ethanol, using a 100 cm³ beaker. Use the heating plate located in the hood (fume chamber). When the crystallization is over (wait long enough and scratch if necessary), collect the crystals in a Büchner funnel, and air dry them.

Give your entire product to the supervisor who will measure its mass and melting-point.

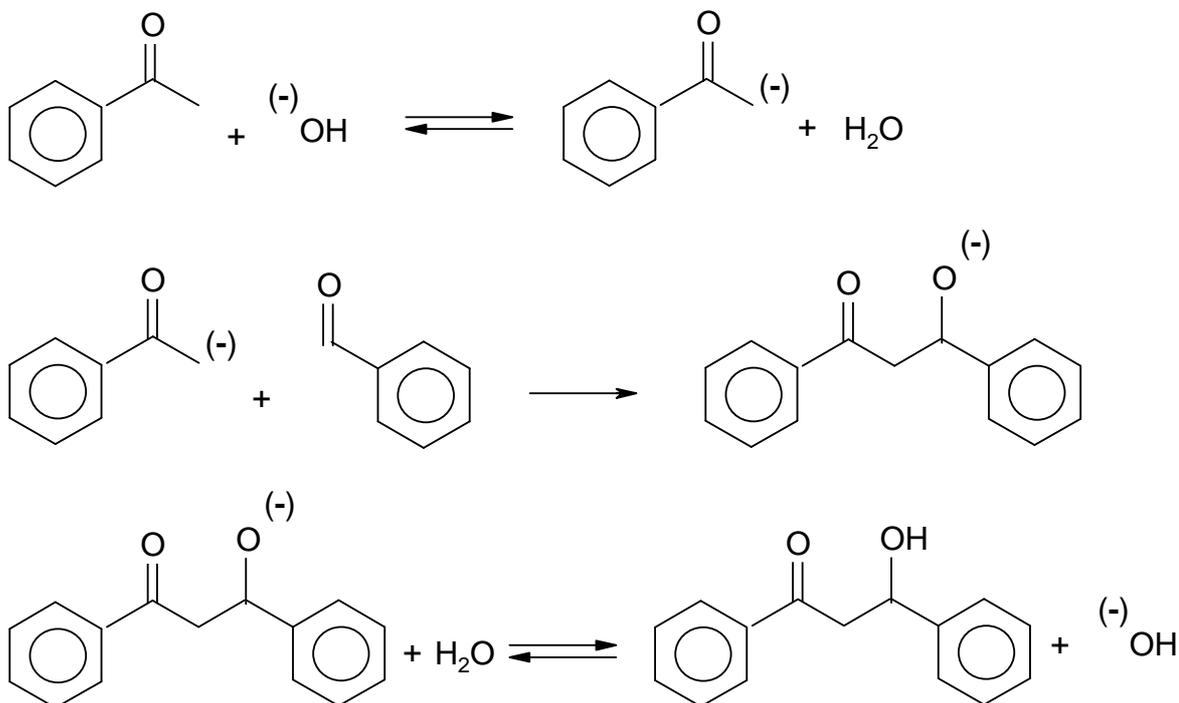
Do not breathe the vapour while recrystallizing and measuring the melting point. It contains irritating chalcone!!!

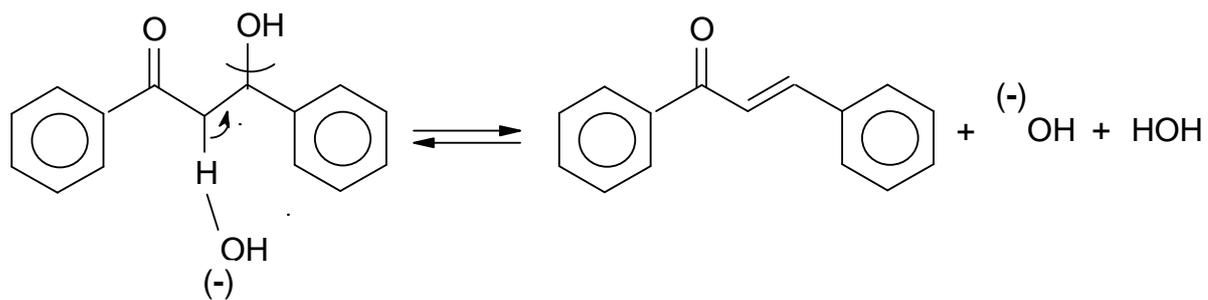
Questions:

- 1.1 Write the mechanism for this reaction.
- 1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.
- 1.3 Calculate the yield of recrystallized product based on starting material and calculate the efficiency of the recrystallization process.

SOLUTION

1.1





PROBLEM 2 (Practical)Qualitative Analysis

Equipment:

Five flasks are labelled 2.1 through 2.5. Each contains an aqueous solution of a colourless metal nitrate. Except for silver nitrate, the concentrations of the nitrates used to prepare these solutions, are all 0.1 mol dm^{-3} .

The solutions are: aluminium(III) nitrate
 calcium(II) nitrate
 lead(II) nitrate
 silver(I) nitrate
 zinc(II) nitrate

Moreover, available are pH indicator paper and the following three reagents of a concentration of about 5 mol dm^{-3} , contained in flasks labelled 2.6 through 2.8.

2.6 : hydrochloric acid,

2.7 : aqueous ammonia solution,

2.8 : sodium hydroxide solution.

Beware: these solutions are all concentrated and corrosive.

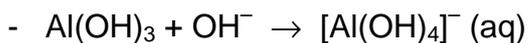
Tasks:

- 2.1 Carry out reactions between each reagent and each solution. For each of the solutions 2.1 through 2.5, record your observations for each reaction observed.
- 2.2 Write the name of the cation contained in each of the solutions 2.1 through 2.5 in the corresponding space on the answer sheet.
- 2.3 For each cation identified, write the equation for each reaction observed.

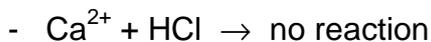
SOLUTION

2.1 Aluminium(III) nitrate

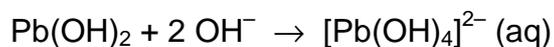
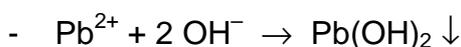
- $\text{Al}^{3+} + \text{HCl} \rightarrow \text{no reaction}$
- $\text{Al}^{3+} + 3 \text{NH}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 \downarrow + 3 \text{NH}_4^+$
- $\text{Al}^{3+} + 3 \text{OH}^- \rightarrow \text{Al}(\text{OH})_3 \downarrow$



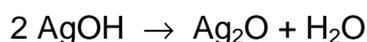
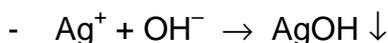
calcium(II) nitrate



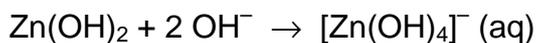
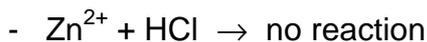
lead(II) nitrate



silver(I) nitrate



zinc(II) nitrate



PROBLEM 3 (Practical)Titration of Oxygen Dissolved in Water

(Winkler's method)

In aqueous alkaline solution, dissolved oxygen oxidizes manganese(II) hydroxide to hydrated manganese(III) oxide (written as $\text{Mn}(\text{OH})_3$ for simplification). In acidic solution, manganese(III) ions oxidize iodide ions to iodine. The iodine formed is titrated with a sodium thiosulphate solution.

Data:

Redox couple	Electrode potentials (in V)	
	at $pH = 0$	at $pH = 14$
$\text{Mn}^{3+} / \text{Mn}^{2+}$	1.51	
$\text{Mn}(\text{OH})_3 / \text{Mn}(\text{OH})_2$		0.13
$\text{O}_2 / \text{H}_2\text{O}$	1.23	0.39
I_2 / I^-	0.62	0.62
$\text{S}_4\text{O}_6^{2-} / \text{S}_2\text{O}_3^{2-}$	0.09	0.09

Solubility products: $K_{sp}(\text{Mn}(\text{OH})_2) = 1 \times 10^{-13}$

$$K_{sp}(\text{Mn}(\text{OH})_3) = 1 \times 10^{-36}$$

Gas constant: $R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ *Procedure:*

Preliminary remarks: To reduce volume variations, the reagents are added either as solids (sodium hydroxide pellets ...), or as concentrated solutions (sulphuric acid).

1. The water to be tested is stored in a large container located on the general-use bench. Place two glass beads into a 250 cm^3 ground top Erlenmeyer (conical) flask. Fill it to the rim with the water to be tested. At this stage of the manipulation the

Erlenmeyer flask should be standing in the basin provided to avoid overflow of water onto the bench. Measure the temperature of the water.

2. Add to the water, avoiding any loss of reagent:
 - a) 2 g of manganese(II) chloride, preweighed within a decigram and contained in the bag.
 - b) about 8 pellets of sodium hydroxide (yielding a basic medium, $pH = 14$). The pellets will be found on the general-use bench.
3. Stopper the Erlenmeyer flask, avoiding air bubbles, and swirl it until complete dissolution of the sodium hydroxide and of the manganese chloride has occurred. A brown precipitate forms.
4. Let the flask stand for at least 30 minutes.
5. Open the Erlenmeyer flask, add concentrated sulphuric acid dropwise, stirring with a glass rod until the solution is definitely acidic (check with the pH indicator paper); make sure that nearly all the precipitate has disappeared.
Sulphuric acid will be found on the general-use bench.
6. Add to the Erlenmeyer flask 3 g of potassium iodide, preweighed within a decigram and contained in a bag. Stopper the flask and shake it until the potassium iodide has dissolved. The solution should now be clear.
7. Remove a 50 cm^3 sample of the solution and titrate it with a $X \text{ mol dm}^{-3}$ sodium thiosulphate solution (the numerical value of X will be shown on the board). For this titration, the endpoint can be determined using the indicator thiodene which is equivalent to starch. A small quantity of this solid indicator should be dissolved in the solution being titrated just prior to the endpoint.

Questions:

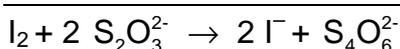
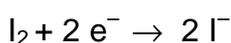
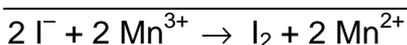
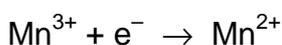
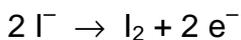
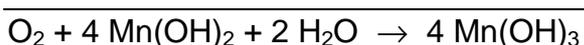
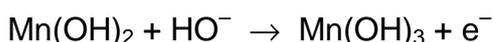
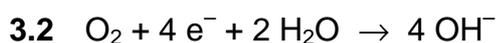
- 3.1 Justify that the oxidation of manganese(II) by dissolved oxygen is possible only in alkaline solution.
- 3.2 Write the equation of the reaction between:
 - dissolved oxygen and manganese(II) hydroxide (in alkaline solution),
 - manganese(III) ions and iodide ions,
 - iodine and thiosulphate.
- 3.3 Record the volume of thiosulphate required to reach the endpoint.

- 3.4 Derive an expression that relates the dissolved oxygen concentration in water (expressed as mol dm⁻³) to the volume in cm³ of thiosulphate added at the endpoint. Determine that concentration for the water tested.

Deduce the volume of oxygen (in cm³), determined at 0 °C and at a pressure of 101,325 Pa, contained in a litre of water (measured at ambient temperature). Give the temperature of the water.

SOLUTION

3.1 $E^0(\text{O}_2/\text{H}_2\text{O}) > E^0(\text{Mn(III)/Mn(II)})$ at $\text{pH} = 14$



3.4 $1 \text{ mol O}_2 \hat{=} 4 \text{ mol Mn(II)} \hat{=} 4 \text{ mol Mn(III)}$

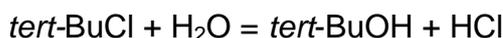
$$4 \text{ mol Mn(III)} \hat{=} 4 \text{ mol I}^- \hat{=} 2 \text{ mol I}_2$$

$$2 \text{ mol I}_2 \hat{=} 4 \text{ mol S}_2\text{O}_3^{2-}$$

$$c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-}) = 4 \times c(\text{O}_2) \times 50$$

PROBLEM 4 (Practical)Kinetics of an S_N1 Reaction

In an aqueous ethanolic solution, *tert*-butyl chloride (2-chloro-2-methylpropane) undergoes an S_N1 nucleophilic substitution reaction leading to the formation of 2-methylpropan-2-ol and hydrochloric acid:



The rate of the reaction is given by

$$\frac{d[\text{HCl}]}{dt} = k_1 [\textit{tert}\text{ BuCl}]$$

The aim of this experiment is to determine the rate constant k_1 at ambient temperature.

Procedure:

- Using a pipette transfer 2.0 cm³ of *tert*-butyl chloride (flask 4.1 on the general-use bench) into a clean and dry 250 cm³ ground neck Erlenmeyer (conical) flask.
- As soon as possible add 148 cm³ (measure with the graduated cylinder) of the aqueous ethanol solution standing on the general-use bench (flask 4.2).
- Stopper the Erlenmeyer flask and stir vigorously using the magnetic stirrer. Start your timer. Note carefully the temperature, T(0), of the solution.
- After approximately 5, 15, 25, 35, 45, 55 min (determined accurately), transfer 10.0 cm³ samples using a pipette into 20 cm³ of a mixture of ice and acetone (propanone).

Add 2 drops of bromothymol blue and titrate the liberated acid with a solution of Y mol dm⁻³ aqueous sodium hydroxide (Y will be shown on the board).

Questions:

- 4.1** The concentrations of *tert*-BuCl at time $t = 0$ and at time t are linked by the following relationship:

$$\ln \frac{[\textit{tert}\text{BuCl}]_0}{[\textit{tert}\text{BuCl}]_t} = k_1 \cdot t$$

Establish the theoretical expression:

$$\ln \frac{V_\infty}{V_\infty - V} = k_1 t$$

where V stands for the volume of sodium hydroxide used at time t and $V(8)$ for the corresponding value at $t(8)$.

$$t_{\infty} = t(8); \quad V_{\infty} = V(8)$$

4.2 Calculate $V(8)$ (density of *tert*-BuCl at 20 °C: 850 kg m⁻³, molar mass of *tert*-BuCl: 92.5 g mol⁻¹).

4.3 Fill in the table on the answer sheet whose columns will be:

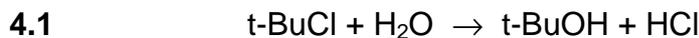
$$t(\text{min}), \quad V(\text{cm}^3), \quad V_{\infty}, \quad V, \quad \frac{V_{\infty}}{V_{\infty} - V}, \quad \ln \frac{V_{\infty}}{V_{\infty} - V}$$

Draw the curve

$$\ln \frac{V_{\infty}}{V_{\infty} - V} = f(t)$$

4.4 Determine the value of k_1 (give the value of $t(0)$).

SOLUTION



$t = 0$	$(\text{t-BuCl})_0$	
t	(t-BuCl)	$(\text{t-BuCl})_0 - (\text{t-BuCl})$
$t(8)$		$(\text{t-BuCl})_0$

$$\frac{d(\text{HCl})}{dt} = -\frac{d(\text{t-BuCl})}{dt} = k_1 (\text{t-BuCl})$$

$$\ln \frac{(\text{t-BuCl})_0}{(\text{t-BuCl})} = k_1 t$$

t :

$$c(\text{HCl}) = c_0(\text{t-BuCl}) - c(\text{t-BuCl}) = \frac{V(\text{NaOH}) \times c(\text{NaOH})}{V(\text{HCl})} = \frac{V \times Y \times 10^{-2}}{10}$$

$t(8)$:

$$c(\text{HCl}) = c_0(\text{t-BuCl}) = \frac{a Y}{10}$$

$$c(\text{t-BuCl}) = \frac{(a - V) Y}{10}$$

$$\ln \frac{c_0(\text{t-BuCl})}{c(\text{t-BuCl})} = \ln \frac{a}{a - V} = k_1 t$$

$$4.2 \quad n_0(\text{t-BuCl}) = \frac{1.70}{92.5} \quad M(\text{t-BuCl}) = 92.5 \text{ g mol}^{-1}$$

$$Y \times a \times 10^{-3} = \frac{10}{150} \times n_0(\text{t-BuCl})$$

$$a_{(\text{ml})} = \frac{170}{Y \times 10^{-3} \times 15 \times 92.5}$$

23rd



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE TWENTY-THIRD INTERNATIONAL CHEMISTRY OLYMPIAD 7–15 JULY 1991, LODZ, POLAND

THEORETICAL PROBLEMS

PROBLEM 1

- 1.1 Show that 0.1 mol of Ti_2S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.
- 1.2 Show that 0.1 CuS dissolves in a 1 M HNO_3 but not in a 1 M HCl solution.

Information:

Assume that Cu^{2+} ions do not form stable complexes with chloride ions in aqueous solutions.

$$E^0(\text{S}/\text{S}^{2-}) = -0.48 \text{ V} \quad E^0(\text{NO}_3^-/\text{NO}_{(\text{aq})}) = 0.96 \text{ V}$$

$$pK_a(\text{H}_2\text{S}) = 7 \quad pK_a(\text{HS}^-) = 13$$

$$K_{sp}(\text{Ti}_2\text{S}) = 1 \times 10^{-20} \quad K_{sp}(\text{CuS}) = 1 \times 10^{-35}$$

Solubility of NO in water (298 K): $2.53 \times 10^{-2} \text{ mol dm}^{-3}$

Solubility of H_2S in water (298 K): 0.1 mol dm^{-3}

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad F = 96\,487 \text{ C mol}^{-1}$$

SOLUTION

- 1.1 Solubility condition: $[\text{Ti}^+]^2 [\text{S}^{2-}] \leq 1 \times 10^{-20}$

$$[\text{Ti}^+] = c(\text{Ti}^+) = 0.2 \text{ mol dm}^{-3}$$

$$c(\text{S}^{2-}) = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}] = [\text{S}^{2-}] \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right) = 0.1 \text{ mol dm}^{-3}$$

$$[S^{2-}] = \frac{0.1}{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}} \Rightarrow$$

For a strong monoprotic acid (1 mol dm⁻³) and [H⁺] ≈ 1.

Then

$$1 + 10^{13} [H^+] \ll 10^{20} [H^+]^2 \quad \text{and} \quad [S^{2-}] \approx \frac{0.1}{1 \times 10^{20}}$$

$$[Ti^{+}]^2 [S^{2-}] = \frac{(0.2)^2 \times 0.1}{1 \times 10^{20}} = 4 \times 10^{-23} < K_s(Ti_2S)$$

Thus, 0.1 mol of Ti₂S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.

1.2

- Dissolving CuS in 1 M solution HCl (non-oxidizing and non-complexing acid):

$$c(Cu^{2+}) = 0.1 \text{ mol dm}^{-3}$$

$$[Cu^{2+}] = 0.1$$

$$c(S^{2-}) = 0.1 \text{ mol dm}^{-3}$$

Similarly as in part (1.1):

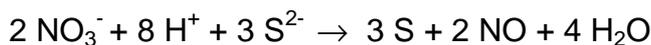
$$[S^{2-}] = \frac{0.1}{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}}$$

$$[S^{2-}] \approx \frac{0.1}{1 \times 10^{20}}$$

$$[Cu^{2+}] [S^{2-}] = \frac{(0.1)^2 \times 0.1}{1 \times 10^{20}} \approx 1 \times 10^{-23} > K_s(CuS)$$

Conclusion: 0.1 mol CuS does not dissolve in 1 M solution HCl.

- When dissolving 0.1 mol CuS in 1 M HNO₃ an additional redox process occurs: the oxidation of S²⁻ to S.



The emf of this reaction is $\Delta E = E_1^0 - E_2^0 = (0.96 + 0.48) = \underline{1.44 V}$

$$\log K = \frac{\Delta G}{RT} = \frac{nF}{RT} \Delta E = \frac{n_1 n_2 (E_1^0 - E_2^0)}{0.0591} \cong 144 \quad K = 1 \times 10^{144}$$

The equilibrium constant of this process can also be written in the form:

$$K = \frac{[\text{NO}]^2}{[\text{NO}_3^-]^2 [\text{H}^+]^8 [\text{S}^{2-}]^3}$$

From the above equilibrium follows that $[\text{S}^{2-}] = \sqrt[3]{\frac{K [\text{NO}_3^-]^2 [\text{H}^+]^8}{[\text{NO}]^2}}$

Since $[\text{NO}_3^-] = [\text{H}^+] = 1$

$$[\text{S}^{2-}] = \sqrt[3]{\frac{K}{[\text{NO}]^2}}$$

$c_{\text{CuS}} = [\text{S}] + [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$

$$[\text{S}^{2-}] = \frac{c_{\text{CuS}}}{1 + \frac{[\text{H}^+]}{K_1} + \frac{[\text{H}^+]^2}{K_1 K_2} + \sqrt[3]{\frac{K}{[\text{NO}]^2}}}$$

However

$$1 + \frac{[\text{H}^+]}{K_1} + \frac{[\text{H}^+]^2}{K_1 K_2} \ll \sqrt[3]{\frac{K}{[\text{NO}]^2}} = \sqrt[3]{\frac{1 \times 10^{144}}{(0.0253)^2}} = 1.16 \times 10^{49}$$

$$[\text{S}^{2-}] = \frac{0.1}{1.16 \times 10^{49}} = 8.62 \times 10^{-51}$$

$$[\text{Cu}^{2+}] [\text{S}^{2-}] = 0.1 \times 8.62 \times 10^{-51} = 8.62 \times 10^{-52} \ll K_{\text{sp}}(\text{CuS}) (= 1 \times 10^{-35})$$

Conclusion: CuS dissolves in 1 M solution of HNO₃.

PROBLEM 2

A polymer **X** contains 88.25 % C and 11.75 % H. In dilute solutions it reacts with bromine and ozone. The thermal degradation of **X** produces a volatile liquid **Y** in 58 % yield. **Y** starts boiling at 34 °C and contains 88.25 % C and 11.72 % H. Some higher boiling products are formed both from the cracking of **X** and from Diels-Alder type cyclization of **Y**. The vapour of **Y** was 34 times as dense as hydrogen.

The product of bromination of **Y** yields a compound containing 82.5 % bromine by mass. Ozonolysis of **Y** followed by mild reduction gave **A** and **B** in a molar ratio **A** : **B** = 2 : 1. Only compound **B** gave a positive result for the iodoform reaction.

2.1 Determine the molecular formula and the molar mass of **Y**.

2.2 Show the structures of compounds **Y**, **A**, and **B**.

2.3 Give an equation for the reaction of **Y** with bromine.

In the catalytic hydrogenation of 13.6 g of **X**, 0.2 mole of hydrogen was absorbed. Ozonolysis of **X** followed by mild reduction yielded compound **Z** (60.0 % C, 8.0 % H).

2.4 Give the molecular formula of **Z** and the degree of unsaturation of **X**.

Compound **Z** gave a positive reaction with Fehling's solution. Mild oxidation of **Z** gave an acid **C**. A solution of acid **C** was titrated with aqueous KOH solution (phenolphthalein as indicator). 0.001 mol KOH was necessary for neutralization of 0.116 g of **C**.

In the iodoform reaction a probe 2.90 g of **C** yielded 9.85 g of iodoform. In addition, the alkaline filtrate yielded compound **D** upon acidification.

2.5 What is the molar mass of **C** and what functional groups are present in **Z**?

When heated, **D** loses water to form **E**. Both **D** and **E** react with an excess of acidified ethanol to **F** (C₈H₁₄O₄).

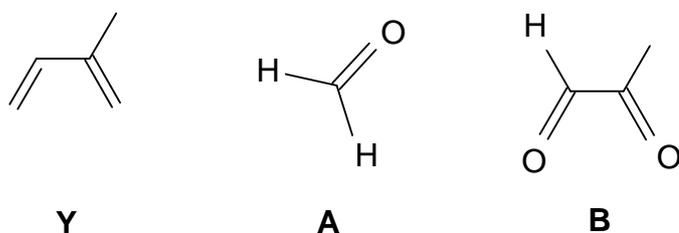
2.6 Sketch the structures of **C**, **D**, **E**, **F** and **Z**.

2.7 **X** exists in isomeric forms which are stereoregular. Show the structure (containing at least 3 monomer units) for two possible stereoisomers of **X**.

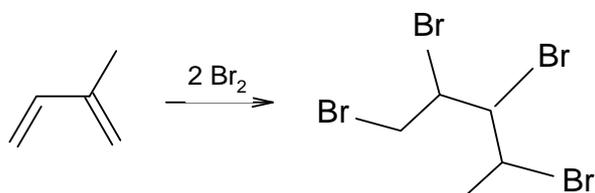
SOLUTION

2.1 $Y = \text{Isoprene, } C_5H_8, M = 68 \text{ g mol}^{-1}$

2.2



2.3

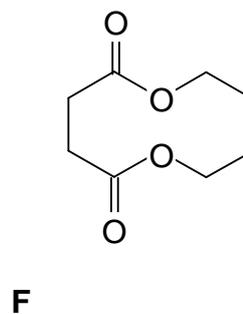
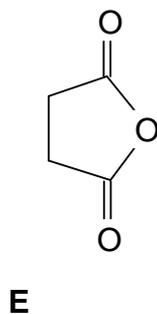
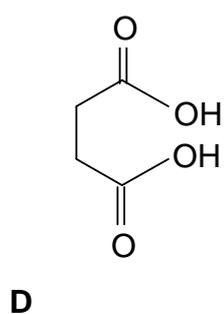
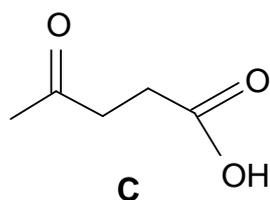


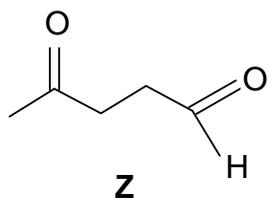
2.4 $Z = C_5H_8O_2$

There is one double bond per monomer unit.

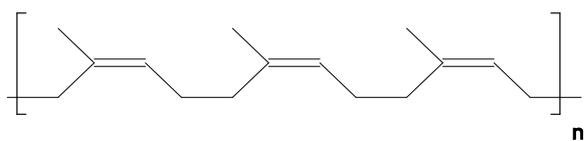
2.5 The molar mass of **C** is 116 g mol^{-1} . **Z** must be a keto aldehyde since it contains an aldehyde functional group and a methyl group next to the carbonyl group.

2.6

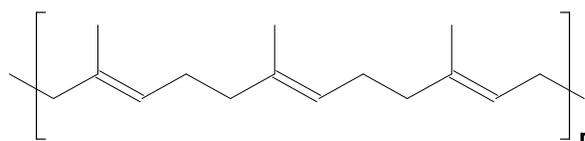




2.7 There are two isomeric form (all cis or all trans) possible:



all-cis (natural caoutchouc)



all-trans

PROBLEM 3

Type II electrodes that are made of a metal covered with a sparingly soluble salt of the metal are dipped into a soluble salt solution containing an anion of the sparingly soluble salt. The silver/silver chloride (Ag, AgCl/Cl⁻) and the calomel electrode (Hg, Hg₂Cl₂/Cl⁻) are examples of such electrodes. The standard emf of a cell built of those electrodes (-) Ag,AgCl/Cl⁻ || Hg₂Cl₂/Hg (+) is $E^0 = 0.0455 \text{ V}$ at $T = 298 \text{ K}$. The temperature coefficient for this cell is $dE^0/dT = 3.38 \times 10^{-4} \text{ V K}^{-1}$.

3.1 Give the equations of the reactions taking place at both the cell electrodes and the overall cell reaction.

3.2 Calculate the Gibbs free energy change (ΔG^0) for the process taking place in the cell at 298 K. What does its sign imply?

3.3 Calculate the enthalpy change for the process taking place at 298 K.

$$\Delta S = n F \Delta E / \Delta T.$$

3.4 Knowing the standard potential of Ag/Ag⁺ electrode is $E^0 = 0.799 \text{ V}$ and the solubility product of AgCl $K_{sp} = 1.73 \times 10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between $E^0(\text{Ag}/\text{Ag}^+)$ and $E^0(\text{Ag}, \text{AgCl}/\text{Cl}^-)$.

3.5 Calculate the solubility product of Hg₂Cl₂ knowing that the standard potential of the calomel electrode is $E^0 = 0.798 \text{ V}$.

$$F = 96487 \text{ C mol}^{-1}, \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad T = 298 \text{ K}$$

SOLUTION

3.1 Reduction (calomel electrode (+)): $1/2 \text{ Hg}_2\text{Cl}_2 + e^- \rightarrow \text{Hg} + \text{Cl}^-$
 Oxidation (silver/silver chloride electrode (-)): $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + e^-$
 Summary reaction: $\text{Ag} + 1/2 \text{ Hg}_2\text{Cl}_2 \rightarrow \text{Hg} + \text{AgCl}$

3.2 $\Delta G^0 = -n F E^0 = -96497 \text{ C mol}^{-1} \times 0.0455 \text{ V} = -4.39 \text{ kJ mol}^{-1}$;

Since ΔG^0 is negative, the reaction is spontaneous.

3.3 The change of enthalpy is related to the Gibbs-Helmholtz equation:

$$\begin{aligned}\Delta H &= \Delta G + T\Delta S = -nFE + TnF\left(\frac{\Delta E^0}{\Delta t}\right) = -nF\left(E - T\left(\frac{\Delta E^0}{\Delta t}\right)\right) = \\ &= -96487 \text{ C mol}^{-1} (0.0455 \text{ V} - 298 \text{ K} \times 3.38 \times 10^{-4} \text{ V K}^{-1}) = 5.36 \text{ kJ mol}^{-1}\end{aligned}$$

3.4 For the Ag | Ag⁺ electrode: $E = E^0 + 0.0591 \log[\text{Ag}^+]$

For the Ag, AgCl | Cl⁻ electrode [Ag⁺] is determined by the solubility product:

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]}$$

$$E^0(\text{Ag, AgCl} | \text{Cl}^-) = E^0(\text{Ag} | \text{Ag}^+) + 0.0591 \log K_{sp} = 0.799 - 0.577 = 0.222 \text{ V}$$

3.5 $E^0(\text{Hg, Hg}_2\text{Cl}_2 | \text{Cl}^-) = E^0(\text{Hg} | \text{Hg}^{2+}) + \frac{0.0591}{2} \log K_{sp}(\text{Hg}_2\text{Cl}_2)$

The standard potential of the calomel electrode is equal to $0.0455 + 0.222 = 0.2675 \text{ V}$.

Thus, $\log K_{sp}(\text{Hg}_2\text{Cl}_2)$ can be calculated as:

$$\log K_{sp}(\text{Hg}_2\text{Cl}_2) = \frac{2(0.2675 - 0.798)}{0.0591} = -17.99$$

$$K_{sp} = 1.03 \times 10^{-18}$$

PROBLEM 4

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18 \times 10^{-18} / n^2$ [J] where n denotes the principal quantum number.

4.1 Calculate the energy differences between $n = 2$ (first excited state) and $n = 1$ (ground state) and between $n = 7$ and $n = 1$.

4.2 In what spectral range is the Lyman series lying?

4.3 Can a single photon, emitted in the first and/or sixth line of the Lyman series, ionize:

- another hydrogen atom in its ground state?
- a copper atom in the Cu crystal?

The electron work function of Cu is $\Phi_{\text{Cu}} = 7.44 \times 10^{-19}$ J.

4.4 Calculate the de Broglie wavelength of the electrons emitted from a copper crystal when irradiated by photons from the first line and the sixth line of the Lyman series.

$$h = 6.6256 \times 10^{-34} \text{ J s}; \quad m_e = 9.1091 \times 10^{-31} \text{ kg}; \quad c = 2.99792 \times 10^8 \text{ m s}^{-1}$$

SOLUTION

4.1 $\Delta E_{n \rightarrow 1} = E_n - E_1 = 2.18 \times 10^{-18} (1 - n^2)$

$$\Delta E_{2 \rightarrow 1} = 1.635 \times 10^{-18} \text{ J}$$

$$\Delta E_{7 \rightarrow 1} = 2.135 \times 10^{-18} \text{ J}$$

4.2 The Lyman series is due to $\Delta E_{n \rightarrow 1}$ varying from 1.635×10^{-18} J ($n = 1$) to 2.135×10^{-18} J ($n \rightarrow \infty$), which corresponds to 121.5 nm and to 93.0 nm, respectively. This is in the UV-region.

4.3 a) The ionisation energy is equal to $\Delta E_{\infty \rightarrow 1} = 2.18 \times 10^{-18}$ J. Both $\Delta E_{2 \rightarrow 1}$ and $\Delta E_{7 \rightarrow 1}$ are smaller than $\Delta E_{\infty \rightarrow 1}$ and a single photon emitted from these transitions is not able to ionize a hydrogen atom.

b) Ionization of copper in a Cu-crystal is related to the photoelectric effect:

$$h\nu = \Phi_{\text{Cu}} + E_{\text{kin}} = \Phi_{\text{Cu}} + \frac{1}{2} m_e v^2$$

Because $\Delta E_{2 \rightarrow 1} > \Phi_{\text{Cu}}$ and $\Delta E_{7 \rightarrow 1} > \Phi_{\text{Cu}}$ both photons are indeed able to ionize a Cu-atom in the crystal.

The kinetic energy of the emitted electrons is:

$$\Delta E_{\text{kin}}(2 \rightarrow 1) = \Delta E_{2 \rightarrow 1} - \Phi_{\text{Cu}} = 8.91 \times 10^{-19} \text{ J}$$

$$\Delta E_{\text{kin}}(7 \rightarrow 1) = \Delta E_{7 \rightarrow 1} - \Phi_{\text{Cu}} = 13.91 \times 10^{-19} \text{ J}$$

4.4 The wavelength of an electron is:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2 E_{\text{kin}} m_e}}$$

$$(p = m_e v_e \text{ and } E_{\text{kin}} = \frac{p^2}{2 m_e})$$

$$\Delta E_{2 \rightarrow 1}: \quad \lambda_1 = 4.16 \times 10^{-10} \text{ m} = 4.16 \text{ \AA}$$

$$\Delta E_{7 \rightarrow 1}: \quad \lambda_2 = 5.20 \times 10^{-10} \text{ m} = 5.20 \text{ \AA}$$

PROBLEM 5Halogen derivatives of hydrocarbons

After passing 0.25 mol of hydrocarbon **A** over heated pumice (950 K) in an iron pipe, compound **B** in yield of 80 % (i. e. 15.4 g) and 2.4 dm³ of hydrogen, (295 K, 102 kPa) were obtained.

B and hydrogen are the only products. A mixture of halogen derivatives **C**, **D**, **E**, **F** and **G** is produced from **B** by reaction with a halogen in presence of a Lewis acid. Compounds **C** to **G** contain each one halogen atom more then the preceding compound. For the compounds **C** to **F** only one of the possible isomers is formed. In compound **G** there is no such preference and its three isomers **G**₁, **G**₂ and **G**₃ are found in the mixture. Compounds **C** to **F** racemize easily so that no optical isomerism occurs. However racemization is difficult for **G**₁, **G**₂, and especially for **G**₃. In the mass spectrum of **E** only three isotopic peaks were observed. Their relative intensities are 1: 1: 0.3.

Information:

- $k_{ortho} > k_{para}$ in compound **B**.
- The effect of the first halogen in the ring: $k_{para} > k_{ortho}$.
- Compounds **D** and **F** in one of their conformations have a center of symmetry.
- The contribution of carbon and hydrogen isotopes in the mass spectrum of **E** are negligible.
- Natural abundance of halogen isotopes:
 - $^{19}\text{F} = 100\%$;
 - $^{35}\text{Cl} = 75.53\%$; $^{37}\text{Cl} = 24.47\%$;
 - $^{79}\text{Br} = 50.54\%$; $^{81}\text{Br} = 49.46\%$;
 - $^{127}\text{I} = 100\%$.

5.1 Give the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G**₁, **G**₂ and **G**₃.

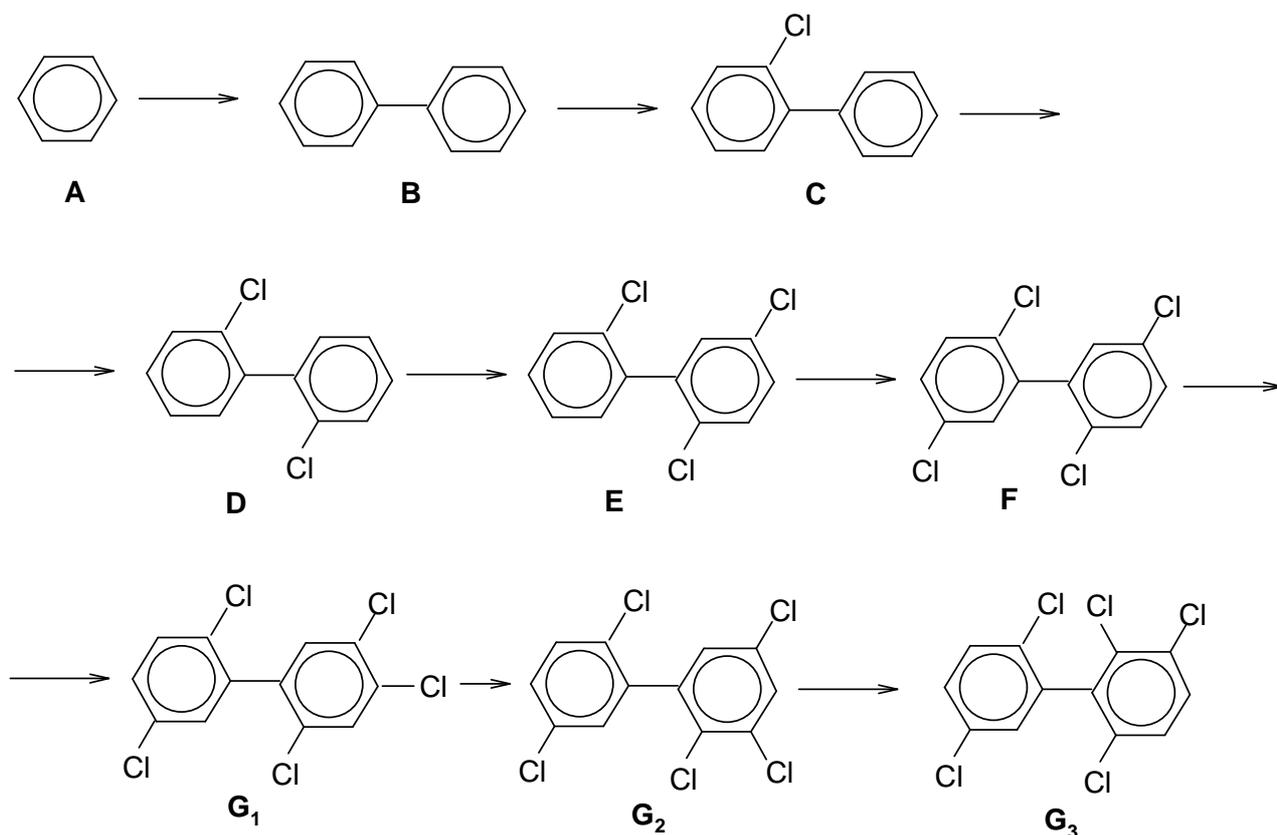
5.2 Explain your choice for the halogen.

5.3 Draw and label stereo-formulas of the rotational isomers of **D** for $\Phi = 0, \pi/2, \pi,$ and $3\pi/2$, where Φ denotes the dihedral or torsional angle in radians and $\vartheta = 0$ describes the configuration with maximal energy.

- 5.4 Draw profiles of the energy changes as a function of the angle of rotation around the C-C bond for compounds **C** and **D**.
- 5.5 Give a sequence of **G**₁, **G**₂, **G**₃ according to their increasing difficulty of racemization. Explain your answer.
- 5.6 Draw stereo-formulas of the enantiomers of **G**₃.
- 5.7 Suggest a chemical reaction or a biological method by which compounds like these can be destroyed.

SOLUTION

5.1



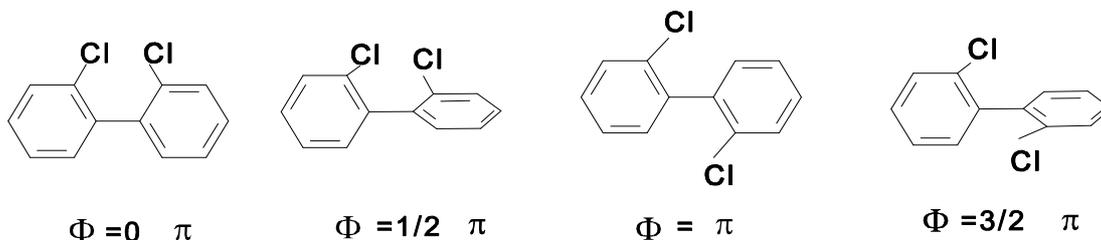
5.2 For the determination of the halogen of **E** we consider the ratio of the isotopic peaks in the mass spectrum.

$$\text{For } \mathbf{E} \text{ (} n = 3 \text{) we have: } (x + y)^3 = x^3 + 3x^2y + 3xy^2 + y^3.$$

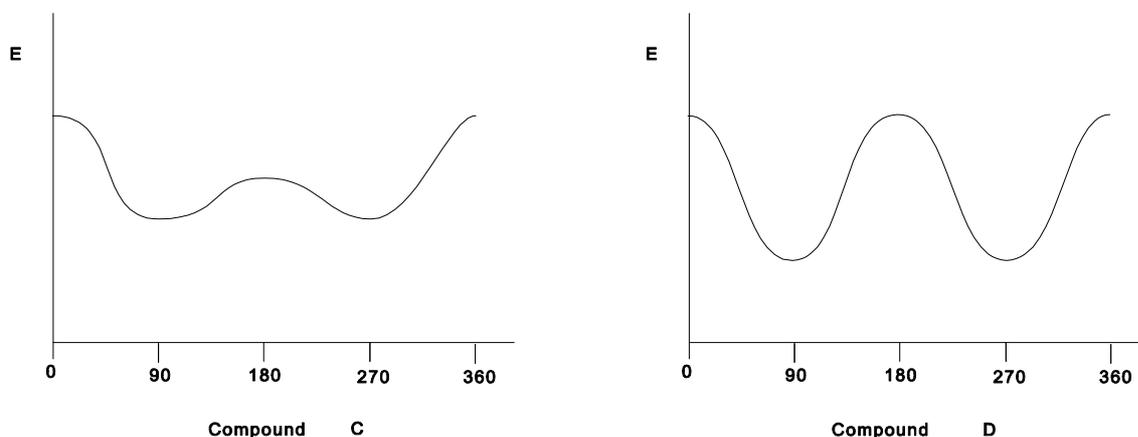
Therefore, with Br we would obtain: $x : y = 50.54 : 49.46 \cong 1 : 1$ hence $(x + y)^3 = 1 + 3 + 3 + 1$ and the ratio would be $1 : 3 : 3 : 1$ which is not in agreement with the text.

For chlorine the isotopic ratio is $75.53 : 24.47 \cong 1 : 3$ and therefore $(x + y)^3 = 3^3 + (3 \times 3^2 \times 1) + (3 \times 3 \times 1^2)$, which yields to a ratio of $1 : 1 : 0.33 : 0.04$. So, the X-atom is chlorine.

5.3



5.4

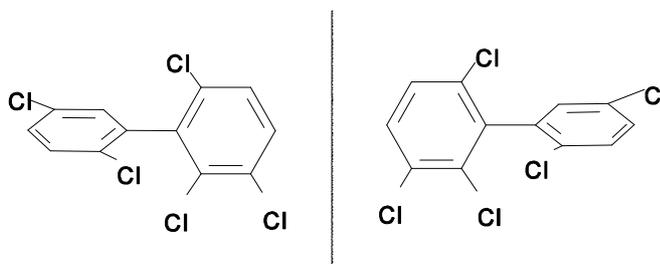


5.5

$$G_1 < G_2 < G_3.$$

Due to the increasing steric hindrance as a result of the interference of the big Van der Waals radii of chlorine, the rotation around the C-C single bond becomes more and more difficult. Therefore racemization is most likely to occur with G_1 , less with G_2 and least with G_3 . This kind of isomerism is called atropisomerism.

5.6



- 5.7** - Complete combustion in chemical incinerator equipped with an afterburner and scrubber.
- Addition of a strong base to obtain corresponding phenols.
 - Transformation into ArOH by OH-radicals in water.
 - Bacteria metabolizing polychlorobiphenyls.
-
-

PROBLEM 6

Sulphuric acid is produced by catalytic oxidation of SO_2 to SO_3 , absorption of SO_3 in concentrated sulphuric acid forming oleum (containing 20 % SO_3 by mass) and appropriate dilution hereafter. The gas leaving the catalyst chamber contains nitrogen, oxygen, a trace of SO_2 and 10 % (by volume) of SO_3 . Sulphur trioxide, SO_3 , is converted into sulphuric acid (98 % by mass) and/or oleum.

- 6.1** Assuming that oleum is the only product formed, calculate the mass of water which is required for 1000 m^3 of gas leaving the catalyst chamber (273 K, 101.3 kPa).
- 6.2** Assuming that only 98 % sulphuric acid is produced, calculate the necessary mass of water and the mass of product produced thereby.
- 6.3** In the industry both oleum and 98 % sulphuric acid are produced in a mass ratio of $x = m_1/m_2$, where m_1 denotes the mass of oleum, m_2 the mass of 98 % sulphuric acid. Find an expression $y = f(x)$ to describe the relation between the mass of water consumed for 1000 m^3 gas (denoted y) and the value of x . Show that the results of 6.1) and 6.2) are in good agreement with your mathematical expression.

SOLUTION

- 6.1** 1000 m^3 of gas contain 4.462 kmol SO_a
 100 kg 20 % oleum contain 0.2498 kmol SO_3 and 0.8157 kmol H_2SO_4
 1.0655 kmol SO_a and 0.8157 kmol (14.70 kg) H_2O are necessary for production of 100 kg 20 % oleum.
 61.56 kg H_2O are necessary for 1000 m^3 of gas.
- 6.2** Assumption that only 98 % sulphuric acid is produced:
 100,0 kg 98 % H_2SO_4 contain 0,9992 kmol H_2SO_4 and 1,1102 kmol H_2O .
 100,0 kg 98 % H_2SO_4 contain 0.9992 kmol SO_3 and 1,1102 kmol (20,01 kg) H_2O .
 89.36 kg H_2O are necessary for 1000 m^3 of gas and 446.56 kg 98 % H_2SO_4 are obtained.
- 6.3** To obtain 1 kg 20 % oleum, 0,1470 kg H_2O are necessary,
 To obtain 1 kg 98 % H_2SO_4 , 0,2001 kg H_2O are necessary.

Thus, for mass of water for production of m_1 kg 20 % oleum and m_2 kg 98 % H_2SO_4 :
 $y = 0,1470 m_1 + 0,2001 m_2$.

Analogically for mass balance of SO_a :

$$4,462 = 1,0655 m_1 + 0,9992 m_2$$

Then:
$$\frac{y}{4.462} = \frac{14.70 m_1 + 20.01 m_2}{1.0655 m_1 + 0.9992 m_2}$$

After substitution: $m_1/m_2 = x$ the above relation may written in the form of a function
 $y = f(x)$:

$$y = \frac{61.65 x + 83.79}{x + 0.9378}$$

Production of oleum: $m_2 = 0$, $y = 61,56$,

production of the acid: $m_1 = 0$, $y = 89,35$,

Results are similar to those obtained in parts **6.1** and **6.2**.

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**Determination of an acid dissociation constant

Reagents:

A solution of a weak monoprotic acid with a concentration of about 0.1 mol dm^{-3} ,
a solution of sodium hydroxide with a concentration of about 0.1 mol dm^{-3} ,
solutions of the indicators: methyl orange and phenolphthalein.

Equipment:

burette 25 cm^3 ,

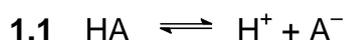
calibrated pipette 20 cm^3 ,

two conical flasks 200 cm^3 ,

access to the *pH*-meter. An assistant will make one measurement only for each participant.

Questions:

- 1.1 Give the expression for the concentration dissociation constant of the acid HA.
- 1.2 Give your reasons for the choice of the indicator.
- 1.3 Give the results of titrations.
- 1.4 Write down your *pH* value (measured by assistant).
- 1.5 Show how you calculate the concentration pK_a value for the acid. Write down the value.

SOLUTION

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (\text{a})$$

1.2 Since the HA is a weak acid the colour transition of the indicator is expected in the basic region ($pH > 7$), and thus phenolphthalein is suitable.

1.3 and 1.4

The results obtained by measuring volumes of the titrand and pH values were expected to be shown in the answer sheet.

1.5 The equation (a) can be transformed to equation (b) as follows:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (b)$$

When $[A^-] = [HA]$, then $pH = pK_a$

Since the concentration of the sodium hydroxide solution is approximate only, it is not possible to calculate the exact concentration of the acid. Nevertheless, the combination of titration and measuring pH values gives the possibility to find the value of dissociation constant K_a .

PROBLEM 2 (Practical)

Determination of the formation (stability) constants of the complex ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$

Equipment:

Two dry beakers with copper and zinc electrodes,
 three bottles with aqueous solutions of CuSO_4 , ZnSO_4 and NH_3 , respectively,
 one beaker with strips of filter paper for making a salt bridge,
 one beaker with an aqueous solution of KNO_3 ,
 three pipettes for delivering CuSO_4 , ZnSO_4 and NH_3 solutions,
 digital voltmeter for the EMF measurements,
 red and blue leads (conductors) for connecting cell electrodes to the digital voltmeter,
 rubber pipette filler,
 appropriately marked glass stirring rods.

a) Procedure for setting up the Daniell cell:

1. Into the dry beakers containing Cu and Zn electrodes deliver 20 cm³ of CuSO_4 and 20 cm³ of ZnSO_4 using marked pipettes in order to get Cu/Cu^{2+} and Zn/Zn^{2+} half-cells.
2. Wet the filter paper strip with KNO_3 solution. The strip should only be moisten with the solution. Then place the strip ends into the CuSO_4 and ZnSO_4 solutions.
3. Connect the leads to the electrodes (red to Cu electrode and blue to Zn electrode).

a)

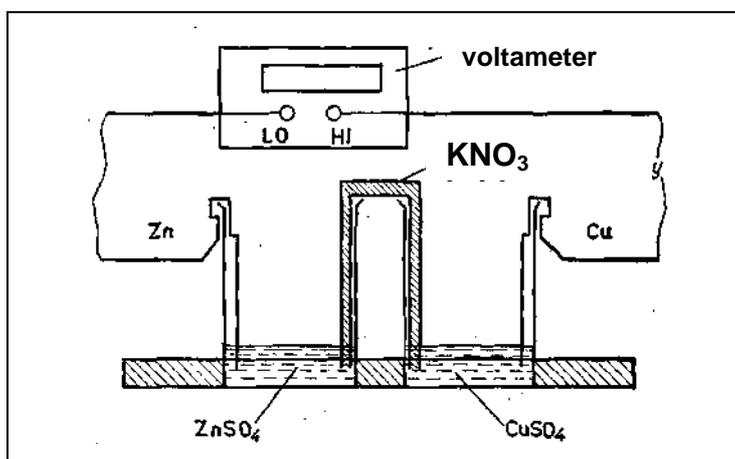


Fig. 1

b) Procedure for the EMF measurement of the Daniell cell (E_A):

Put the appropriately marked glass rods (red - Cu, blue - Zn) into the CuSO_4 and ZnSO_4 solutions. Having stirred the solutions gently with the rods, the rods should be left in the solutions throughout the course of the experiment. Start the EMF measurement of the cell by connecting the red lead to the voltmeter terminal (HI) and the blue one to the negative terminal (LO). If the EMF value changes by no more than 0.001 V, record the EMF (E_A).

c) Procedure for the EMF measurement of the cell (E_B) after the addition of the complexing agent (NH_3 solution) into the Cu/Cu^{2+} half-cell:

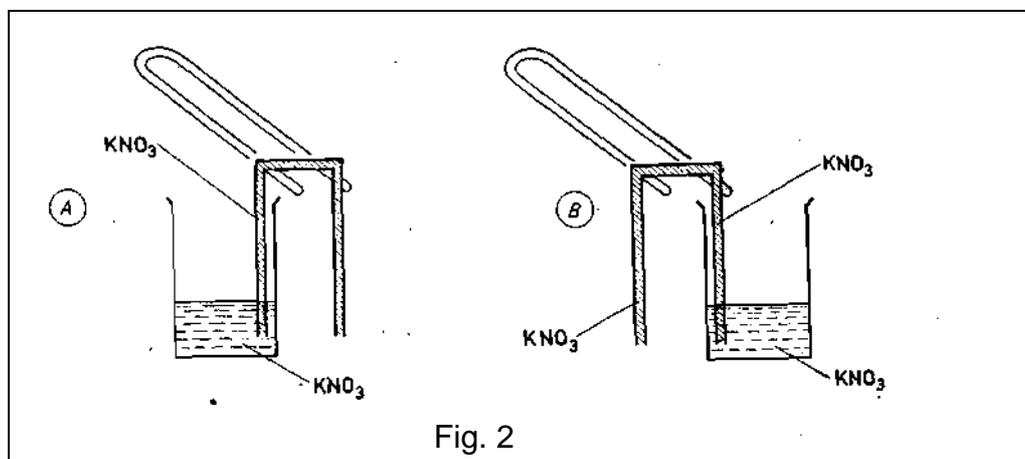


Fig. 2

Pipette 20 cm³ of aqueous NH_3 solution into the CuSO_4 solution. Stir the solution with a glass rod gently until it becomes a clear dark blue. Leave the rod in the solution. Measure and record the new EMF (E_B), in the way described in part b).

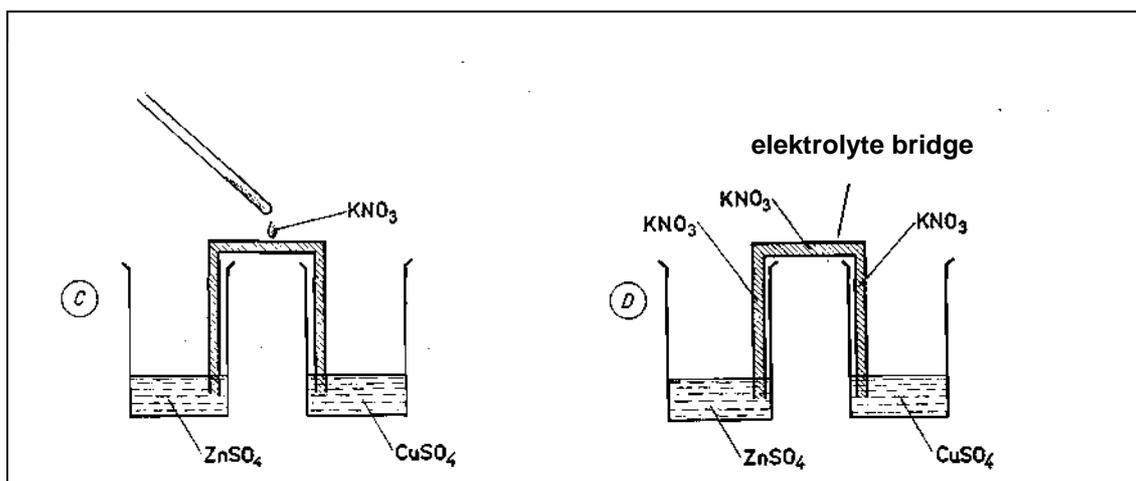


Fig. 3

- d) Procedure for the EMF measurement of the cell (E_C) after the addition of the complexing agent (NH_3 solution) to the Zn/Zn^{2+} half-cell:

Leave the $\text{Cu}/[\text{Cu}(\text{NH}_3)_4]^{2+}$ half-cell unchanged. Add 20 cm^3 of NH_3 solution to the ZnSO_4 half-cell. Carry out the EMF measurement of the cell in the way described in part b). Write down the result (E_C).

Theoretical considerations:

Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Faraday constant $F = 96\,487 \text{ C mol}^{-1}$

- i) The concentrations of CuSO_4 , ZnSO_4 and NH_3 aqueous solutions written on the bottles are expressed in mol kg^{-1} . Therefore they must be converted into appropriate concentrations expressed in mol dm^{-3} . The densities (d) of the solutions as functions of temperature are respectively:
- CuSO_4 : $d_1 = 1.0923 (\text{kg dm}^{-3}) - 0.0002700 (\text{kg dm}^{-3}\text{K}^{-1}) T$
- ZnSO_4 : $d_2 = 1.0993 (\text{kg dm}^{-3}) - 0.0002900 (\text{kg dm}^{-3}\text{K}^{-1}) T$
- NH_3 : $d_3 = 1.0740 (\text{kg dm}^{-3}) - 0.0002800 (\text{kg dm}^{-3}\text{K}^{-1}) T$
- ii) In order to convert concentrations (c_i) into ionic activities (a_i), we need to calculate activities of the ions using the equation $a_i = f_i \cdot c_i$. The activity coefficient values, f_i , of the ions involved are given in the answer sheet. The activity coefficient of ammonia should be assumed to be 1.
- iii) To simplify the calculations it should be assumed that after the addition of the excess of complexing agent (NH_3) only $\text{Cu}^{2+}_{\text{aq}}$, $\text{Zn}^{2+}_{\text{aq}}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions exist in the respective solutions.
- iv) Any diffusion potential occurring between both half-cells when the salt bridge is applied may be neglected in practice.

Questions:

- 2.1** Calculate the values of the concentrations of Cu^{2+} and Zn^{2+} ions in the Daniell cell before the introduction of the complexing agent (NH_3).
- 2.2** Calculate the standard EMF value E^0 of your Daniell cell using the Nernst equation.

- 2.3 Calculate the concentrations of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and NH_3 in the B type cell, i.e. after the addition of NH_3 to the Cu/Cu^{2+} half-cell.
- 2.4 Determine the values of the thermodynamic formation (stability) constants K_B and $\ln K_B$ for the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions.
- 2.5 Calculate the concentrations of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and NH_3 in the type C cell, i. e. after the addition of NH_3 to the Zn/Zn^{2+} half-cell.
- 2.6 Determine the values of the thermodynamic formation (stability) constant K_C and $\ln K_C$ for $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions.

SOLUTION

2.1 The mass of the solutions (kg) can be transformed to volumes of the solutions (dm^3) using the given densities. The concentrations are then given in units mol dm^{-3} .

$$2.2 \quad E = \left(E^0(\text{Cu}^{2+}/\text{Cu}) + \frac{RT}{2F} \ln([\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}}) \right) - \left(E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln([\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}}) \right) - E_{\text{diff}}$$

For $E_{\text{diff}} = 0$:

$$E_A = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}}}{[\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}}}$$

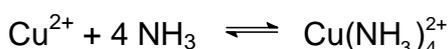
E_A can be measured. All other data required are given in the text of the problem or in the answer sheet.

2.3 Concentrations after the addition of NH_3 :

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = \frac{c(\text{Cu}^{2+}) \times V}{V + V_1}$$

$$[\text{NH}_3] = \frac{(c(\text{NH}_3) \times V_1) - (4 c(\text{Cu}^{2+}) \times V)}{V + V_1}$$

2.4 After the addition of NH_3 the following complex equilibrium is established:



$$\beta_4 = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{[\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}} \times [\text{NH}_3]^4}$$

Then the Nernst equation has the form:

$$E_1' = E^0(\text{Cu}^{2+}/\text{Cu}) = \frac{RT}{2F} \ln \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{\beta_4 \times [\text{NH}_3]^4}$$

$$E_B = E_1' - E_2 = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{[\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}} \times \beta_4 \times [\text{NH}_3]^4}$$

From the above equation β_4 or $\ln\beta_4$ can be calculated since E_B can be measured, and all other data required are given in the text of the problem or in the answer sheet.

2.5 and 2.6

The procedure in the calculation of β_4 or $\ln\beta_4$ for complex $\text{Zn}(\text{NH}_3)_4^{2+}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\text{Cu}(\text{NH}_3)_4^{2+}$.

24th



International Chemistry Olympiad

**9 theoretical problems
1 practical problem**

THE TWENTY-FOURTH INTERNATIONAL CHEMISTRY OLYMPIAD 11–22 July 1992, PITTSBURGH, UNITED STATES OF AMERICA

THEORETICAL PROBLEMS

PROBLEM 1

Diatoms, microscopic organisms, are an abundant food source in the oceans producing carbohydrates from carbon dioxide and water by photosynthesis:



- 1.1 During the first five years of life blue whales gain 75 kg of mass per day by feeding on krill. The whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill. Assuming that the mass gain in the first years of a whale's life is due to the consumption of carbohydrates ($\text{C}_6\text{H}_{12}\text{O}_6$), calculate the volume of CO_2 at STP (0 °C, 101 kPa) that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.
- 1.2 There is 0.23 cm^3 of dissolved CO_2 per one litre sea water (at 24 °C and 101 kPa).
- If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life?
 - What fraction of the total volume of the oceans will be needed to supply the carbon dioxide for the first five years of growth of 1000 blue whales? The volume of the oceans is $1.37 \times 10^{18} \text{ m}^3$.
- 1.3 Three percent of the mass of a $9.1 \times 10^4 \text{ kg}$ adult whale is nitrogen. When a $9.1 \times 10^4 \text{ kg}$ blue whale dies, what is the maximum mass of NH_4^+ that can become available for other marine organisms?
- 1.4 Eighteen percent of a $9.1 \times 10^4 \text{ kg}$ whale's mass is carbon. Carbon can be returned to the atmosphere as CO_2 and then removed from the atmosphere by weathering of rocks containing calcium silicate.



What are the maximum number of grams of CaSiO_3 that can be weathered by the carbon dioxide produced from the decomposition of 1000 blue whales, the number estimated to die annually?

SOLUTION

1.1 In five years a whale eats carbohydrates coming from $5 \times 365 \times 75 \times 10 = 1.4 \times 10^6$ kg krill which themselves need 1.4×10^7 kg of carbohydrates coming from diatoms.

For 180 g $\text{C}_6\text{H}_{12}\text{O}_6$, 6×44 g CO_2 are necessary, and thus

for 1.4×10^7 kg carbohydrates $1.4 \times 10^7 \times (264/180) = 2.00 \times 10^7$ kg of CO_2 are needed,

i. e. 1.0×10^{10} dm³ CO_2

1.2 i) The amount of water is 4×10^{13} dm³.

ii) 3×10^{-5} of the total ocean volume (0.03 ‰).

1.3 The mass of nitrogen from a whale is $0.03 \times 9.1 \times 10^4$ kg = 2.7×10^6 g.

$$n(\text{N}) = n(\text{NH}_4^+) = \frac{2.7 \times 10^6 \text{ g}}{14 \text{ g mol}^{-1}} = 1.9 \times 10^5 \text{ mol}$$

$$m(\text{NH}_4^+) = 1.9 \times 10^5 \text{ mol} \times 18 \text{ g mol}^{-1} = 3 \times 10^6 \text{ g NH}_4^+ = 3 \times 10^3 \text{ kg NH}_4^+$$

1.4 One whale contains 1.6×10^4 kg of carbon. It corresponds to 1.3×10^6 mol of CO_2 .

From the equation: $n(\text{CaSiO}_3) = 6.5 \times 10^5$ mol

$$m(\text{CaSiO}_3) = 6.5 \times 10^5 \text{ mol} \times 116 \text{ g mol}^{-1} = 7.5 \times 10^7 \text{ g CaSiO}_3$$

1000 whales therefore produce 7.5×10^{10} g CaSiO_3 .

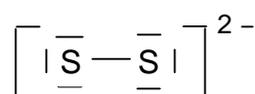
PROBLEM 2

Many streams drain in areas where coal or metallic ores are mined. These streams have become acidic and contain high concentrations of dissolved iron and sulphate, due to sulphur-containing ores being exposed to the atmosphere or to oxygenated waters. The most common sulphur-containing mineral is pyrite, FeS_2 , in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite, FeO(OH) , which coats the stream bottom while the water remains acidic.

- 2.1 Draw the electron dot structure that illustrates the bonding in the ion S_2^{2-} , showing all valence electrons.
- 2.2 Write a balanced chemical equation to show how hydrogen ions (H^+) are generated during the oxidation of pyrite to form a solution of iron(II) and sulphate ions.
- 2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, FeO(OH) .
- 2.4 Calculate how many moles of pyrite would be required to bring 1.0 dm^3 of pure water to a pH of 3.0 if the pyrite was completely converted into FeO(OH) and H^+ ions. Neglect the formation of HSO_4^- .
- 2.5 The concentration of iron as Fe(II) in a stream is 0.00835 M. At a very narrow point in the stream it empties into a large pond, with a flow rate of 20.0 l each minute. The water in this stream is sufficiently aerated that 75 % of the Fe(II) is oxidized to Fe(III). The pH of the pond is high enough (> 7) that the iron(III) precipitates immediately as Fe(OH)_3 which on aging becomes Fe_2O_3 . What mass of Fe_2O_3 will be deposited on the bottom of the pond in two years?

SOLUTION

2.1



2.4 $[\text{H}^+] = 1 \times 10^{-3}$

$n[\text{H}^+] = 1 \times 10^{-3} \text{ mol}$

From both equations: $n(\text{FeS}_2) = 2.5 \times 10^{-4} \text{ mol}$

2.5 Total flow into pond in 2 years =

$$2 \text{ yr} \times 365 \text{ days yr}^{-1} \times 24 \text{ h day}^{-1} \times 60 \text{ min h}^{-1} \times 20.0 \text{ dm}^3 \text{ min}^{-1} = \\ = 2.10 \times 10^7 \text{ dm}^3 \text{ of water}$$

$$n(\text{Fe}^{2+}) \text{ into pond} = 2.10 \times 10^7 \text{ dm}^3 \times 8.35 \times 10^{-3} \text{ mol dm}^{-3} = 1.76 \times 10^5 \text{ mol}$$

$$n(\text{Fe}^{3+}) \text{ produced} = 0.75 \times 1.76 \times 10^5 \text{ mol} = 1.32 \times 10^5 \text{ mol}$$

mass of deposited Fe_2O_3 :

$$m(\text{Fe}_2\text{O}_3) = 0.5 \times 1.32 \times 10^5 \text{ mol} \times 159.7 \text{ g mol}^{-1} = 1.05 \times 10^7 \text{ g}$$

PROBLEM 3

Coniferyl alcohol has the molecular formula $C_{10}H_{12}O_3$. It is isolated from pine trees. Coniferyl alcohol is not soluble in water or aqueous $NaHCO_3$. A solution of Br_2 in CCl_4 is decolorized when added to coniferyl alcohol forming **A** ($C_{10}H_{12}O_3Br_2$). Upon reductive ozonolysis coniferyl alcohol produces vanillin (4-hydroxy-3-methoxybenzaldehyd) and **B** ($C_2H_4O_2$). Coniferyl alcohol reacts with benzoyl chloride (C_6H_5COCl) in the presence of a base to form **C** ($C_{24}H_{20}O_5$). This product rapidly decolorizes $KMnO_4$ (aq) and is insoluble in dilute $NaOH$.

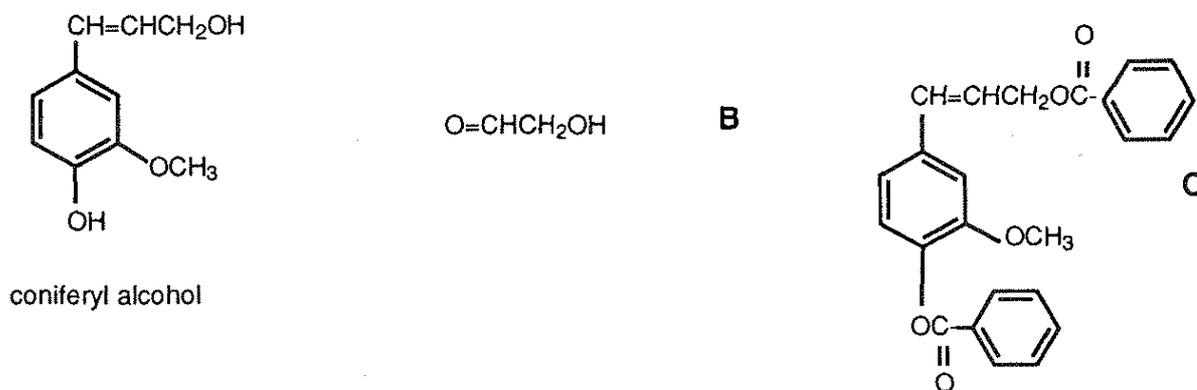
Coniferyl alcohol reacts with cold HBr to form **D** ($C_{10}H_{11}O_2Br$). Hot HI converts $ArOR$ to $ArOH$ and RI . Coniferyl alcohol reacts with excess hot HI to give **E** ($C_9H_9O_2I$) and CH_3I . CH_3I in aqueous base reacts with coniferyl alcohol to form **F** ($C_{11}H_{14}O_3$), which is not soluble in a strong base, but decolorizes Br_2/CCl_4 -solution.

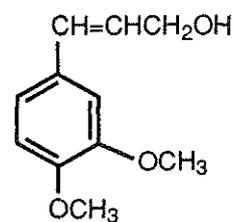
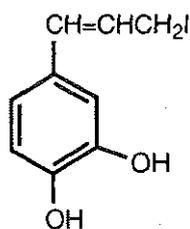
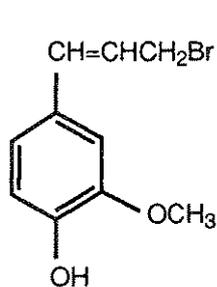
3.1 Draw the structures of coniferyl alcohol and compounds **A - F**.

3.2 There are a number of stereoisomers of compound **A**. Draw structure of compound **A**. Label each chiral centre in compound **A** with an asterisk (*). For all stereoisomers draw Fischer projections and label each chiral center with the proper *R* or *S* designation giving the absolute configuration about the chiral centre.

SOLUTION

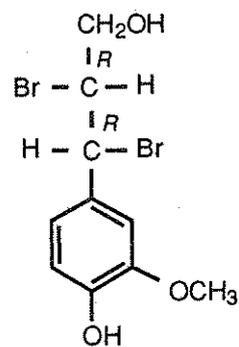
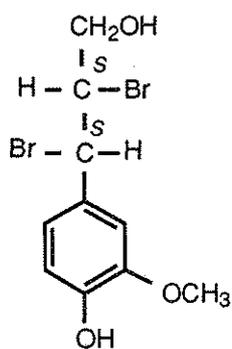
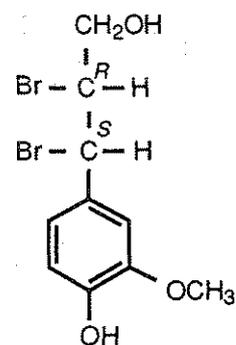
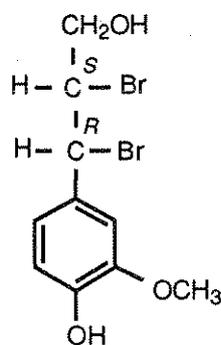
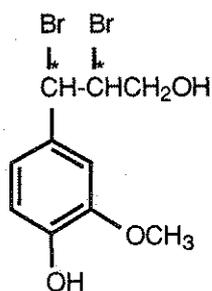
3.1





I

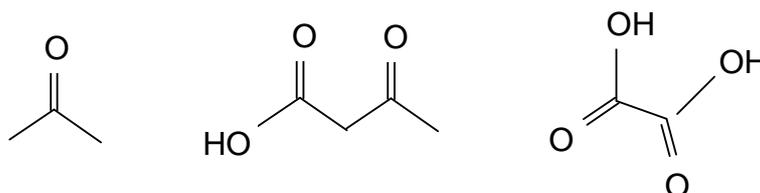
3.2 There are no geometric isomers of compound **A**, but there are 4 diastereomers (2 pairs of enantiomers).



PROBLEM 4

Rose oil is an essential oil obtained from the steam distillation of plant material from roses. It contains a number of terpenes, one of which is geraniol, $C_{10}H_{18}O$ (**A**). Upon oxidation, geraniol can either give a ten-carbon aldehyde or a ten-carbon carboxylic acid. Reaction with two moles of bromine gives a tetrabromide ($C_{10}H_{18}OBr_4$) (**B**). Geraniol reacts with HBr to give two bromides of formula $C_{10}H_{17}Br$.

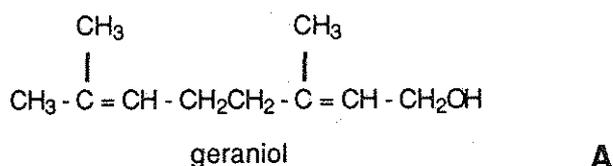
When geraniol is vigorously oxidized, three products are obtained:



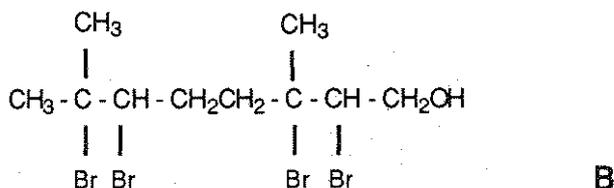
- 4.1 Give the structure of geraniol **A**.
- 4.2 Give the structure of compound **B**.
- 4.3 Give the structures of the two bromides of formula $C_{10}H_{17}Br$.
- 4.4 Indicate which of the two bromides is formed in greater proportions.

SOLUTION

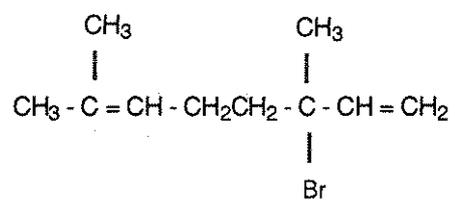
4.1



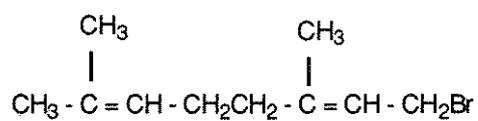
4.2



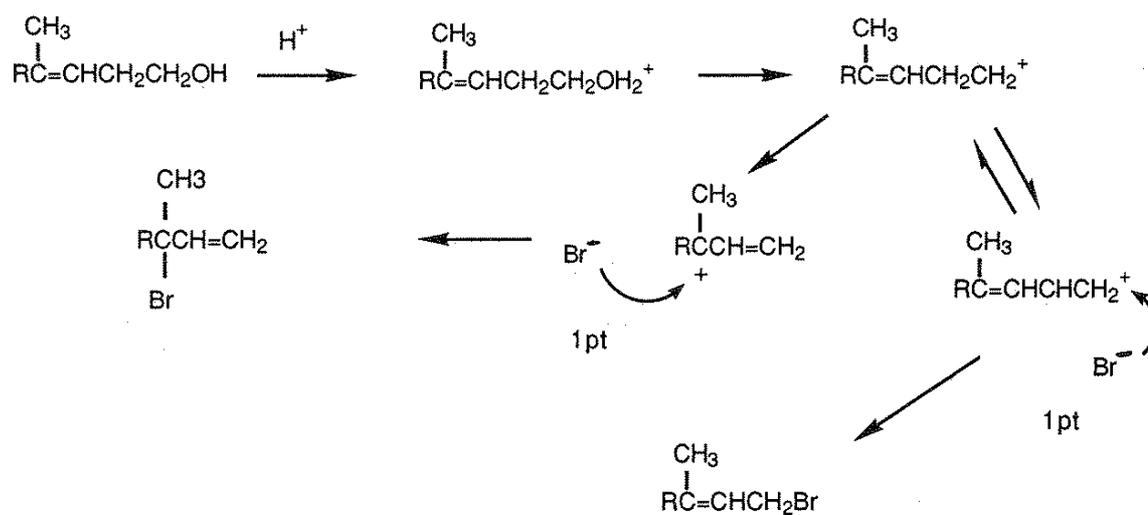
4.3



or

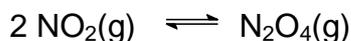


4.4



PROBLEM 5

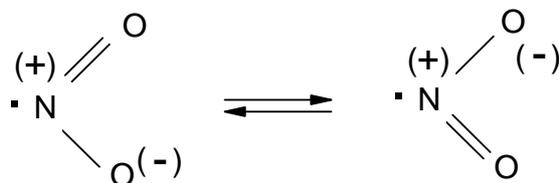
Nitrogen dioxide NO_2 is one of a number of oxides of nitrogen found in our atmosphere. It can dimerize to give N_2O_4 (g):



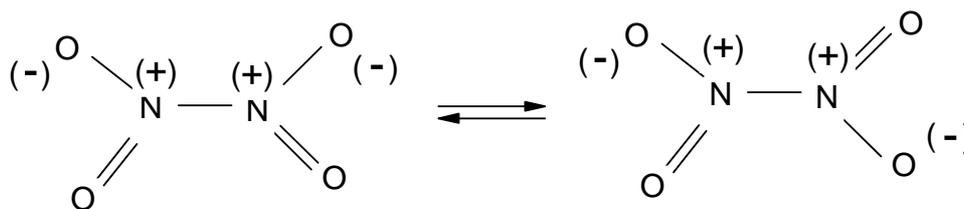
- 5.1** With a diagram, show the bonds present in $\text{NO}_2(\text{g})$ using the concept of resonance if necessary. Nitrogen dioxide, NO_2 , is paramagnetic.
- 5.2** Show, with bonding diagrams, how two molecules of $\text{NO}_2(\text{g})$ combine to give a molecule of N_2O_4 (g) which is not paramagnetic.
- 5.3** At 298 K, the ΔG° of formation for $\text{N}_2\text{O}_4(\text{g})$ is 98.28 kJ, whereas for $\text{NO}_2(\text{g})$ is 51.84 kJ. Starting with one mole of $\text{N}_2\text{O}_4(\text{g})$ at 1.0 atm and 298 K, calculate what fraction will be decomposed if the total pressure is kept constant at 1.0 atm and the temperature is maintained at 298 K.
- 5.4** If ΔH° for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?
- 5.5** The dissociation of $\text{N}_2\text{O}_4(\text{g})$ to give $\text{NO}_2(\text{g})$ is a first order process with a specific rate constant of $5.3 \times 10^4 \text{ s}^{-1}$ at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original N_2O_4 to decompose?
- 5.6** The association of $\text{NO}_2(\text{g})$ to give $\text{N}_2\text{O}_4(\text{g})$ is a second-order process with a specific rate constant of $9.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c , at 298 K for the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

SOLUTION

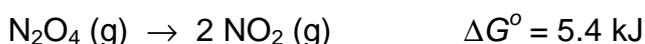
- 5.1** The structure of NO_2 :



- 5.2** The structure of N_2O_4 :



(At very low temperatures there is another structure of N_2O_4 possible: $\text{O}=\text{N}-\text{ONO}_2$, nitrosyl nitrate)



If x denotes the fraction of decomposed N_2O_4 and P_T the partial pressure and X the mole fraction of the corresponding species, we obtain:

$$\Delta G^\circ = -RT \ln K; \quad K = e^{(-5.4 \text{ kJ} / 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})}$$

$$K_p = 0.113 = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(P_T X_{\text{NO}_2})^2}{P_T X_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2x}{1+x}\right)^2}{\left(\frac{1-x}{1+x}\right)} = \frac{4x^2}{1-x^2}$$

wherefrom $x = 0.166$

5.4 If $2 \times 0.166 = 0.332 \text{ mol}$ N_2O_4 decomposes, 0.664 mol NO_2 are formed, thus

$$K_p = \frac{\left(\frac{0.664}{1.332}\right)^2}{\frac{1-0.332}{1.332}} = 0.496$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{0.496}{0.113}\right) = -\frac{58.03 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{T_2} - \frac{1}{298 \text{ K}}\right)$$

$$T_2 = 318 \text{ K}$$

5.5 $\ln \frac{[\text{N}_2\text{O}_4]_t}{[\text{N}_2\text{O}_4]_0} = -kt$

$$\ln 0.80 = -(5.3 \times 10^4 \text{ s}^{-1}) t$$

$$t = 4.2 \times 10^{-6} \text{ s}$$

5.6 $K = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{9.8 \times 10^6}{5.3 \times 10^4} = 1.8 \times 10^2$

PROBLEM 6

The concentration of carbon dioxide in the atmosphere has increased substantially during this century and is predicted to continue to increase. The $[\text{CO}_2]$ is expected to be about 440 ppm (440×10^{-6} atm) in the year 2020.

- 6.1** Calculate the concentration (in mol dm^{-3}) of CO_2 dissolved in distilled water equilibrated with the atmosphere in the year 2020.
- 6.2** Calculate the pH -value of the solution in 6.1.
- 6.3** Calculate the enthalpy of reaction between CO_2 (aq) and H_2O .
- 6.4** If the temperature of an equilibrated solution of CO_2 is increased and the concentration of dissolved carbon dioxide is maintained constant, the pH of the solution may change. Predict whether the pH will increase or decrease.

Data:

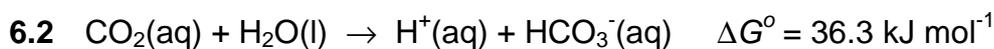
Henry's Law constant for CO_2 at 298 K: $0.0343 \text{ dm}^3 \text{ mol}^{-1} \text{ atm}^{-1}$

Thermodynamic values, in kJ/mol at 298 K are:

	$\Delta_f G^0$	$\Delta_f H^0$
CO_2 (aq)	-386.2	-412.9
H_2O (l)	-237.2	-285.8
HCO_3^- (aq)	-587.1	-691.2
H^+ (aq)	0.00	0.00

SOLUTION

$$6.1 \quad [\text{CO}_2(\text{aq})] = K_{\text{H}} p_{\text{CO}_2} = 0.0343 \text{ M atm}^{-1} \times 440 \times 10^{-6} \text{ atm} = \underline{1.51 \times 10^{-5} \text{ M}}$$



$$K = e^{-\Delta G^\circ / RT} = 4.37 \times 10^{-7}$$

Since $x = [\text{H}^+] = [\text{HCO}_3^-]$,

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x^2}{[\text{CO}_2]}$$

$$\text{Solving for } x \text{ yields } [\text{H}^+] = 2.57 \times 10^{-6}; \quad \underline{\text{pH} = 5.59}$$

$$6.3 \quad \Delta H^\circ = \Delta H_f^\circ(\text{HCO}_3^-) - \Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ(\text{H}_2\text{O}) = \\ = -691.2 - (-412.9) - (-285.8) = \underline{7.5 \text{ kJ mol}^{-1}}$$

6.4 Since the reaction is endothermic, the equilibrium constant will increase with temperature. Therefore, $[\text{H}^+]$ will also increase and the pH will decrease.

PROBLEM 7

When the fresh-water rivers that run into the Chesapeake Bay flood after heavy rains in the spring, the increase in fresh water in the Bay causes a decrease in the salinity in the areas where oysters grow. The minimum concentration of chloride ions needed in oyster beds for normal growth is 8 ppm (8 mg dm^{-3}).

After one week of heavy rain, the following analysis is done on water from the bay. To a 50.00 cm^3 sample of bay water a few drops of a K_2CrO_4 solution are added. The sample is then titrated with 16.16 cm^3 of a 0.00164 M AgNO_3 solution. After AgNO_3 solution has been added to the sample a bright red-orange precipitate forms.

- 7.1 What is the molar concentration of chloride in the sample?
- 7.2 Does the water contain sufficient chloride for the normal growth of oysters? Show your calculation.
- 7.3 Write a balanced equation for the reaction of the analyte with the titrant.
- 7.4 Write a balanced net-ionic equation that describes the reaction responsible for the colour change at the endpoint of the titration. Which compound produces the brick-red colour?
- 7.5 The concentration of chromate at the endpoint is 0.020 M . Calculate the concentration of chloride ions in the solution when the red precipitate forms.
- 7.6 For this titration to work most effectively, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium that would influence the observed endpoint of this titration.

Typically, a buffer is added to the solution being titrated to control the pH if the initial sample is acidic. Suppose the *pH* of the sample of bay water was 5.10, thus too acidic to perform the analysis accurately.

- 7.7 Select a buffer from the list that would enable you to establish and maintain a *pH* of 7.20 in aqueous medium. Show the calculations which lead to your choice.

	Buffer systems	K_a of weak acid
1.	0.10 M lactic acid / 0.10 M sodium lactate	1.4×10^{-4}
2.	0.10 M acetic acid / 0.10 M sodium acetate	1.8×10^{-5}

3. 0.10 M sodium dihydrogen phosphate /
/ 0.10 M sodium hydrogen phosphate 6.2×10^{-8}
4. 0.10 M ammonium chloride / 0.10 M ammonia 5.6×10^{-10}

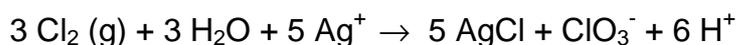
7.8 Using the selected buffer system, calculate the mass (in g) of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 cm³ of a stock solution buffered at a pH of 7.2.

7.9 The chloride concentration in another 50.00 cm³ sample of bay water was determined by the Volhard method. In this method an excess of AgNO₃ is added to the sample. The excess Ag⁺ is titrated with standardized KSCN, forming a precipitate of AgSCN. The endpoint is signalled by the formation of the reddish-brown FeSCN²⁺ complex that forms when Ag⁺ is depleted. If the excess Ag⁺ from the addition of 50.00 cm³ of 0.00129 M AgNO₃ to the water sample required 27.46 cm³ of 1.41 · 10⁻³ M KSCN for titration, calculate the concentration of chloride in the bay water sample.

In natural waters with much higher concentration of Cl⁻, the Cl⁻ can be determined gravimetrically by precipitating the Cl⁻ as AgCl. A complicating feature of this method is the fact that AgCl is susceptible to photodecomposition as shown by the reaction:



Furthermore, if this photodecomposition occurs in the presence of excess Ag⁺, the following additional reaction occurs:



If 0.010 g of a 3.000 g sample of AgCl contaminated with excess Ag⁺ undergoes photodecomposition by the above equations

7.10 Will the apparent weight of AgCl be too high or too low? Explain your answer showing by how many grams the two values will differ.

Data: $K_{sp}(\text{AgCl}) = 1.78 \times 10^{-10}$
 $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.00 \times 10^{-12}$

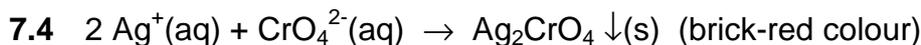
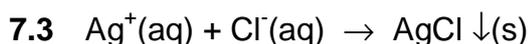
SOLUTION

$$7.1 \quad n(\text{Ag}^+) = n(\text{Cl}^-)$$

$$c(\text{Cl}^-) = \frac{0.01616 \text{ dm}^3 \times 0.00164 \text{ mol dm}^{-3}}{0.050 \text{ dm}^3} = 5.30 \times 10^{-4} \text{ mol dm}^{-3}$$

$$7.2 \quad \text{Concentration in mg dm}^{-3} = 5.30 \times 10^{-4} \text{ mol dm}^{-3} \times 35.5 \text{ g mol}^{-1} = 0.0188 \text{ g dm}^{-3} = 18.8 \text{ mg dm}^{-3}$$

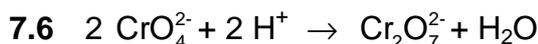
Thus the chloride concentration is sufficiently high for normal oyster growth.



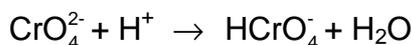
$$7.5 \quad K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 4x^3 \text{ if } x = [\text{Ag}^+] \Rightarrow$$

$$[\text{Ag}^+] = 7.07 \times 10^{-6}; \quad [\text{CrO}_4^{2-}] = 2 \times 10^{-2}$$

$$[\text{Cl}^-] = \frac{K_{sp}(\text{AgCl})}{[\text{Ag}^+]} = \frac{1.78 \times 10^{-10}}{7.07 \times 10^{-6}} = 2.5 \times 10^{-5}$$



either/or



7.7 A buffer system has its maximum buffer capacity when $\text{pH} = \text{pK}_a$. So, the system 3 would be best since $\text{pK}_a = 7.2$

$$7.8 \quad m(\text{NaH}_2\text{PO}_4) = 0.10 \text{ mol dm}^{-3} \times 0.500 \text{ dm}^3 \times 119.98 \text{ g mol}^{-1} = 6.0 \text{ g}$$

$$m(\text{Na}_2\text{HPO}_4) = 0.10 \text{ mol dm}^{-3} \times 0.500 \text{ dm}^3 \times 141.96 \text{ g mol}^{-1} = 7.1 \text{ g}$$

$$7.9 \quad \text{mol Ag}^+ \text{ added: } n(\text{Ag}^+)_{\text{ad}} = 0.05 \text{ dm}^3 \times 0.00129 \text{ mol dm}^{-3} = 6.45 \times 10^{-5} \text{ mol}$$

$$\text{mol Ag}^+ \text{ left over: } n(\text{Ag}^+)_{\text{left}} = 0.02746 \text{ dm}^3 \times 0.0141 \text{ mol dm}^{-3} = 3.87 \times 10^{-5} \text{ mol}$$

mol Cl^- in sample:

$$n(\text{Cl}^-) = n(\text{Ag}^+)_{\text{ad}} - n(\text{Ag}^+)_{\text{left}} = (6.45 \times 10^{-5} \text{ mol}) - (3.87 \times 10^{-5} \text{ mol}) = 2.58 \times 10^{-5} \text{ mol}$$

$$\Rightarrow [\text{Cl}^-] = \frac{2.58 \times 10^{-5}}{0.050} = 5.16 \times 10^{-4} \text{ mol dm}^{-3}$$

7.10 $n(\text{AgCl})$ lost: $\frac{0.010 \text{ g AgCl}}{143.35 \text{ gmol}^{-1}} = 6.98 \times 10^{-5} \text{ mol}$

$n(\text{Cl}_2)$ produced: $\frac{1}{2} (6.98 \times 10^{-5} \text{ mol}) = 3.49 \times 10^{-5} \text{ mol}$

$n(\text{AgCl})$ new prod.: $\frac{5}{3} (3.49 \times 10^{-5} \text{ mol}) = 5.82 \times 10^{-5} \text{ mol} \equiv 8.34 \text{ mg}$

The amount of Ag formed is equal to the amount of AgCl lost, thus

$[\text{Ag}]_{\text{formed}} = 6.98 \times 10^{-5} \text{ mol} \times 107.9 \text{ g mol}^{-1} = 7.53 \times 10^{-3} \text{ g}$

The mass of the sample is equal to $3.0 \text{ g} - 0.010 \text{ g} + 0.00834 \text{ g} + 0.00753 \text{ g} = 3.006 \text{ g}$. Therefore the total mass of the solid (AgCl + Ag) will be too high and the difference is 6 mg.

PROBLEM 8

The Pourbaix diagrams for water, nitrogen and manganese are depicted in Fig. 1.

8.1 Write the formula of the species of nitrogen that is predominant

- in O₂-rich lakes of pH ≈ 6,
- in highly O₂-depleted lakes that are strongly contaminated with acid rain (pH ≈ 3),

8.2 Which species of manganese is predominant

- in O₂-rich lakes of pH ≈ 6,
- in highly O₂-depleted lakes that are strongly contaminated with bases (pH ≈ 12)?

8.3 People often find that clear, slightly acidic (pH ≈ 5) water drawn from wells deposits a black manganese-containing solid on standing in toilet bowls.

- Write the chemical formula of the black solid?
- Write the formula for the species of manganese found in well water while it is still underground ?

8.4 According to Pourbaix diagrams two species of nitrogen should oxidize Mn(s) to Mn²⁺(aq).

- Write the formulas of these two nitrogen species.
- Which of the two species of nitrogen does not oxidize Mn(s) (in practice) at room temperature ?

8.5 According to the Pourbaix diagrams, some of the chemical forms of manganese should oxidize NH₃(aq) or NH₄⁺(aq) to N₂(g).

Choose in the following list the forms of Mn that should do it:

Mn, Mn(OH)₂, Mn²⁺, Mn₃O₄, Mn₂O₃, MnO₂, MnO₄²⁻, MnO₄⁻

8.6 Ammonium permanganate, NH₄MnO₄, is a well-known salt, but ammonium manganate, (NH₄)₂MnO₄, is a rarely known salt.

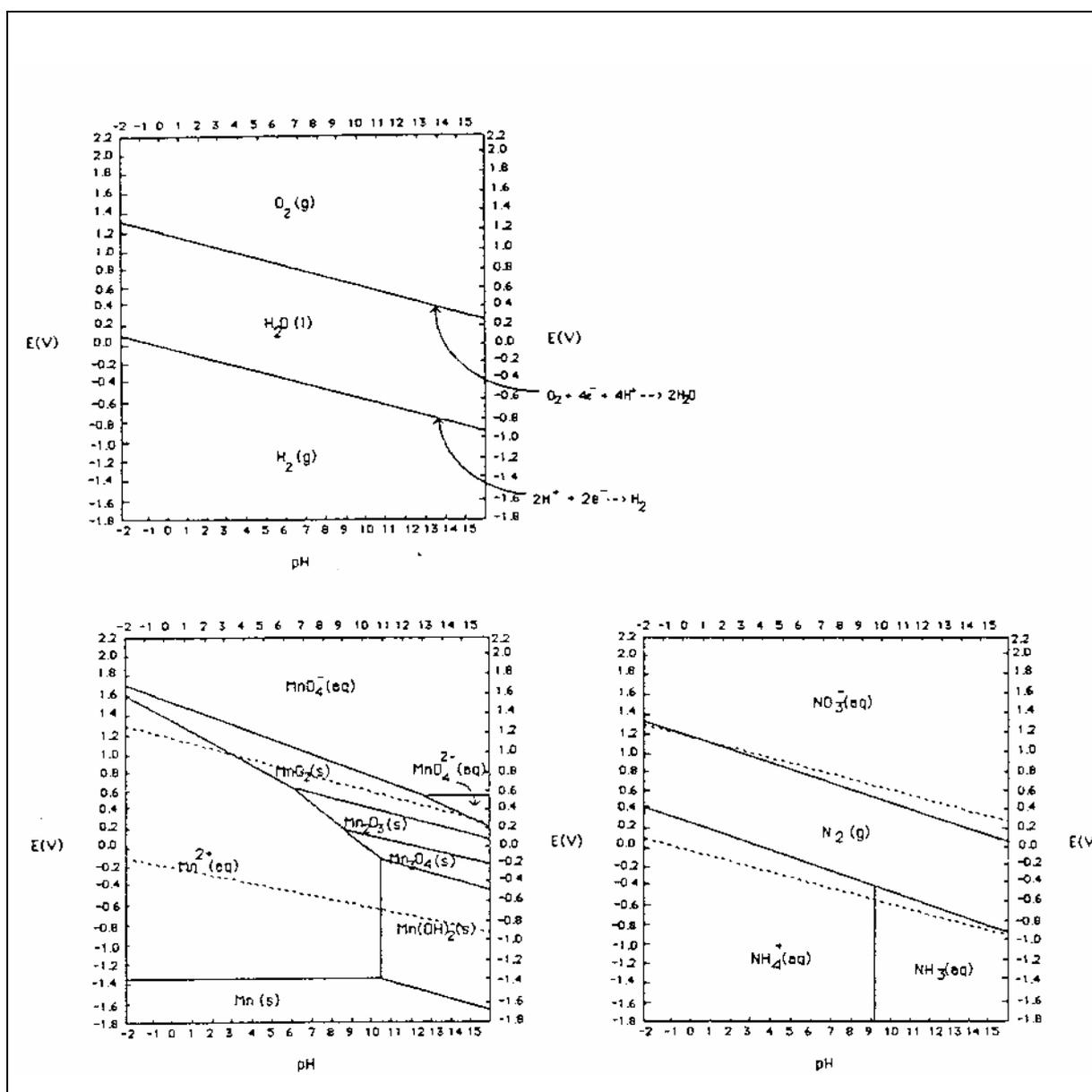
- Is NH₄MnO₄ expected to be thermodynamically stable? (YES or NO)
- Is (NH₄)₂MnO₄ expected to be thermodynamically stable? (YES or NO)
- Write and balance an equation for the decomposition of NH₄MnO₄ to give MnO₂ and N₂.
- Write and balance an equation for the decomposition of (NH₄)₂MnO₄ to give Mn and N₂.

8.7 According to the Pourbaix diagrams, is it dangerous to grind together in a mortar and pestle

- i) potassium nitrate and manganese metal,
- ii) potassium nitrate and manganese dioxide?

8.8 The standard reduction potential, E^0 , for the reduction of MnO_4^- to MnO_2 is 1.692 V. Applying the Nernst equation calculate the reduction potential, E , for the reduction of 0.00100 M MnO_4^- solution at a $\text{pH} = 4.0$.

Figure 1



SOLUTION8.1 i) N₂ ii) NO₃⁻8.2 i) MnO₂ ii) Mn(OH)₂8.3 i) MnO₂, ii) Mn²⁺

8.4 NO₃⁻ and N₂. In practice only NO₃⁻ would oxidize Mn, since the activation energy for N₂ in order to break the triple bonds is very high.

8.5 Mn₃O₄, Mn₂O₃, MnO₂, MnO₄²⁻, MnO₄⁻8.6 i) NH₄MnO₄: YESii) (NH₄)₂MnO₄: NOiii) 2 NH₄MnO₄ → 4 H₂O + 2 MnO₂ + N₂iv) (NH₄)₂MnO₄ → 4 H₂O + Mn + N₂

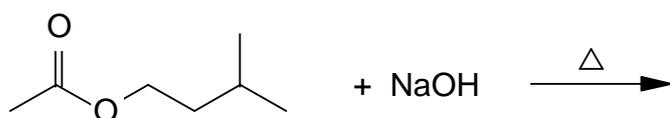
8.7 According to the diagrams, KNO₃ is easily reduced by Mn whereas the potential of MnO₂ is more positive than the potential of NO₃⁻. So a mixture of KNO₃ and Mn could be explosive.

$$\begin{aligned}
 8.8 \quad E &= E^{\circ} + \frac{0.0591}{3} \log[\text{MnO}_4^-] + \frac{0.0591}{3} \log[\text{H}^+]^4) = \\
 &= 1.692 + 0.0197 \log 0.001 - 0.0788 \text{ pH} = 1.633 - 0.0788 \text{ pH} = \underline{1.34 \text{ V}}
 \end{aligned}$$

PROBLEM 9

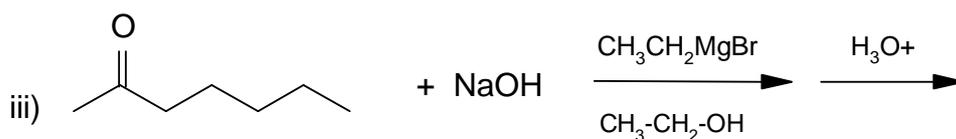
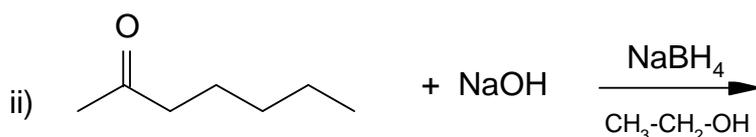
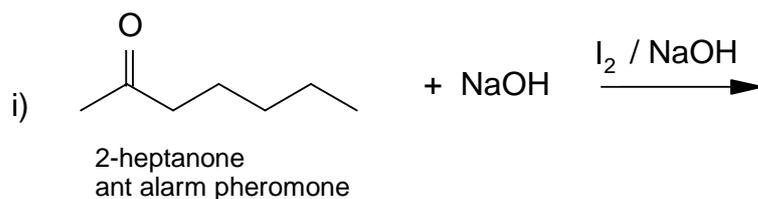
Pheromones are chemicals or mixtures of certain chemicals secreted by insects and some animals for communication. They bring about certain responses in another individual of the same species. In the problem below you will find a number of pheromones undergoing reactions which were used in determining their structures. In each case give the structure or structures of the products produced. Show geometric (cis/trans) isomers where appropriate (in part (9.5)). You may ignore other forms of stereoisomerism.

9.1

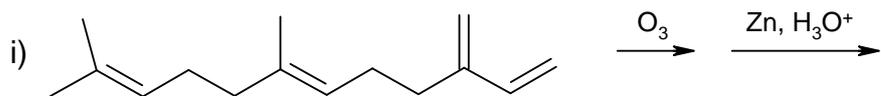


isoamyl acetate,
bee alarm pheromone

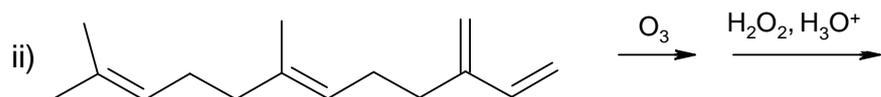
9.2



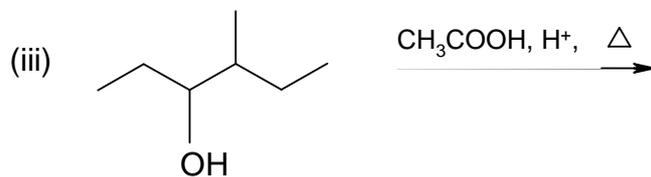
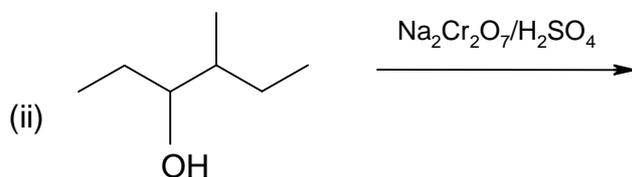
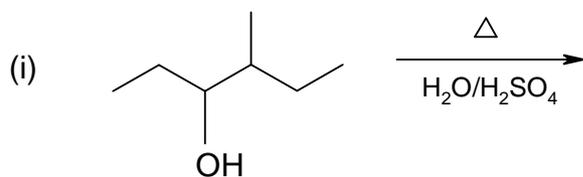
9.3



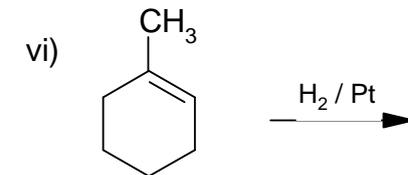
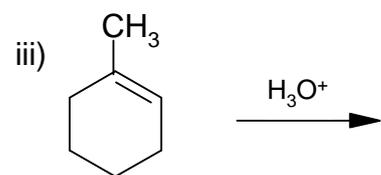
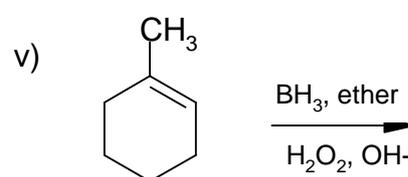
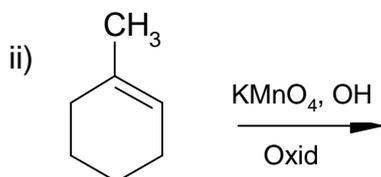
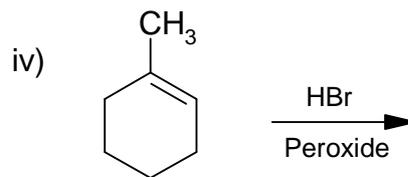
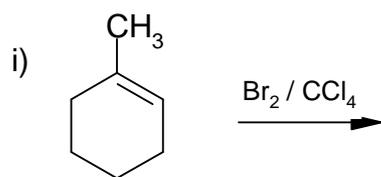
green peach -
aphid pheromone



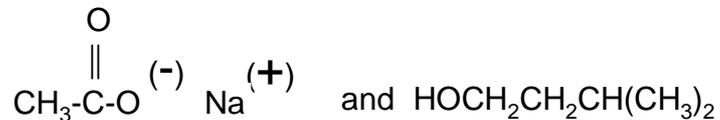
9.4



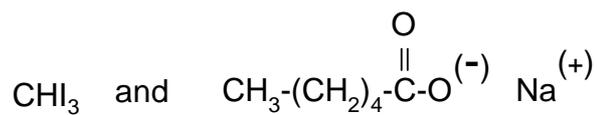
9.5


SOLUTION

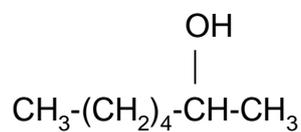
9.1



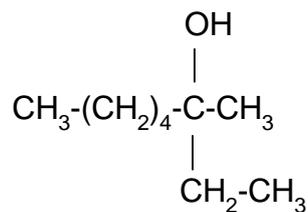
9.2 i)



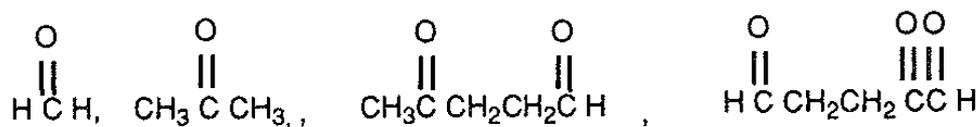
ii)



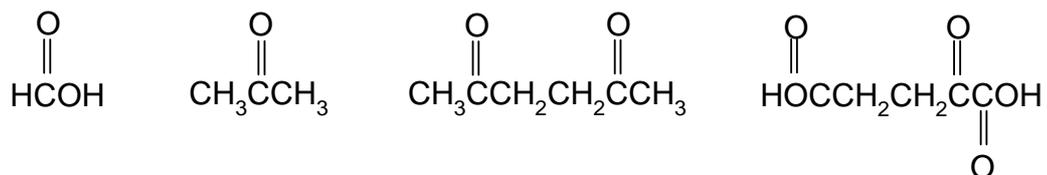
iii)



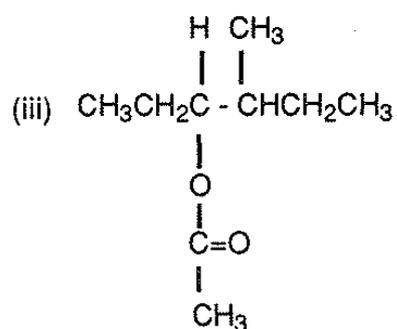
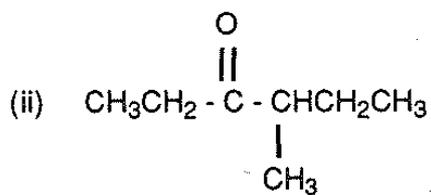
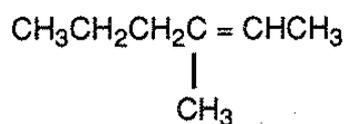
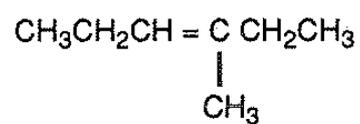
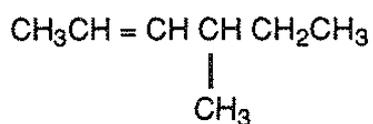
9.3 i)



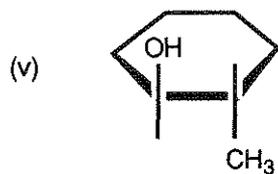
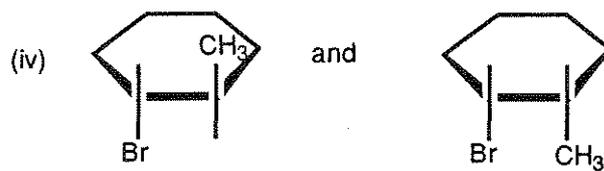
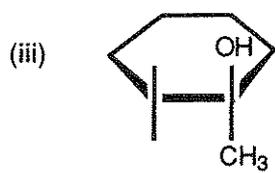
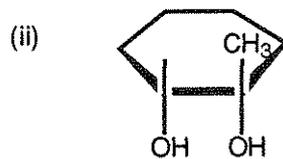
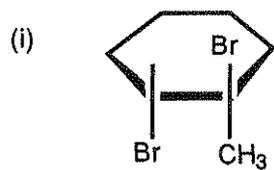
ii)



9.4 i)



9.5



PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**Effects of CO₂ on Solubility

Calcium carbonate is a partially soluble material commonly known as limestone, marble, chalk, or calcite. In the presence of CO₂-rich groundwater, calcium carbonate dissolves to form cavities and caves in limestone formations.

In this experiment you will determine the solubility of calcium carbonate in an aqueous solution saturated with carbon dioxide and in solution free of carbon dioxide. The [Ca²⁺] will be determined by complexometric titration with EDTA (ethylenediamine-tetraacetic acid).

- a) Procedure for the determination of [Ca²⁺]
1. Calibrate your *pH* meter.
 2. Measure and record the *pH* of the sample equilibrated with solid CaCO₃ and CO₂ gas.
 3. Filter all your sample into a second 250 cm³ plastic bottle to remove any suspended CaCO₃. Quickly cap the bottle when the filtering is complete.
 4. Uncap the bottle long enough to measure and record the *pH* of the filtered solution and recap the bottle until you are ready for the next step.
 5. As rapidly as possible, transfer three 25 cm³ aliquots of this sample to three Erlenmeyer flasks. Recap the sample bottle after removing each 25 cm³ aliquot.
 6. Add 15 drops of 6 M HCl to each of the three flasks with stirring. Any CaCO₃ that may have formed should dissolve. Before proceeding with the next step, make sure there is no solid CaCO₃ in the Erlenmeyer flasks. If a flask has some solid present, then more stirring is necessary.
 7. To one, and only one flask, add 5 cm³ of a *pH* 10 NH₃ buffer. Proceed immediately with steps 8 - 10.
 8. Add 20 drops of 0.001 M Mg²⁺/EDTA⁴⁻ solution to the flask in order for the indicator to function properly.
 9. Add 5 drops of Calmagite indicator to the sample.

10. Titrate the sample with an approximately 0.01 M EDTA solution provided (to be standardized as directed below) to a colour change from red to blue. You may wish to make a reference for colour with water, buffer, two drops EDTA and indicator.
11. Quickly repeat steps 7 - 10 for each remaining flask, one at a time.
12. After steps 1 - 11 have been completed to your satisfaction, transfer the remaining filtered, saturated solution from step 3 to a suitable beaker. Heat this solution to 96 – 99 °C and allow it to remain at that temperature, with magnetic stirring, for 5 minutes. A stirrer setting on 6 is adequate, and an initial high setting of heat will be required. You should see CO₂ being evolved and some CaCO₃ may precipitate.
13. At the end of the five minutes heating period, use the beaker tongs to remove the beaker from the hot plate and place it in an ice bath. Allow the solution to cool to room temperature.
14. Measure and record the *pH* of the cooled solution.
15. Filter the solution to remove any suspended CaCO₃.
16. Transfer three 25 cm³ aliquots of this filtered solution to three Erlenmeyer flasks. Add about 25 cm³ of deionized water to each flask, followed by 15 drops of 6 M HCl.
17. Titrate each sample according to steps 7 - 11.

b) Procedure for standardization of EDTA

1. Weigh approximately 0.35 g of dried primary standard CaCO₃, (molar mass 100.09 g mol⁻¹) which will be found in the weighing bottle in the desiccator. Note: CaCO₃ is hygroscopic.
2. Add 25 cm³ of deionized water to the CaCO₃, then carefully add 5 cm³ of 6 M HCl. Quickly cover with a watch glass.
3. When the CaCO₃ has dissolved, quantitatively transfer the solution to a 250 cm³ volumetric flask and dilute to the mark.
4. Transfer three 25 cm³ aliquots of the standard Ca²⁺ solution to three Erlenmeyer flasks.
5. Proceed to titrate each sample according to steps 7 - 11, following each step in sequence.

Tasks:

- 1.1 Calculate the solubility of calcium carbonate (expressed in mol dm⁻³) in a solution saturated with both CaCO₃ and CO₂ and in solution free of CO₂.
 - 1.2 List all the ionic species that increase in concentration as a result of the dissolving of CaCO₃ in water.
 - 1.3 Given below are brief descriptions of two solutions. Circle the one in which the concentration of CO₃²⁻ would be highest:
 - a) a solution produced by dissolving CaCO₃(s) in CO₂-saturated water
 - b) a solution produced by dissolving CaCO₃(s) in CO₂-free water
 - 1.4 Will the solubility of CaCO₃ increase or decrease in a solution from which the CO₂ has been removed?
-

SOLUTION

- 1.1 The results of the titration (volumes of titrants, mass of CaCO₃) and calculation of the concentration of the standardized EDTA solution were required to be written on the Answer Sheet.
Moreover, it was necessary to measure and record *pH* values of the sample at steps 2, 4, and 14.
It was expected to show the calculation of the solubility of CaCO₃ in its saturated solutions containing CO₂ and in those without CO₂.

The other tasks to be solved:

- 1.2 The ionic species mentioned above are as follows: Ca²⁺, HCO₃⁻, OH⁻.
 - 1.3 Correct answer: (b) A solution produced by dissolving CaCO₃(s) in CO₂-free water.
 - 1.4 The solubility of CaCO₃ will decrease.
-
-

25th



International Chemistry Olympiad

**5 theoretical problems
2 practical problems**

THE TWENTY-FIFTH INTERNATIONAL CHEMISTRY OLYMPIAD 11–22 JULY 1993, PERUGIA, ITALY

THEORETICAL PROBLEMS

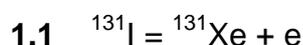
PROBLEM 1

^{131}I is a radioactive isotope of iodine (e^- emitter) used in nuclear medicine for analytical procedures to determine thyroid endocrine disorders by scintigraphy. The decay rate constant, k , of ^{131}I is $9.93 \times 10^{-7} \text{ s}^{-1}$.

Questions:

- 1.1 Write the decay reaction of ^{131}I .
- 1.2 Calculate the half-life of ^{131}I expressed in days.
- 1.3 Calculate the time necessary (expressed in days) for a sample of ^{131}I to reduce its activity to 30 % of the original value.
- 1.4 Knowing that a Geiger counter detects activities of the order of $10^{-4} \mu\text{c}$, calculate the minimum amount of ^{131}I (in grams) which could be detected by this counter.
1 Curie (c) is the amount of a radioisotope that produces 3.7×10^{10} disintegrations s^{-1} .

SOLUTION



1.2 Decay reactions are first order reactions. Then:

$$k = \frac{\ln 2}{t_{1/2}} \quad t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{0.693}{9.93 \times 10^{-7} \times 86400 \text{ s d}^{-1}} = 8.08 \text{ d}$$

1.3 For a first order reaction:

$$\ln \frac{C_0}{C} = k t$$

where c_0 and c are the concentrations at time 0 and time t , respectively. Then:

$$\ln \frac{100}{30} = 9.93 \times 10^{-7} \times t$$

$$t = \frac{1.212 \times 10^6}{8.64 \times 10^4} = 14.03 \text{ d}$$

1.4 1 Curie (c) is the amount of a radioisotope that produces 3.7×10^{10} disintegrations s^{-1}

$$1 \text{ mc} = 3.7 \times 10^7 \text{ dis s}^{-1}$$

$$1 \text{ } \mu\text{c} = 3.7 \times 10^4 \text{ dis s}^{-1}$$

Then:

$$10^{-4} \mu\text{c} \times 3.7 \times 10^4 \text{ dis s}^{-1} = 3.7 \text{ dis s}^{-1} = - \frac{dN}{dt}$$

$$t_{1/2} \text{ of } ^{131}\text{I} \text{ expressed in seconds is } = 8.08 \text{ d} \times 86400 \text{ s d}^{-1} = 6.98 \times 10^5 \text{ s}$$

$$m = - \frac{dN}{dt} \times \frac{t_{1/2} \times A_r(\text{I})}{\ln 2 \times N_A} = \frac{3.7 \times 6.98 \times 10^5 \times 131}{0.693 \times 6.02 \times 10^{23}} = 8.11 \times 10^{-16} \text{ g}$$

PROBLEM 2

The reflux of bile duodenal matter is suspected to be the major cause of gastritis and medical therapy is based on the treatment with antiacida that buffer the *pH* of gastric juices by binding bile acids and lysolecithin. Two bile acids, i. e. cholic acid (CA) and glycocholic acid (GCA), were chosen to study the properties of some antiacida commercial formulations. Separation and determination of the two acids in artificial and natural gastric juices were required and high performance liquid chromatography (HPLC) was used as analytical technique.

Two chromatographic columns (A and B, respectively) were selected on the base of published literature data and preliminary tests were carried out to choose the column (between A and B) which would yield the best separation of the aforementioned compounds. The retention times (*t*) of the two acids, of a substance not retained by the chromatographic columns and of a compound used as internal standard (i.s.) are shown in the first two columns of the Table. Both chromatographic columns are 25 cm long and show the efficiency of 2.56×10^4 theoretical plates per meter ($N\ m^{-1}$).

In actual analysis, an artificial gastric juice was extracted with an appropriate solvents mixture and then final solution ($1\ cm^3$) contained 100 % of the two acids present in the original mixture. $100\ \mu cm^3$ of the extract with $2.7\ \mu moles$ of the internal standard were analysed by HPLC using the selected column. The response factors (F) of CA and GCA with respect to the i.s. and the chromatographic peak areas of the two compounds are reported in the Table.

	Column A <i>t</i> (s)	Column B <i>t</i> (s)	F	Area
Unretained compound	120	130	-	-
Cholic Acid (CA)	380	350	0.5	2200
Glycocholic Acid (GCA)	399	395	0.2	3520
Internal standard	442	430	-	2304

In answering to the questions remember that:

$$R = \frac{\sqrt{N}}{4} \times \frac{\alpha - 1}{\alpha} \frac{K'}{K' + 1} \quad (1)$$

$$\alpha = \frac{t_2'}{t_1'} = \frac{t_2 - t_0}{t_1 - t_0} \quad (2)$$

$$K' = K_2' = \frac{t_2'}{t_0} = \frac{t_2 - t_0}{t_0} \quad (3)$$

Questions:

- 2.1** Using R , α and K' values, demonstrate which of the two chromatographic columns would you use, considering that an accurate determination requires the best possible (baseline) separation of all compounds (do not take into account the unretained compound)?
- 2.2** Calculate the amounts of each acid in the extract solution.

SOLUTION

Nowadays, chromatography is the most powerful technique for the separation and quantification of organic compounds from volatiles to high molecular weight substances. In conjunction with a mass-spectrometer, it can lead to the undoubted identification of compounds even in extremely complex mixtures. Liquid chromatography (HPLC) is becoming a routine analytical technique in a large variety of fields and in particular in biochemistry and in medicine where compounds are unsuitable for gas chromatographic analysis.

- 2.1** Baseline separation requires $R \geq 1.5$ for each pair of peaks (GCA/CA, i.s./GCA). N can be calculated from $N \text{ m}^{-1}$ value taking into account that the column length is 25 cm:

$$N = 2.56 \times 10^4 \times (25/100) = 64 \times 10^2$$

By substituting of α , K and N values in equation 1, the resolution for each pair of peaks can be found.

For column A:

$$\alpha_{GCA/CA} = \frac{399 - 120}{380 - 120} = \frac{279}{260} = 1.07$$

$$K'_{GCA} = \frac{399 - 120}{120} = 2.32$$

$$R_{GCA/CA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.07}{1.07} \times \frac{2.32}{3.32} = 0.91$$

$$\alpha_{i.s./GCA} = \frac{422 - 120}{399 - 120} = \frac{322}{279} = 1.15$$

$$K'_{i.s.} = \frac{442 - 120}{120} = 2.68$$

$$R_{i.s./GCA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.15}{1.15} \times \frac{2.68}{3.68} = 1.9$$

For column B:

$$\alpha_{GCA/CA} = \frac{395 - 130}{350 - 130} = \frac{265}{220} = 1.20$$

$$K'_{GCA} = \frac{395 - 130}{130} = 2.04$$

$$R_{GCA/CA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.20}{1.20} \times \frac{2.04}{3.04} = 2.2$$

$$\alpha_{i.s./GCA} = \frac{430 - 130}{395 - 130} = \frac{300}{265} = 1.13$$

$$K'_{i.s.} = \frac{430 - 130}{130} = 2.31$$

$$R_{i.s./GCA} = \frac{\sqrt{64 \cdot 10^2}}{4} \times \frac{0.13}{1.13} \times \frac{2.31}{3.31} = 1.6$$

For column B the minimum value of R is 1.6 (>1.5) so that complete separation is obtained. For column A, $R = 0.91$ (<1.5) for the pair GCA/CA which, then, is not completely separated. Therefore column B should be used.

2.2 The amount of acid in the extract solution (1 cm³) can be calculated from the relationship:

$$\frac{\mu\text{moles}_{\text{acid}}}{\mu\text{moles}_{\text{i.s.}}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F}$$

where F is the response factor.

Therefore:

$$\mu\text{moles}_{\text{acid}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F} \times \mu\text{moles}_{\text{i.s.}} \times \frac{1000}{100}$$

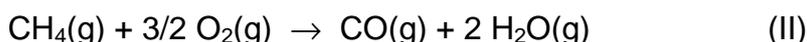
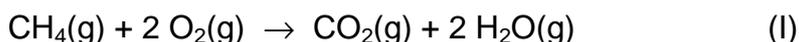
$$n(\text{CA}) = \frac{2200}{2304} \times \frac{1}{0.5} \times 2.7 \times 10 = 51.6 \mu\text{mol}$$

$$n(\text{GCA}) = \frac{3520}{2304} \times \frac{1}{0.2} \times 2.7 \times 10 = 206 \mu\text{mol}$$

PROBLEM 3

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The student may be aware that the acceptable concentration of CO in air is ≤ 5 ppm and the maximum tolerable level is 50 ppm.

The following reactions occur in methane burner:



Compound	CH ₄	O ₂	CO ₂	CO	H ₂ O
ΔH_f° (kJ mol ⁻¹)	-74.9	0	-393.5	-110.5	-241.8
S° (J K ⁻¹ mol ⁻¹)	186.2	205.0	213.6	197.6	188.7

Questions:

- 3.1** Calculate the equilibrium constants for both reactions at $T = 1500$ K assuming that the values ΔH° and ΔS° are independent of the temperature.
- 3.2** Find the relationship between the mole numbers of oxygen and carbon monoxide at equilibrium ($T = 1500$ K, $p = 1$ atm) when air is admitted into the burner in such amount that the mole ratio CH₄ : O₂ is 1 : 2.

Assume the following volume composition of air: 80 % N₂ and 20 % O₂.

Make the approximation that $n(\text{CH}_4) \cong 0$ at equilibrium and justify it on the bases of the answers to the question 3.1.

- 3.3** Calculate the equilibrium mole fraction x of CO in the conditions given in the question 3.2. Assume that the mole fraction of CO is very small in comparison with that of CO₂ and consequently, the total number of moles does not appreciably vary during the combustion. Justify this assumption.

- 3.4** Repeat the calculations of items 3.2 and 3.3 assuming that twice the amount of air (compared to the conditions in question 3.2) is admitted into the burner (4 mol O₂: 1 mol CH₄).
- 3.5** Calculate the concentrations of CO (expressed as ppm by volume) in the fumes after condensation of water vapour under the conditions of question 3.2 and 3.4, assuming that the composition does not change appreciably during the cooling from 1500 K to room temperature and neglecting the contribution of water vapour to the composition of the gas phase.

SOLUTION

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The problem involves the calculation of equilibrium constants, consideration of simultaneous equilibria and simple stoichiometric calculations.

$$\mathbf{3.1} \quad \Delta_1 H^0 = 74.9 - 393.5 - (2 \times 241.8) = -802.2 \text{ kJ mol}^{-1}$$

$$\Delta_1 S^0 = -186.2 - (2 \times 205.0) + 213.6 + (2 \times 188.7) = -5.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_1 = \exp -\frac{\Delta_1 H^0 - T\Delta_1 S^0}{RT} = \exp \frac{802.2 - 1.5 \times 5.2}{8.314 \times 1.5} = 4.62 \times 10^{27}$$

$$\Delta_{II} H^0 = 74.9 - 110.5 - (2 \times 241.8) = -519.2 \text{ kJ mol}^{-1}$$

$$\Delta_{II} S^0 = -186.2 - (1.5 \times 205.0) + 197.6 + (2 \times 188.7) = 81.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_{II} = \exp \frac{519.2 - 1.5 \times 81.3}{8.314 \times 1.5} = 2.13 \times 10^{22}$$

- 3.2** Since K_1 and K_{II} are very large, both equilibria are completely shifted to the right so that $n_{\text{CH}_4} = 0$.

$$\text{At equilibrium: } n_{\text{CH}_4} = 0; \quad n_{\text{H}_2\text{O}} = 2; \quad n_{\text{N}_2} = 8; \quad n_{\text{CO}_2} + n_{\text{CO}} = 1;$$

$$n_{\text{O}_2} = 2 - (2 n_{\text{CO}_2} + 1.5 n_{\text{CO}}) = 0.5 n_{\text{CO}}$$

- 3.3** In reaction I the total number of moles does not vary; in reaction II it changes from 8.5 to 9 (taking into account the presence of N₂), but this change affects the total number of moles only negligibly since $K_{II} \ll K_1$.

Before reaction: $n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{O}_2} + n_{\text{N}_2} = 1 + 2 + 8 = 11$

$$\frac{K_{\text{II}}}{K_{\text{I}}} = \frac{p_{\text{CO}} p_{\text{O}_2}^{1/2}}{p_{\text{CO}_2}} = \frac{x_{\text{CO}} (x_{\text{O}_2} p)^{1/2}}{x_{\text{CO}_2}}$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{tot}}} = \frac{1 - n_{\text{CO}}}{n_{\text{tot}}} = \frac{1}{11} \quad \text{since } n_{\text{CO}} \ll n_{\text{CO}_2} \text{ as a consequence of } K_{\text{II}} \ll K_{\text{I}}$$

$$x_{\text{CO}}^{3/2} = \frac{K_{\text{II}} (2/p)^{1/2}}{K_{\text{I}} \cdot 11} = \frac{2.13 \times 10^{22} \times 1.414}{4.62 \times 10^{27} \times 11} = 5.93 \times 10^{-7}$$

$$x_{\text{CO}} = 7.06 \cdot 10^{-5}$$

3.4 $n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{O}_2} + n_{\text{N}_2} = 1 + 4 + 16 = 21$

At equilibrium: $n_{\text{O}_2} = 4 - (2 n_{\text{CO}_2} + 1.5 n_{\text{CO}}) = 2 + 0.5 n_{\text{CO}} = 2$

$$n_{\text{CO}_2} = 1 - n_{\text{CO}}$$

$$\frac{K_{\text{II}}}{K_{\text{I}}} = \frac{x_{\text{CO}} (x_{\text{O}_2} p)^{1/2}}{x_{\text{CO}_2}} = x_{\text{CO}} (2/21)^{1/2} \times 21 = (42)^{1/2} x_{\text{CO}}$$

$$x_{\text{CO}} = 42^{-1/2} \frac{K_{\text{II}}}{K_{\text{I}}} = 42^{-1/2} \times \frac{2.13 \times 10^{22}}{4.62 \times 10^{27}} = 7.11 \times 10^{-7}$$

3.5 As a consequence of the condensation of water vapour, the number of moles in the gaseous phase changes from 11 to 9 in case c), and from 21 to 19 in case d).

Therefore the mole fraction of CO changes to:

$$x_{\text{CO}} = 7.06 \times 10^{-5} \times \frac{11}{9} = 8.63 \times 10^{-5} \quad \text{and to:}$$

$$x_{\text{CO}} = 7.11 \times 10^{-7} \times \frac{21}{19} = 7.86 \times 10^{-7} \quad \text{in case 3.4}$$

These values correspond to 86 and 0.8 ppm, respectively.

PROBLEM 4

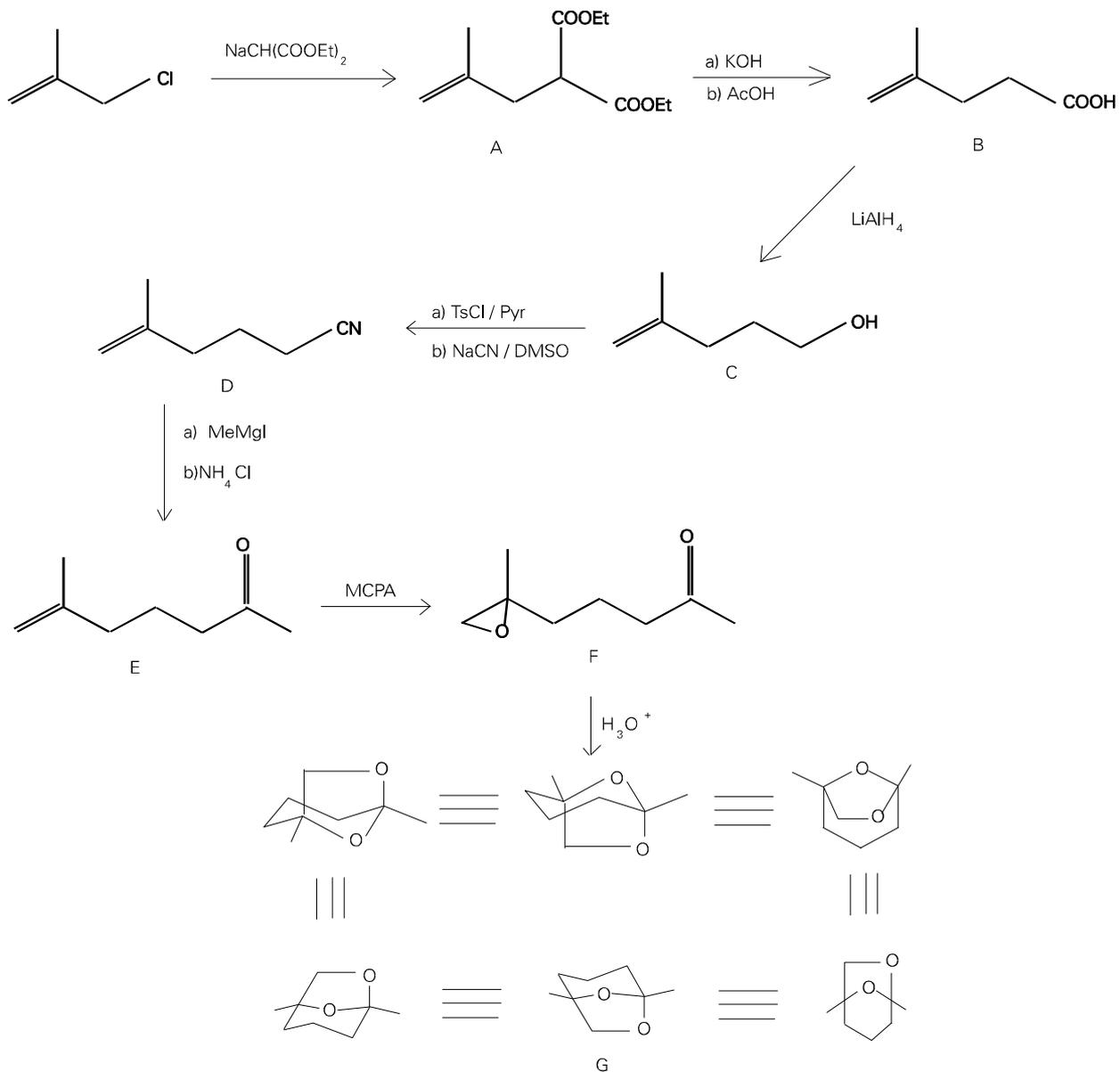
- i) Frontalin is a pheromone of the western pine beetle with composition C 67.58 %, H 9.92 %, O 22.50 %. It is an acetal that can be prepared through a rather long synthesis starting from sodium diethylmalonate (sodium salt of propanedioic acid, diethyl ester) and 3-chloro-2-methylpropene.
- ii) The product **A** resulting from this first step is subsequently hydrolyzed by conc. potassium hydroxide and then decarboxylated by treatment with hot acetic acid to give a compound **B**. The latter reacts with aq NaHCO₃ (gas evolution is observed) as well as with cold aq KMnO₄ which turns to a brown colour.
- iii) The compound **B** is then converted by LiAlH₄ into a new compound **C** (C₆H₁₂O).
- iv) Treatment of **C** with p-toluenesulfonyl chloride in pyridine and then sodium cyanide in dimethylsulfoxide, affords **D** (C₇H₁₁N).
- v) The subsequent reaction of **D** with methylmagnesium iodide, followed by hydrolysis, yield **E** (C₈H₁₄O). **E** shows IR absorption at ca 1700 cm⁻¹.
- vi) The epoxidation of **E** with metachloroperbenzoic acid then affords **F** (C₈H₁₄O₂) which, by treatment with diluted acids is converted to frontalin acetal **G**.

Questions:

4.1 Draw the structures of compounds **A - G**.

SOLUTION

4.1



PROBLEM 5

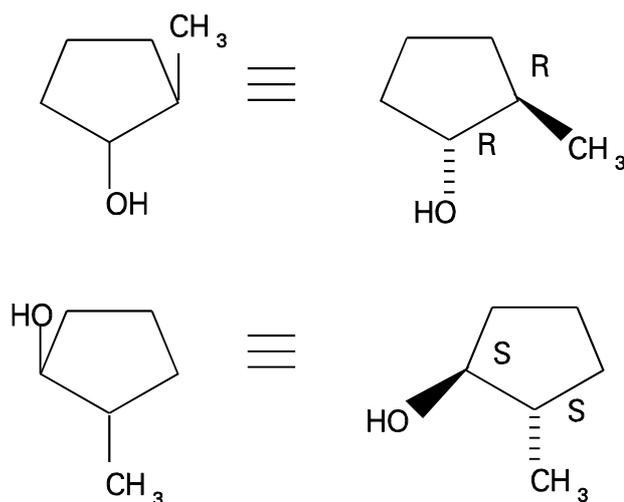
By treatment with a chiral optically active hydroborating agent (R_2^*BH) and subsequent oxidative work-up, 1-methylcyclopentene affords a mixture of alcohols that rotates the plane of the polarized light.

Questions:

- 5.1 Write the structures of the alcohols.
- 5.2 Assign the configurations (R , S) to the chiral centres.
- 5.3 Explain in a sentence why the obtained mixture of alcohols exhibits optical activity.

SOLUTION

5.1, 5.2



- 5.3 Due to the chirality of the hydroborating agent, one enantiomer prevails against the other.

In alternative: $R,R > S,S$ or $S,S > R,R$

PRACTICAL PROBLEMS

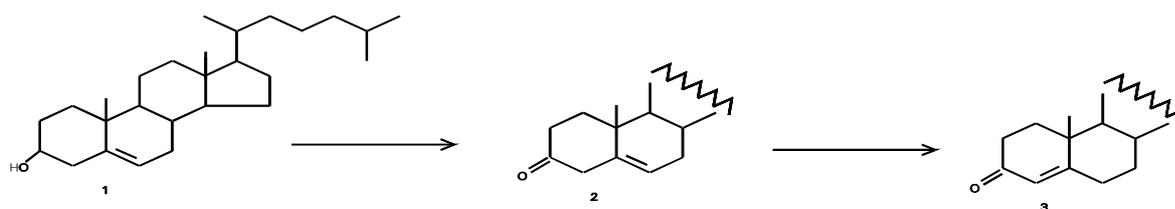
PROBLEM 1 (Practical)

Synthesis

Cholesterol (1) is a natural sterol metabolite present in animal and vegetal organisms. This compound can be oxidized by Jones' reagent into its corresponding 3-ketoderivative (2). The latter, when treated with bases, undergoes isomerization of the carbon-carbon double bond leading to α,β -unsaturated ketone (3).

The conversion of Δ^5 -3 β -hydroxy steroids into their corresponding Δ^4 -3-ketones is an important reaction in steroid chemistry and represents the last step of the synthesis of a variety of commercial hormones.

You will be marked for the purity of the product (3).



Procedure:

- Dissolve your pre-weighed sample of cholesterol (386 mg, 1 mmol) contained in a 50 cm³ flask A with acetone (20 cm³) warming gently the flask in a bath tub of hot water. When the sample is completely dissolved, cool the flask containing the solution to the temperature by cold water.
- Add dropwise 0.40 cm³ of Jones' reagent to the solution, gently swirling the flask in a bath of cold water. The formation of a green precipitate [Cr₂(SO₄)₃] is observed during the addition of Jones' reagent.
- Remove the green precipitate by filtration with paper filter.
- Add slowly water (10 cm³) to the clean filtrate. The ketone (2) begins to precipitate.
- Filter the precipitate over the Büchner funnel under reduced pressure, washing the crystals with small portions of a 2 : 1 acetone/water mixture.
- Dissolve the ketone (2) in methanol (15 cm³). Add to the solution just one drop of 5 % methanolic NaOH solution and warm the mixture in a bath of hot water for 10 min.

- g) The Δ^4 -3-ketosteroid (3) precipitates spontaneously, upon addition of water (ca. 2 cm³) to the cooled reaction mixture. Filter the crystals over the Büchner funnel under reduced pressure and recrystallize the product by methanol. If you do not get the crystals, add a few drops of water. *Remember! You are getting a mark for the purity, not the yield.*
- h) Dry carefully the crystals on a porous plate. Determine the melting point of the ketone (3) and write its value on your student's report. Taking into account the correction reported on the top of the thermometer (see example at the end).
- i) Put the crystals in the plastic vial B, write on it your personal identification number (see the left corner of your badge), and deliver it to one of the supervisors.

The melting point of the ketone (3) will be checked by the lab supervisors.

SOLUTION

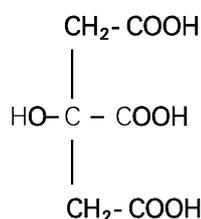
Points were given accordingly to the amount of product.

Some additional points were given for melting point measurements.

PROBLEM 2 (Practical)Analysis

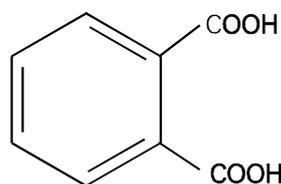
Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is widely distributed in plants and in animal tissues. Lemon juice contains from 5 to 8% of this acid. It is produced by mycological fermentation on an industrial scale using crude sugar solutions, such as molasses, and stains of *Aspergillus niger*.

It is utilized as an acidulant and antioxidant in several beverages.



MM = 192.12 g/mol

$\text{pK}_1 = 3.06$; $\text{pK}_2 = 4.74$; $\text{pK}_3 = 5.40$



MM = 204.23 g/mol

- a) Standardization of NaOH solution (ca 0.1 mol dm⁻³) by potassium hydrogen phthalate

Procedure:

A preweighed quantity (2.050 g) of potassium hydrogen phthalate is in the 100 cm³ volumetric flask B. Dilute this sample with water to the mark. Phenolphthalein indicator (2 - 3 drops) is added to an aliquot of 25.0 cm³ of the resulting solution and the solution is then titrated with the NaOH solution that has to be standardized.

Give the concentration of the NaOH solution.

- b) Titrimetric determination of citric acid

Procedure:

The unknown sample of citric acid is in the 100 cm³ volumetric flask C. Dilute the sample with water to the mark. Transfer 25.0 cm³ of the resulting solution into a 250 cm³ Erlenmeyer flask and dilute with water. Add 2 – 3 drops of phenolphthalein indicator and titrate with the previously standardized NaOH solution.

Give the mass of citric acid.

SOLUTION

Marks were given accordingly to determined mass of citric acid.

Some additional points were given for correct calculations.

26th



**8 theoretical problems
2 practical problems**

THE TWENTY-SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 3–11 JULY 1994, OSLO, NORWAY

THEORETICAL PROBLEMS

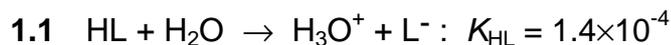
PROBLEM 1

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written as HL is monoprotic, and the acid dissociation constant is $K_{\text{HL}} = 1.4 \times 10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{\text{a}1} = 4.5 \times 10^{-7}$ and $K_{\text{a}2} = 4.7 \times 10^{-11}$. All carbon dioxide remains dissolved during the reactions.

- 1.1 Calculate pH in a 3.00×10^{-3} M solution of HL.
- 1.2 Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.
- 1.3 3.00×10^{-3} mol of lactic acid (HL) is added to 1.00 dm^3 of 0.024 M solution of NaHCO_3 (no change in volume, HL completely neutralized).
 - i) Calculate the value of pH in the solution of NaHCO_3 before HL is added.
 - ii) Calculate the value of pH in the solution after the addition of HL.
- 1.4 pH in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having $pH = 7.40$ and $[\text{HCO}_3^-] = 0.022$ represent blood in the following calculation. How many moles of lactic acid have been added to 1.00 dm^3 of this solution when its pH has become 7.00 ?
- 1.5 In a saturated aqueous solution of $\text{CaCO}_3(\text{s})$ pH is measured to be 9.95 . Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5×10^{-9} .
- 1.6 Blood contains calcium. Determine the maximum concentration of "free" calcium ions in the solution ($pH = 7.40$, $[\text{HCO}_3^-] = 0.022$) given in 1.4.

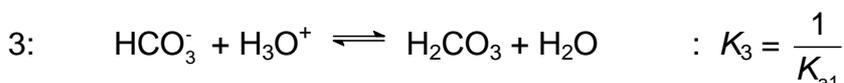
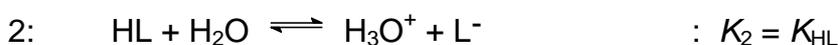
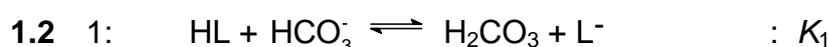
SOLUTION

$$c_0 - x \qquad \qquad x \qquad x$$

$$K_a = \frac{x^2}{c_0 - x} = 1.4 \times 10^{-4} \qquad c_0 = 3.00 \times 10^{-3}$$

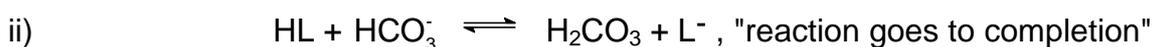
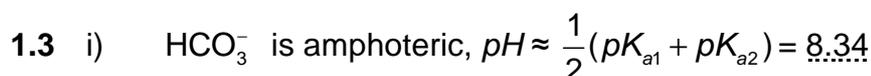
Assumption $c_0 \gg x$ gives $x = 6.5 \cdot 10^{-4}$, not valid

Quadratic formula: $x = 5.8 \times 10^{-4}$, $[\text{H}_3\text{O}^+] = 5.8 \times 10^{-4}$, $\text{pH} = 3.24$



Reaction 1 = 2 + 3, $K_1 = K_2 \cdot K_3 = 311 \quad (3.1 \times 10^2)$

$$\text{Alternative: } K_1 = \frac{[\text{H}_2\text{CO}_3][\text{L}^-]}{[\text{HL}][\text{HCO}_3^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]} \times \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}$$

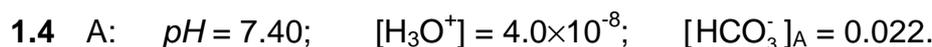


Before: 0.0030 0.024 0 0

After: 0 0.021 0.0030 0.0030

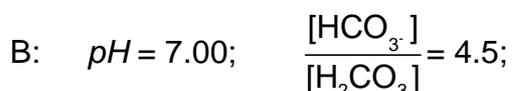
Buffer: $\text{pH} \approx \text{p}K_{a1} + \log \frac{0.021}{0.0030} = 6.35 + 0.85 = 7.20$

(Control: $\frac{K_{\text{HL}}}{[\text{H}_3\text{O}^+]} = \frac{[\text{L}^-]}{[\text{HL}]} = 2.2 \times 10^3$, assumption is valid)



From K_{a1} : $[\text{H}_2\text{CO}_3]_{\text{A}} = 0.0019$;

$$(1) [\text{HCO}_3^-]_{\text{B}} + [\text{H}_2\text{CO}_3]_{\text{B}} = 0.0239 \quad (0.024)$$



$$(2) \quad [\text{HCO}_3^-]_{\text{B}} = 4.5 [\text{H}_2\text{CO}_3]_{\text{B}}$$

$$\text{From (1) and (2):} \quad [\text{HCO}_3^-]_{\text{B}} = 0.0196$$

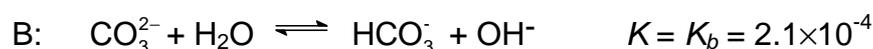
$$[\text{H}_2\text{CO}_3]_{\text{B}} = 0.0043$$

$$n(\text{HL}) = \Delta n(\text{H}_2\text{CO}_3) = \Delta c(\text{H}_2\text{CO}_3) \times 1.00 \text{ dm}^3 = 2.4 \times 10^{-3} \text{ mol}$$

$$1.5 \quad [\text{OH}^-] = 8.9 \times 10^{-5} \quad [\text{H}_2\text{CO}_3] \text{ of no importance}$$



$$c_0 \qquad c_0$$



$$c_0 - x \qquad x \qquad x$$

$$\text{From B:} \quad [\text{HCO}_3^-] = [\text{OH}^-] = 8.9 \times 10^{-5}$$

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-][\text{OH}^-]}{K_b} = 3.8 \times 10^{-5}$$

$$[\text{Ca}^{2+}] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.3 \times 10^{-4}$$

$$c_0(\text{Ca}^{2+}) = 1.3 \times 10^{-4} \text{ mol dm}^{-3} = \text{solubility}$$

$$1.6 \quad K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 1.3 \times 10^{-4} \times 3.8 \times 10^{-5} = 4.9 \times 10^{-9} = 5 \times 10^{-9}$$

$$\text{From } K_{a2}: \quad [\text{CO}_3^{2-}] = \frac{K_{a2} [\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} = 2.6 \times 10^{-5}$$

$$Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]; \quad \text{Precipitation when } Q > K_{sp} = 5 \times 10^{-9}$$

No precipitation when $Q < K_{sp}$

Max. concentration of "free" Ca^{2+} ions:

$$[\text{Ca}^{2+}]_{\text{max}} = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = 1.9 \times 10^{-4}$$

PROBLEM 2

Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

- 2.1** 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 cm³ of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 cm³ of 0.1050 M sodium hydroxide. Calculate the concentration of nitrogen in the sample, in percent by mass.
- 2.2** Calculate the *pH* of the solution which is titrated in 2.1 when 0 cm³, 9.65 cm³, 19.30 cm³ and 28.95 cm³ of sodium hydroxide have been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid. K_a for ammonium ion is 5.7×10^{-10} .
- 2.3** Draw the titration curve based on the calculations in b).
- 2.4** What is the *pH* transition range of the indicator which could be used for the back titration.
- 2.5** The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting 0.2345 g of the pure acid and distilling ammonia released into 50.00 cm³ of 0.1010 M hydrochloric acid. A titration volume of 17.50 cm³ was obtained for the back titration with 0.1050 M sodium hydroxide. Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

SOLUTION

$$\mathbf{2.1} \quad [(50.00 \times 0.1010) - (19.30 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2515} = 16.84 \% \text{ N}$$

$$\mathbf{2.2} \quad 0 \text{ cm}^3 \text{ added:} \quad [\text{H}^+] = \frac{19.30 \cdot 0.1050}{50} = 0.04053$$

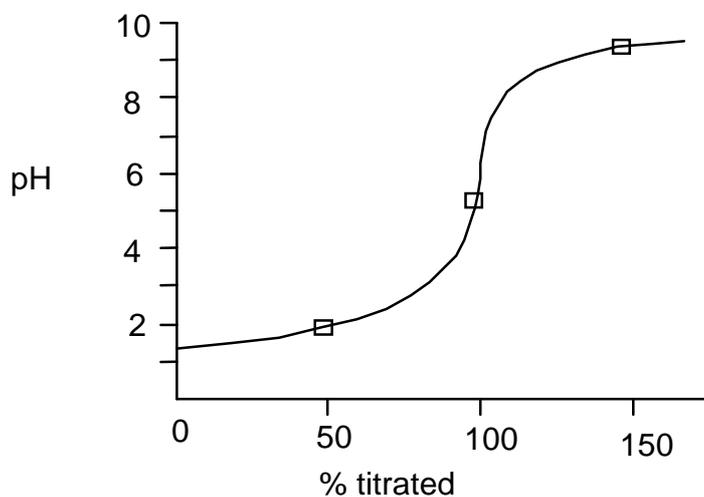
$$pH = 1.39$$

9.65 cm³ added: $[H^+] = 0.01699$
 $pH = 1.77$

19.30 cm³ added: $[H^+] = \sqrt{5.7 \cdot 10^{-10} \times \frac{50.000 \times 101019 \times 300 \times 1050}{50 + 19.30}}$
 $pH = 5.30$

28.95 cm³ added: $pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.24 + \log \frac{1.01}{2.01} = 8.94$

2.3



2.4 Indicator pH transition range: $pH 5.3 \pm 1$

2.5 $[(50.00 \times 0.1010) - (17.50 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2345} = 19.19 \% N$

1 N: $M_r = 73.01$

2 N: $M_r = 146.02$

PROBLEM 3

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

- 3.1** Write Lewis structures for molecules SCl_2 , SO_3 , SO_2ClF , SF_4 , and SBrF_5 .
- 3.2** Carefully draw the geometries of the 5 molecules. (Disregard small deviations from "ideal" angles.)
- 3.3** A compound, consisting of sulphur (one atom per molecule), oxygen and one or more atoms of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests?

- i) Addition of HNO_3 and AgNO_3 .
- ii) Addition of $\text{Ba}(\text{NO}_3)_2$.
- iii) Adjustment to $\text{pH} = 7$ with NH_3 and addition of $\text{Ca}(\text{NO}_3)_2$.

Write the equations for the possible reactions in the tests:

- iv) Addition of KMnO_4 followed by $\text{Ba}(\text{NO}_3)_2$ to an acid solution of the substance.
- v) Addition of $\text{Cu}(\text{NO}_3)_2$.

- 3.4** In practice, the tests in 3.3 gave the following results:

- i) A yellowish precipitate.
- ii) No precipitate.
- iii) No visible reaction.
- iv) The main features were that the characteristic colour of permanganate disappeared, and a white precipitate was formed upon addition of $\text{Ba}(\text{NO}_3)_2$.
- v) No precipitate.

Write the formulas of the possible compounds, taking the results of these tests into account.

- 3.5** Finally, a simple quantitative analysis was undertaken:

7.190 g of the substance was weighed out and dissolved in water to give 250.0 cm³ of a solution. To 25.00 cm³ of this solution, nitric acid and enough AgNO_3 was added

to secure complete precipitation. After washing and drying the precipitate weighed 1.452 g. Determine the formula of the compound.

3.6 Write the equation describing the reaction of the substance with water.

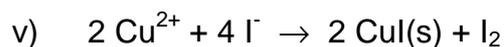
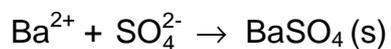
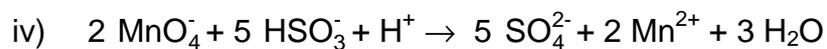
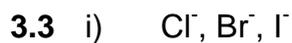
If you have not found the formula for the compound, use SOClF.

SOLUTION

3.1

3.2

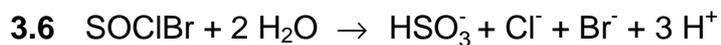
SCl ₂		<p>Bent</p>
SO ₃		<p>Trigonal planar</p>
SO ₂ ClF		<p>Tetrahedral</p>
SF ₄		<p>Trigonal bipyramidal - 1 corner</p>
SBrF ₅		<p>Octahedral</p>



3.4 SOClBr and SOBr_2

3.5 SOClBr

[SOClBr : 1.456g, and SOBr_2 : 1.299g]



PROBLEM 4

Platinum(IV) oxide is not found in the nature, but it can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas at 1 atm ($= 1.01325 \times 10^5$ Pa) and 650 °C.

4.1 This suggests that the conditions on the Earth, when the minerals we know were formed, were:

[1] $p(\text{O}_2) = 1$ atm, $t = 650$ °C;

[2] $p(\text{O}_2) < 1$ atm, $t < 650$ °C;

[3] $p(\text{O}_2) > 1$ atm, $t < 650$ °C;

[4] $p(\text{O}_2) < 1$ atm, $t > 650$ °C;

[5] $p(\text{O}_2) > 1$ atm, $t > 650$ °C

Mark the most probable alternative [1] – [5] on the answer sheet. Please note that the marking of only one alternative will be accepted.

4.2 What are ΔG and K_p for the formation of platinum(IV) oxide at oxygen pressure of 1 atm and temperature of 650 °C?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process $\text{PtO}_2 \cdot n \text{H}_2\text{O}$ is formed and this is in turn converted to platinum(IV) oxide upon subsequent filtering and heat treatment. In the following we assume $n = 4$.

$\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$ or $\text{Pt}(\text{OH})_4 \cdot 2 \text{H}_2\text{O}$ can be dissolved in acids and strong bases.

4.3 Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.

4.4 Write the balanced equations for the dissolution of $\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$ in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in the nature as the metal (in mixture or in alloying with other precious metals). Platinum is dissolved in aqua regia under the formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3 : 1, and of the nitrosylchloride (NOCl) and the atomic chlorine which are formed upon the mixing. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV) and by thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

- 4.5** Write the balanced equations for the formation of aqua regia and its reaction with platinum.
- 4.6** Write the balanced equation of the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ which occurs in *cis* ($\Delta H_f^0 = -467.4 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -228.7 \text{ kJ mol}^{-1}$) and *trans* ($\Delta H_f^0 = -480.3 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -222.8 \text{ kJ mol}^{-1}$) form.

- 4.7** The occurrence of the isomers shows that $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has geometry:
- [1] linear,
 - [2] planar,
 - [3] tetrahedral,
 - [4] octahedral geometry.

Mark the correct alternative of [1] – [4] on the answer sheet.

- 4.8** Is the *cis* form or *trans* form thermodynamically more stable?

Platinum is used as a catalyst in modern automobiles. In the catalyst carbon monoxide ($\Delta H_f^0 = -110.5 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -137.3 \text{ kJ mol}^{-1}$) reacts with oxygen to carbon dioxide ($\Delta H_f^0 = -393.5 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -394.4 \text{ kJ mol}^{-1}$).

- 4.9** Is the reaction spontaneous at 25 °C?

[1] yes, or

[2] no.

Is the reaction:

[3] endothermic, or

[4] exothermic?

Calculate ΔS° for the reaction.

Establish whether the entropy of the reaction system

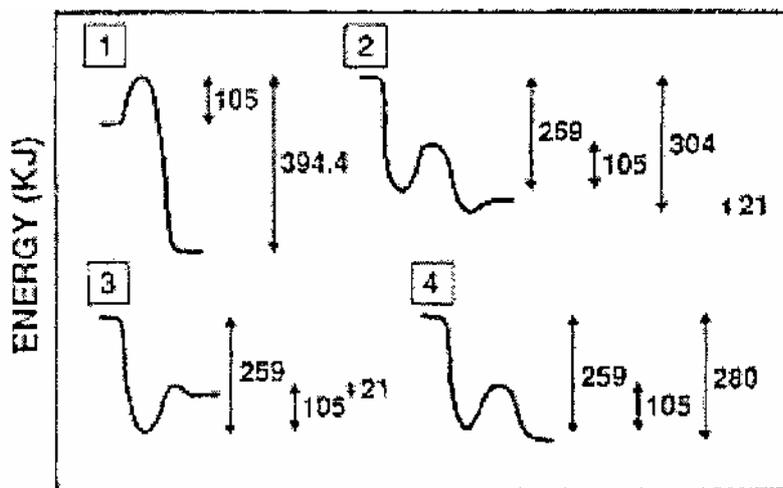
[5] increases, or

[6] decreases.

4.10 Establish an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the homogeneous phase is very complicated with a large number of reaction steps, and the course is difficult to control owing to a distinct chain character. With platinum as catalyst the significant reaction steps are: (i) Adsorption of CO and adsorption/dissociation of O₂ ($\Delta H = -259$ kJ per mol CO + O), (ii) their activation (105 kJ per mol CO + O) and (iii) the reaction and the desorption of CO₂ ($\Delta H = 21$ kJ per mol CO₂).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:

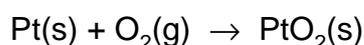


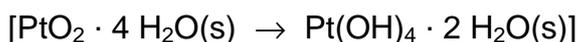
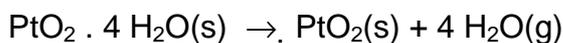
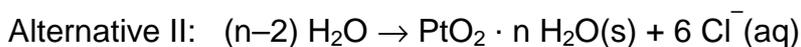
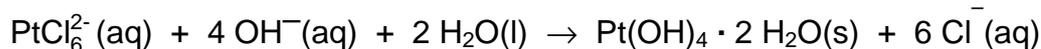
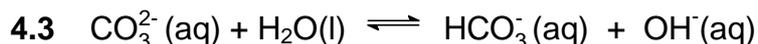
4.11 Mark the correct alternative of [1] – [4] on the answer sheet.

SOLUTION

4.1 Correct answer is No 4.

4.2 $\Delta G = 0$ kJ and $K_p = 1$ according to the chemical equation

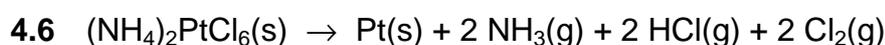
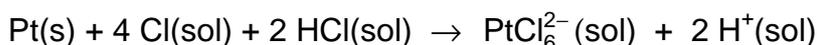
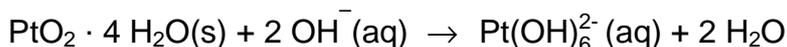




4.4 In hydrochloric acid:



In sodium hydroxide:

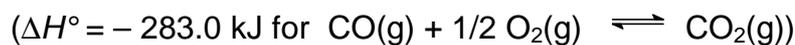


4.7 Correct is No 2.

4.8 The cis form is thermodynamically more stable.



[4] The reaction is exothermic.



[6] is correct.



As seen from the sign for ΔS° as well as for the reaction enthalpy the entropy of the system decreases.

4.10 $\ln K_p = 34037 / T - 10.45$ for $\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$

Alternative: $K_p = \exp^{(34037 / T - 10.45)}$

4.11 No 2 is correct.

PROBLEM 5

There is only one correct answer to each question

5.1 What is the correct systematic name (IUPAC name) for the compound below?

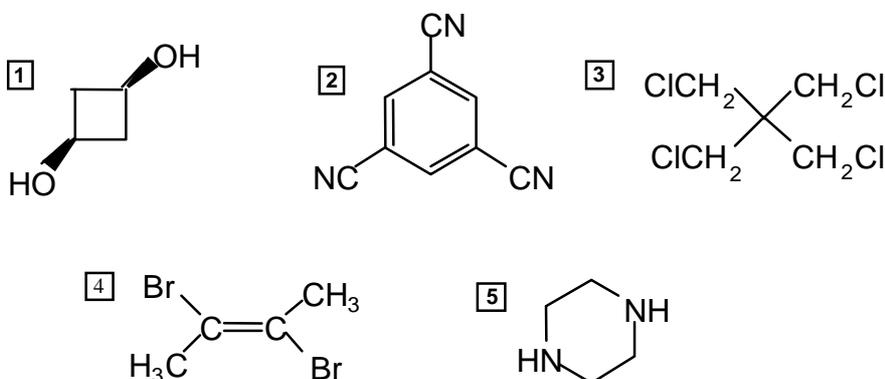


- 1 3-Isopropylhexane
- 2 2-Methyl-3-propylpentane
- 3 Ethyl isopropyl propyl methane
- 4 3-Hexylpropane
- 5 3-Ethyl-2-methylhexane

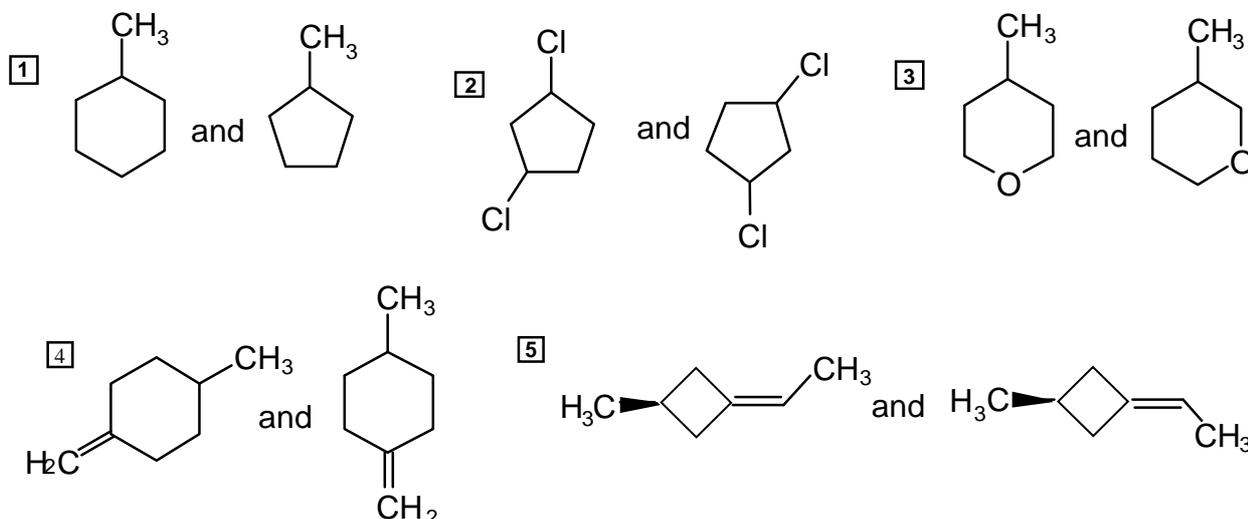
5.2 How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for C_5H_{10} ?

- 1 4 isomers 2 5 isomers 3 6 isomers
- 4 7 isomers 5 8 isomers

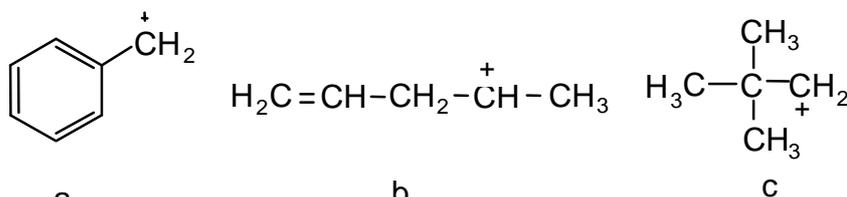
5.3 Which one of the following compounds has a dipole moment significantly different from zero?



5.4 Which of the following is a pair of structural isomers?

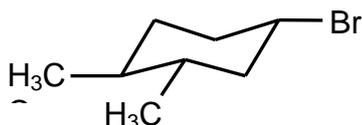


5.5 Which of the following five options is the correct order of relative stabilities of cations a, b and c as written below (most stable first)?



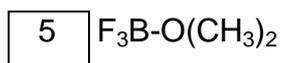
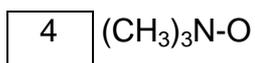
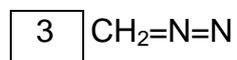
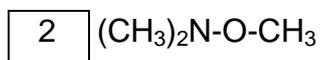
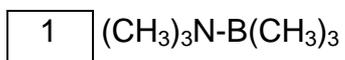
- 1 a>b>c 2 b>c>a 3 c>a>b 4 a>c>b 5 b>a>c

5.6 What is the correct stereochemical descriptor of the optically active compound drawn below?



- 1 1*R*,3*R*,4*R* 2 1*R*,3*R*,4*S* 3 1*R*3*S*,4*R* 4 1*S*,3*S*,4*R* 5 1*S*,3*S*,4*S*

5.7 All the molecules drawn below are neutral compounds. Which one does not contain a formal positive charge and a formal negative charge?



SOLUTION

	1	2	3	4	5
5.1	X				X
5.2				X	
5.3	X				
5.4			X		
5.5	X				
5.6					X
5.7		X			

PROBLEM 6

An optical active compound **A** ($C_{12}H_{16}O$) shows amongst other a strong IR-absorption at $3000 - 3500\text{ cm}^{-1}$, and two medium signals at 1580 and 1500 cm^{-1} . The compound does not react with 2,4-dinitrophenylhydrazine (2,4-D). Upon treatment with $I_2/NaOH$, **A** is oxidized and gives a positive iodoform reaction.

Ozonolysis of **A** (1. O_3 ; 2. Zn, H^+) gives **B** ($C_9H_{10}O$) and **C** ($C_3H_6O_2$). Both **B** and **C** give precipitation when treated with 2,4-D, and only **C** gives positive reaction with Tollens reagent. Nitration of **B** (HNO_3/H_2SO_4) may give two mono-nitro compounds **D** and **E**, but in practical work only **D** is formed.

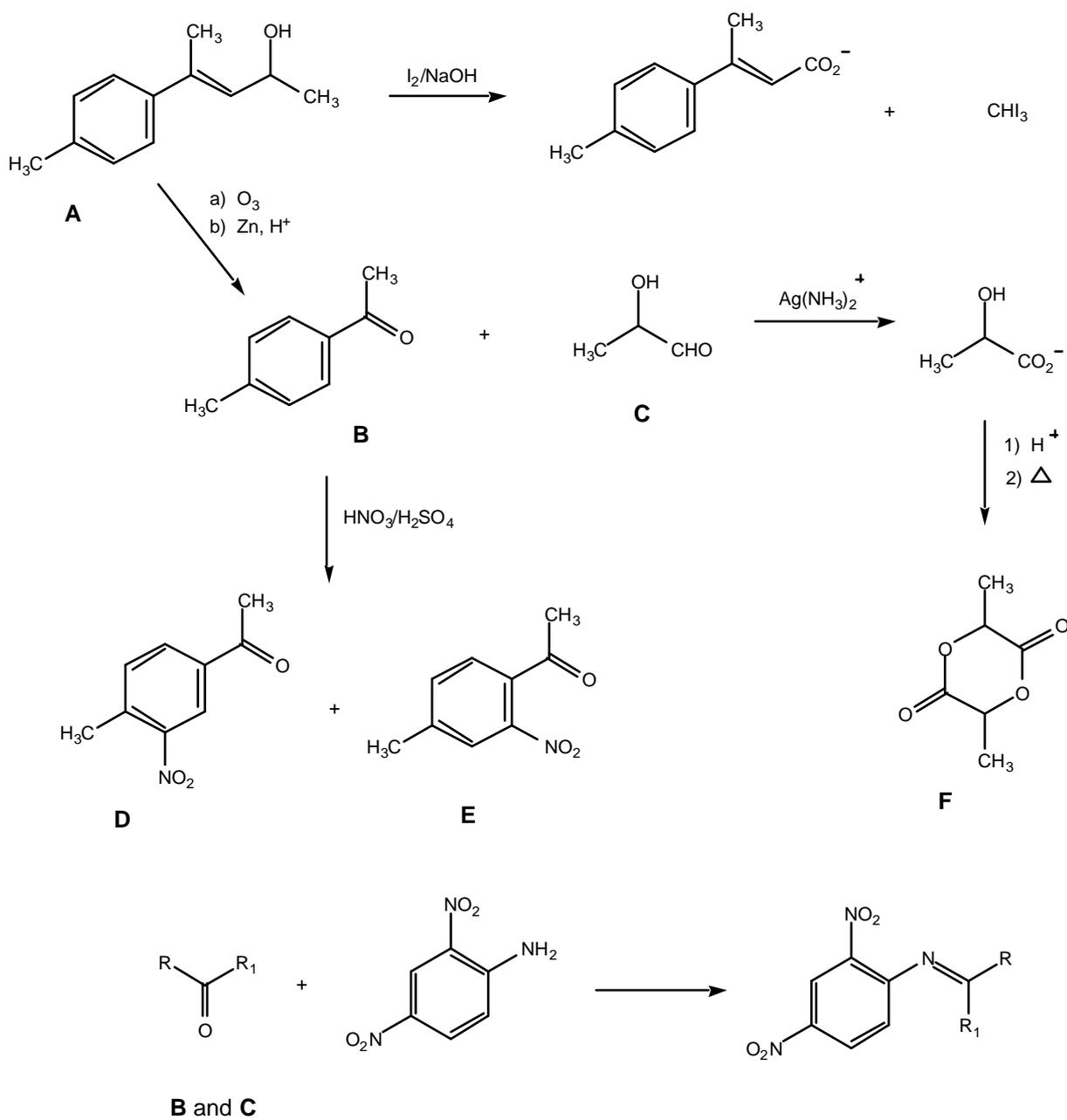
Acidification followed by heating of the product formed by the Tollens reaction on **C** gives compound **F** ($C_6H_8O_4$). The compound gives no absorption in IR above 3100 cm^{-1} .

- 6.1** Based on the above information draw the structure formula(e) for the compounds **A – F** and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.
- 6.2** Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a **D** or L configuration.

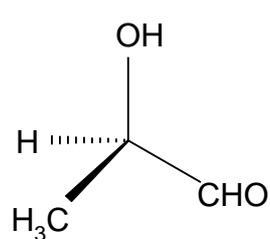
SOLUTION

(See the next page.)

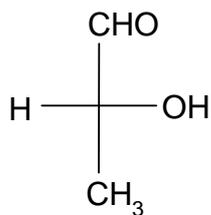
6.1



6.2



R-configuration



D-configuration

PROBLEM 7

7.1 When an ideal, monatomic gas expands reversibly from a volume V_1 to a volume V_2 , a work

$$w = - \int_{V_1}^{V_2} p \, dV$$

is performed on the system by the surroundings. In this equation, w is the work and p is the pressure of the gas.

Determine the performed work when one mole ideal gas expands isothermally from $V_1 = 1.00 \text{ dm}^3$ to $V_2 = 20.0 \text{ dm}^3$ at the temperature $T = 300.0 \text{ K}$.

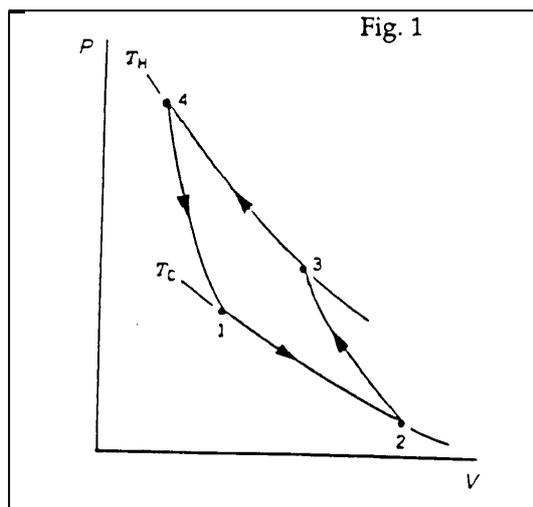
Given: The gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

7.2 Determine how much heat must be added to the gas during the process given under 7.1.

7.3 The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

1	The volume of the gas is constant
2	The expansion is always irreversible
3	No heat is supplied to the gas

7.4 The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here, T_H and T_C represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.



SOLUTION

7.1 Work performed on the gas is

$$w = - \int_{V_1}^{V_2} p \, dV = - RT \int_{V_1}^{V_2} \frac{dV}{V} = - RT \ln \frac{V_2}{V_1}$$

$$= -8,314 \, \text{J K}^{-1} \text{ mol}^{-1} \times 300 \, \text{K} \times \ln \frac{20.00}{1.00} = -7472 \, \text{J mol}^{-1} = -7.47 \, \text{kJ mol}^{-1}$$

7.2 Because this is an isothermal expansion of an ideal monatomic gas, there is no change in internal energy. From the first law of thermodynamics, we then have that $\Delta U = q + w = 0$

where q is the amount of supplied heat and w is performed work. This leads to $\underline{q} = -w = 7.47 \, \text{kJ mol}^{-1}$.

7.3 (3) No heat is supplied to the gas.

7.4	isotherm	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	adiabat	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>

PROBLEM 8

Avogadro's Number: $6.022 \cdot 10^{23}$

8.1 An atom of ^{238}U disintegrates by a series of α -decays and β^- -decays until it becomes ^{206}Pb , which is stable.

i) How many α -decays and how many β^- -decays does an atom starting as ^{238}U undergo before it becomes stable?

ii) One of the following ten nuclides is formed from a series of disintegrations starting at ^{238}U . Which one ?

^{235}U , ^{234}U , ^{228}Ac , ^{224}Ra , ^{224}Rn , ^{220}Rn , ^{215}Po , ^{212}Po , ^{212}Pb , ^{211}Pb .

8.2 In a thermal neutron-induced fission process, ^{235}U reacts with a neutron and breaks up into energetic fragments and (normally) 2-3 new neutrons.

We consider one single fission event:



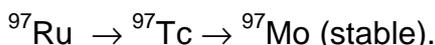
Identify the fragment X.

8.3 The half-life of ^{238}U is 4.5×10^9 years, the half-life of ^{235}U is 7.0×10^8 years. Natural uranium consists of 99.28 % ^{238}U and 0.72 % ^{235}U .

i) Calculate the ratio in natural U between the disintegration rates of these two uranium isotopes.

ii) A mineral contains 50 weight percent uranium. Calculate the disintegration rate of ^{238}U in 1.0 kg of this mineral.

8.4 We have the following radioactive sequence:



Halflives: ^{97}Ru : 2.7 days; ^{97}Tc : 2.6×10^6 years

At $t = 0$ a radioactive source containing only ^{97}Ru has a disintegration rate of 1.0×10^9 Bq.

i) What is the total disintegration rate of the source at $t = 6.0$ days?

ii) What is the total disintegration rate of the source at $t = 6000$ years?

SOLUTION

8.1 i) 8 α 's and 6 β^- 's (only α 's gives ^{206}Os , to come from Os to Pb requires 6 β^- 's).

ii) ^{234}U , all other answers are incorrect.

8.2 ⁹⁷Zr

8.3 i) $D = \lambda N$, i.e. $D_1 / D_2 = \lambda_1 N_1 / \lambda_2 N_2 = \text{abund.}(1)T_{1/2}(2) / \text{abund.}(2)T_{1/2}(1)$
 $= (99.28 \times 7.0 \times 10^8) / (0.72 \times 4.5 \times 10^9) = 21.4$ (0.047 is also of course correct)

ii) $N = (m/AW(U)) \times \text{abundance}(238) \times N_A = (500 / 238.01) \times 0.9928 \times 6.022 \times 10^{23}$
 $= 1.26 \times 10^{24}$

$$D = N \ln 2 / T_{1/2} = 1.26 \times 10^{24} \times \ln 2 / (4.5 \times 10^9 \text{ (y)} \times 3.16 \times 10^7 \text{ (s/y)}) = 6.1 \cdot 10^6 \text{ Bq}$$

8.4 i) $\lambda = \ln 2 / 2.7(\text{d}) = 0.26 \text{ d}^{-1}$

$$D = D_0 e^{-\lambda t} = 1.0 \times 10^9 \times e^{-(0.26 \times 6.0)} = 2.1 \times 10^8 \text{ Bq}$$

ii) Number of ⁹⁷Ru atoms in the source:

$$N = D T_{1/2}({}^{97}\text{Ru}) / \ln 2 = 1.0 \times 10^9 \text{ (Bq)} \times 2.7 \text{ (d)} \times 24 \text{ (h/d)} \times 3600 \text{ (s/h)} / 0.6931 =$$

$$= 3.4 \times 10^{14} \text{ atoms}$$

When all ⁹⁷Ru has disintegrated, these atoms have all become ⁹⁷Tc, and the disintegration rate of this nuclide is

$$D = N \ln 2 / T_{1/2}({}^{97}\text{Tc}) = (3.4 \times 10^{14} \times 0.6931) / (2.6 \cdot 10^6 \text{ y} \times 3.16 \times 10^7 \text{ s y}^{-1}) =$$

$$= 2.9 \text{ Bq}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Fatty Acids

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 cm³ of this solution contain a total of 1.00 g acid plus ester). By titration the acid number¹⁾, the saponification number²⁾ and the iodine number³⁾ of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

Note: The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 cm³). There will be no supplementation.

- 1) Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.
- 2) Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.
- 3) Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Relative atomic masses:

$$A_r(\text{I}) = 126.90 \quad A_r(\text{O}) = 16.00$$

$$A_r(\text{K}) = 39.10 \quad A_r(\text{H}) = 1.01$$

1) Determination of the Acid Number

Reagents and Apparatus

Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1 : 1 mixture), burette (50 cm³), Erlenmeyer flasks (3 x 250 cm³), measuring cylinder (100 cm³), graduated pipette (2 cm³), funnel.

Procedure:

Pipette out aliquots (2.00 cm³) from the unknown mixture into Erlenmeyer flasks (250 cm³). Add first ca. 100 cm³ of an ethanol/ether mixture (1:1) and then add the indicator (5 drops).

Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

2) Determination of the Saponification Number*Reagents and Apparatus*

Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 cm³), round bottom flask (250 cm³), Liebig condenser, burette (50 cm³), Erlenmeyer flasks (3 x 250 cm³), volumetric pipette (25 cm³), volumetric pipette (10 cm³), graduated pipette (2 cm³), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

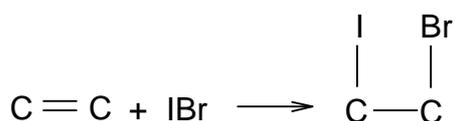
Procedure

Pipette out a 2.00 cm³ aliquot of the unknown sample into a round bottom flask (250 cm³) and add 25.0 cm³ 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for 30 min in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 cm³ volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm³ and titrate with 0.1000 M HCl using phenolphthalein as indicator (5 drops).

Calculate the saponification number.

3) Determination of the Iodine Number

In this experiment iodobromine adds to the double bond.



The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I₂, (IBr + I⁻ → I₂ + Br⁻) which in turn is determined by standard thiosulphate solution.

Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.

Reagents and Apparatus

Unknown sample, 0.2000 M Hanus solution, dichloro-methane, 15 % KI solution in distilled water, distilled water, 0.2000 M sodium thiosulphate, starch indicator, Erlenmeyer flasks (3 x 500 cm³), buret (50 cm³), graduated pipette (2 cm³), measuring cylinders (10 and 100 cm³), volumetric pipette (25 cm³), aluminium foil.

Procedure

Pipette out aliquots (1.00 cm³) of the unknown mixture into Erlenmeyer flasks (500 cm³) and add 10 cm³ of dichloromethane. With a pipette add 25.0 cm³ Hanus solution, cover the opening with aluminium foil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 cm³ of the 15 % KI solution, shake thoroughly and add 100 cm³ of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm³) and continue titration until the blue colour entirely disappears.

Calculate the iodine number.

4) Use the results from 1) 2) and 3) to:

- i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester.
- ii) Calculate the number of double bonds in the unsaturated acid.

PROBLEM 2 (Practical)**Volumetric Determination of Bromide by Back-titration with Thiocyanate after Precipitation with Silver Ions in Excess**

Moments worth considering:

- The candidates must consider the number of significant figures that will be reasonable in the results.
- The candidates must be able to carry out the whole analysis by using the delivered portions of silver nitrate and potassium thiocyanate. Supplementation of these two solutions will not be available.
- Only *one* 25 cm³ pipette will be at disposal for each candidate.

Principle

Bromide is precipitated as silver bromide after a known amount of silver ions has been added in excess.

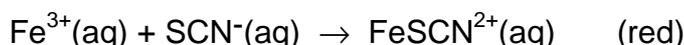


The excess of silver ions is titrated with thiocyanate with a known concentration, after a previous standardization of the thiocyanate solution.

During the titration of the following reaction takes place resulting in the precipitation of silver thiocyanate:



Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:

**a) Procedures**

Every candidate has got a 0.5 dm³ brown bottle with screw cap, containing the potassium thiocyanate solution (about 0.08 M) and also a 0.25 dm³ brown bottle with screw cap, containing the silver nitrate solution. The concentration of this solution is 0.1000 M. The exact concentration of the KSCN solution is to be determined by the candidates.

i) Determination of bromide in the unknown sample solution

Fill the 250 cm³ volumetric flask containing the bromide sample solution to the mark with water. Transfer three 25.00 cm³ portions (pipette) of the sample solution to three Erlenmeyer flasks. Add about 5 cm³ of 6 M nitric acid (measuring cylinder) to each flask. Transfer 25.00 cm³ (pipette) of the accurately known silver solution and about 1 cm³ of iron(III) indicator (ind.) (measuring cylinder) to each solution.

Titrate the contents of the three aliquots with the potassium thiocyanate solution. The end-point of the titration is detected when the solution (including the precipitate) becomes permanently *very faint* brownish. It is important to shake the contents vigorously near the end-point and rinse the walls of the flask with water. The colour should be stable for at least one minute.

ii) Standardization of the potassium thiocyanate solution

Transfer 25.00 cm³ (pipette) of the silver nitrate solution to an Erlenmeyer flask, add about 5 cm³ of 6 M nitric acid and about 1 cm³ of the iron(III) indicator solution and about 25 cm³ of water (use measuring cylinders for these solutions). Titrate the contents with the thiocyanate solution and determine the end-point according to the instruction given in the "Determination" procedure.

Atomic mass: $A_r(\text{Br}) = 79.90$

b) Exercise

At the equivalent point the solution is saturated with respect to both AgBr and AgSCN. Find the molar concentration of free (unprecipitated) Br⁻ in this solution:

$$K_{sp}(\text{AgBr}) = 5.00 \times 10^{-13} \quad K_{sp}(\text{AgSCN}) = 1.00 \times 10^{-12}$$

Ignore the effect of *pH* and Fe(III) species.

Note:

On the answer sheet, not only the required final results shall be given, but also exemplifications of how the calculations are carried out.

27th



International Chemistry Olympiad

**6 theoretical problems
3 practical problems**

1.2 Rate constants k_c for reaction (c) were measured at various temperatures in a simulation experiment in order to obtain its kinetic parameters. On the basis of the data given below answer the following questions:

t / °C	25	40
k_c / mol dm ⁻³ s ⁻¹	1.29×10^{-4}	2.50×10^{-4}

- Write the equation for calculating the activation energy of reaction (c) and find the value.
- Assign the overall reaction order of reaction (c).
- Knowing that the rate determining step of reaction (c) is the monolayer adsorption of O₂ (g) on solid CuCl, write the overall rate equation of this heterogeneous reaction (c). Under what condition might the reaction order be the same as that you have given in ii)? Assume only O₂ can be adsorbed.

1.3 A copper plate was divided into two parts, Cu(1) and Cu(2). Cu(1) was then hammered so that Cu(1) and Cu(2) are different in certain thermodynamic properties.

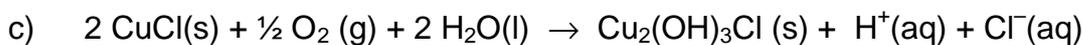
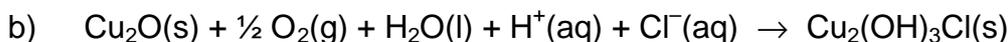
- An galvanic cell with Cu(1) and Cu(2) was designed as Cu(1)|CuSO₄(aq)|Cu(2) and the electromotive force E of the above cell was expressed as $E = \Phi_R - \Phi_L$, where Φ_R and Φ_L being the right and left electrode potentials (i. e. half-cell potentials), respectively. Please choose the correct E value from the following and give the thermodynamic reason for your choice.
(A) $E < 0$ (B) $E = 0$ (C) $E > 0$ (D) It cannot be decided
- Write the net cell reaction for the cell.

1.4 In a Cu-Zn alloy the molar fractions of Cu and Zn are 0.750 and 0.250, respectively. The structure type of the alloy is the same as that of pure copper, except Zn atoms substitute some Cu atoms randomly and statistically, i. e. at every atomic position, the probability of the occupation of Cu and Zn is proportional to the composition of the alloy. In this sense the alloy can be considered as composed of statistical atoms Cu_xZn_{1-x}. X-ray analysis shows that the arrangement of atoms in the alloy is of the cubic face-centred close packing type. Density of the alloy $d = 8.51$ g cm⁻³. Calculate the radius of the statistical atoms in the alloy.

Given: $A_r(\text{Cu}) = 63.5$, $A_r(\text{Zn}) = 65.4$.

SOLUTION

1.1 i)



ii) a) $\Delta G^0 = 69 \text{ kJ mol}^{-1}$

b) $\Delta G^0 = -824 \text{ kJ mol}^{-1}$

c) $\Delta G^0 = -755 \text{ kJ mol}^{-1}$

iii) Calculation (dilute HCl solution can be considered as an ideal solution)

$$\Delta_r G = \Delta_r G^0 + 2 RT \ln [\text{H}^+][\text{Cl}^-] = -22.3 \text{ kJ mol}^{-1} < 0$$

Spontaneous: to the right

1.2 i) Formula: $\ln \frac{k_c(T_2)}{k_c(T_1)} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$E_a = 34.2 \text{ kJ mol}^{-1}$$

ii) overall reaction order = 0

when $b p(\text{O}_2) \gg 1$

$$r = k_c \theta = \frac{k_c b p(\text{O}_2)}{1 + b p(\text{O}_2)}; \quad r = k_c \quad \text{zero order}$$

1.3 i) (C) $E > 0$ ii) Net cell reaction: $\text{Cu(1)} = \text{Cu(2)}$ Thermodynamic reason for choosing 3 (C) is $\Delta_r G < 0$, $\Delta_r G = -nFE$ and $E > 0$

1.4 $r = 1.30 \times 10^{-10}$

formula: $a = 2\sqrt{2r}$

$$d = \frac{4(63.5 \times 0.75 + 65.4 \times 0.25) \times 10^{-3}}{a^3 N_A} = 8.51 \times 10^{-3} \text{ kg m}^{-3}$$

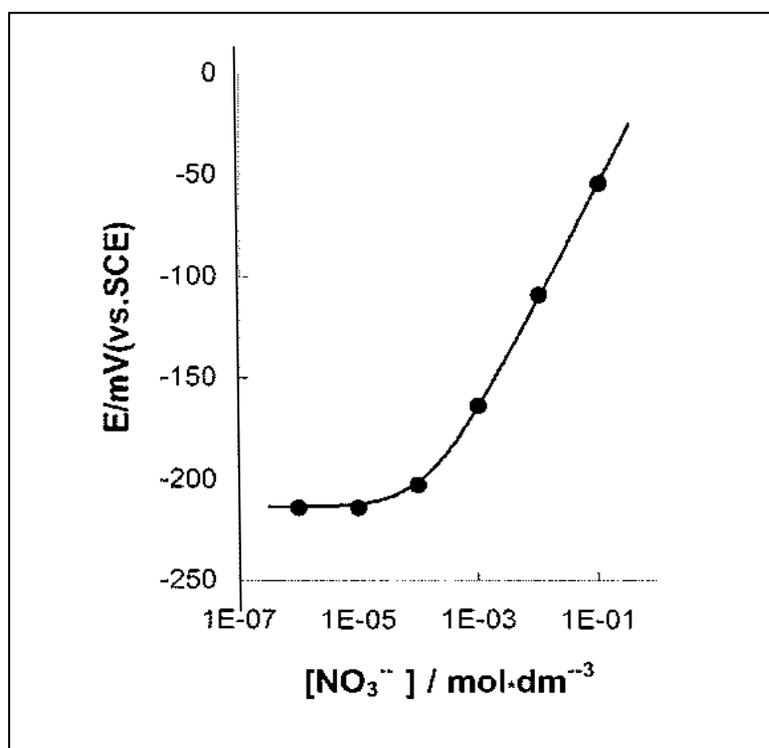
$$r^3 = 2.209 \times 10^{-30} \text{ m}^3$$

$$r = 1.30 \times 10^{-10} \text{ m}$$

PROBLEM 2

To control the quality of milk serum, a dairy by-product, the concentration of NO_3^- ion in serum is monitored by means of an ion selective electrode. Generally there is about 15 mg NO_3^- ion per litre in serum, measured on the basis of nitrogen mass.

2.1 For a nitrate ion selective electrode a calibration curve as shown below was obtained using a series of standard nitrate solutions containing $0.5 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$, $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cl}^-$ ion as the background. Decide whether it is feasible to measure concentration NO_3^- in serum under the above conditions.



2.2 Given are selective coefficients of Cl^- , SO_4^{2-} and ClO_4^- versus NO_3^- as follow

$$K_{\text{NO}_3, \text{Cl}^-} = \frac{c_{\text{NO}_3^-}}{c_{\text{Cl}^-}} = 4.9 \times 10^{-2} \quad K_{\text{NO}_3, \text{SO}_4^{2-}} = \frac{c_{\text{NO}_3^-}}{c_{\text{SO}_4^{2-}}^{1/2}} = 4.1 \times 10^{-3}$$

$$K_{\text{NO}_3, \text{ClO}_4^-} = \frac{c_{\text{NO}_3^-}}{c_{\text{ClO}_4^-}} = 1.0 \times 10^{-3}$$

where the units of the concentrations are in mol dm^{-3} which is the best to reduce the interference of Cl^- to NO_3^- determination, so as to control the error in the NO_3^- concentration within 1 %, when there are $1.40 \times 10^{-3} \text{ mol dm}^{-3} \text{ NO}_3^-$ and $1.60 \times 10^{-2} \text{ mol dm}^{-3} \text{ Cl}^-$ in serum:

- (a) AgNO_3 (b) Ag_2SO_4 (c) AgClO_4

Calculate the amount of the salt that should be added to 1 dm^3 of the sample solution to be measured.

- 2.3** The NO_3^- ion concentration was determined by this method at 298 K. For 25.00 cm^3 sample solution the electronic potential, E , is measured to be -160 mV . After adding 1.00 cm^3 $1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ NO}_3^-$ standard solution to the above solution, E changes to -130 mV . Find the $p\text{NO}_3$ of the serum.
- 2.4** The selective coefficient of CH_3COO^- versus NO_3^- $K(\text{NO}_3^-/\text{CH}_3\text{COO}^-) = 2.7 \times 10^{-3}$. If AgCH_3COO instead of Ag_2SO_4 is added to the sample solution of question 2.2, find the upper limit of the pH value below which the same requirement in question 2.2 can be met.

$$K_{\text{sp}}(\text{AgCl}) = 3.2 \times 10^{-10} \quad K_{\text{sp}}(\text{Ag}_2\text{SO}_4) = 8.0 \times 10^{-5}$$

$$K_{\text{sp}}(\text{AgCH}_3\text{COO}) = 8.0 \times 10^{-3} \quad K_{\text{a}}(\text{CH}_3\text{COOH}) = 2.2 \times 10^{-5}$$

$$A_r(\text{N}) = 14.00$$

SOLUTION

2.1 Yes

2.2 B

$$(1.4 \times 10^{-3} \times 0.01) / [\text{Cl}^-] = 4.9 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Cl}^-] = 2.9 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Excess } [\text{Cl}^-] = 1.6 \times 10^{-2} - 2.9 \times 10^{-3} \cong 1.6 \times 10^{-2} \text{ mol dm}^{-3}$$

To reduce the interference of Cl^- at least $1.6 \times 10^{-2} \text{ mol Ag}^+$ ion or $8.0 \times 10^{-3} \text{ mol Ag}_2\text{SO}_4$ has to be added to 1 dm^3 sample solution.

2.3 $\Delta E = E_2 - E_1 = 0.059 \log \{(c_X V_X + c_S V_S)(c_X [V_X + V_S])\}$

$$0.03 = 0.059 \log [(25.00 V_x + 0.10) / (26.00 \times c_x)]$$

$$c_x = 1.7 \times 10^{-3} \text{ mol dm}^{-3}$$

$$p\text{NO}_3 = 2.77$$

2.4 $pH = 4.4$

$$(1.4 \times 10^{-3} \times x) \div 1.6 \times 10^{-2} = 2.7 \times 10^{-3}$$

$$x = 3.1 \% > 1 \%$$

$$(1.4 \times 10^{-3} \times 0.01) \div [\text{CH}_3\text{COO}^-] = 2.7 \times 10^{-3}$$

$$[\text{CH}_3\text{COO}^-] = 5.2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$1.6 \times 10^{-2} - 5.2 \times 10^{-3} = 1.08 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\{[\text{H}^+] \times 5.2 \times 10^{-3}\} \div (1.08 \times 10^{-2}) = 2.2 \times 10^{-5}$$

$$[\text{H}^+] = 4.3 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = 4.4$$

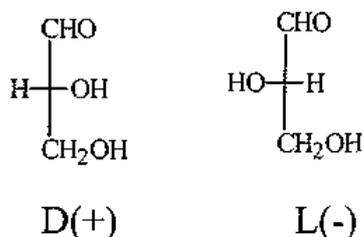
PROBLEM 3

1,3-Dihydroxyacetone can be converted to glyceraldehyde. On standing this glyceraldehyde changes spontaneously into a six member cyclic dimer $C_6H_{12}O_6$. The infrared spectrum of the dimer shows no absorption peak between $1600 - 1800\text{ cm}^{-1}$ and the dipole moment of the dimer is determined to be zero.

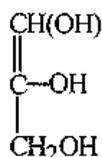
- 3.1 Write the Fischer projection structural formula(e) for the resulting glyceraldehyde and indicate configuration using D(+) and/or L(-).
- 3.2 Write the structural formula for the reaction intermediate of the conversion of 1,3-dihydroxyacetone to glyceraldehyde.
- 3.3 Write the structural formula for the dimer.
- 3.4 Using Haworth projection formula represent the possible stereoisomers which fit the dipole moment data.
- 3.5 Denote each chiral carbon atom in the above formulae with *R* or *S*.

SOLUTION

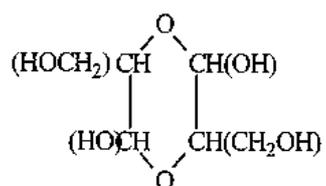
3.1



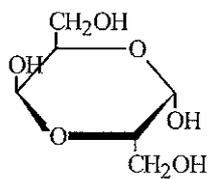
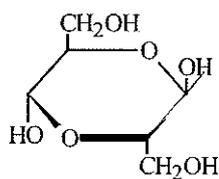
3.2



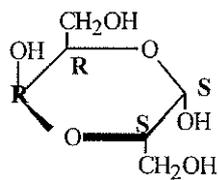
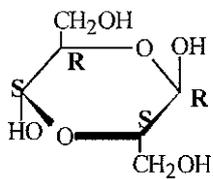
3.3



3.4



3.5



PROBLEM 4

Poly[(R)-3-hydroxyalkanoic acids], PHAs, are synthesized by a variety of bacteria and function as intracellular carbon and energy storage materials. These polymers are also biodegradable in environments, such as soil, anaerobic sewage and sea water. The inherent biologically mediated environmental degradability, useful physical properties, slow hydrolytic degradation and other favourable properties make bacterial polyesters exciting materials for both disposable biodegradable plastics (good for a clean environment) and special medical products.

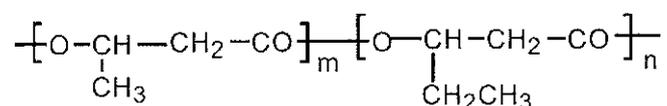
4.1 PHB, Poly(3-hydroxybutanoic acid), produced by bacteria contains only (R)-HB repeating units, while that synthesized by polymer chemists may contain only (R)-HB or only (S)-HB or both (R)-and (S)-HB in an alternating manner or both but in random distributions. Sketch chain structures of the atactic PHB, syndiotactic PHB and isotactic PHBs and denote each chiral carbon with (R) or (S). Five monomeric units are enough for each chain.

{Note: In "PHB", P means "poly" or "polymer of, HB represents the monomeric units contained in poly(3-hydroxybutanoic acid) molecules.)

4.2 Suggest two types of monomers that could be used for polymer chemists to synthesize a PHB, regardless of the stereochemistry of the products.

4.3 Poly[(R)-3-hydroxybutanoic acid] can be synthesized by feeding the bacteria (such as *Alcaligenes Eutrophus*) with sodium acetate in a nitrogen-free media. It is believed that the key steps for the conversion of acetate to PHB are the activation of acetate molecules by coenzyme A and the subsequent formation of the coenzyme A activated acetoacetate, which is then reduced by a reductase to form coenzyme A activated monomer 3-hydroxybutyrate. Polymerization of the monomer is achieved by a polymerase which would build the polymer molecules with unique stereospecificity. Sketch these steps with structural formulae. For coenzyme A the conventional abbreviation, -S-CoA (-CoA is as good), should be used in the sketch.

4.4 If sodium propanoate is used (as the sole carbon source) in the feeding media instead of sodium acetate, the principal product will be a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid with the following generalized structure:

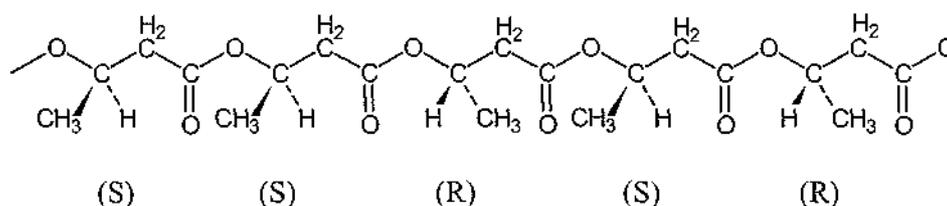


Rationalize the result.

(Note: Two different monomers are needed for the formation of the copolymer. The letters *m* and *n* in the structural formula are numbers of the units and have nothing to do with the answer, in other words, you may leave them out in your answer.)

SOLUTION

4.1

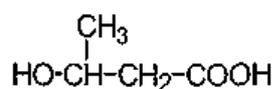


Other arrangements with (*R*) and (*S*) randomly distributed along the chain are correct, e.g. *RSRRS*, *SRSSR*, *RRSRS*, etc.

Syndiotactic PHB: This polymer has (*R*) and (*S*) units positioned along the chain in an alternating manner: *RSRSR* (or *SRSRS*).

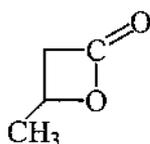
Isotactic PHB: All the chiral centres have the same configuration. There are 2 types of the isotactic PHBs: *SSSSS* and *RRRRR*.

4.2 Monomer 1:

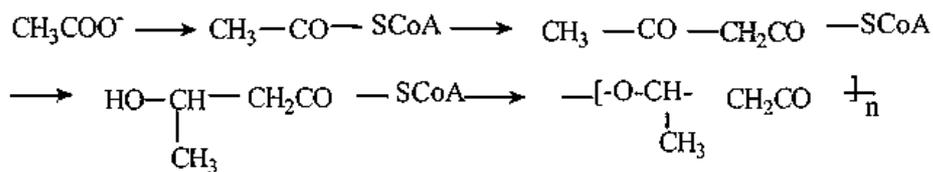


3-hydroxybutanoic acid

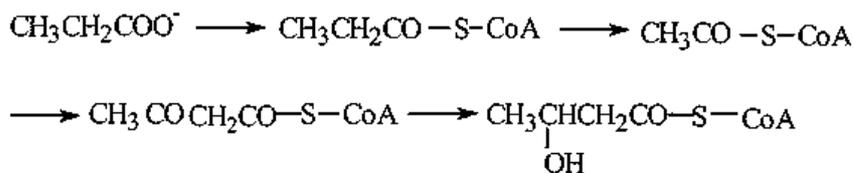
Monomer 2:



4.3

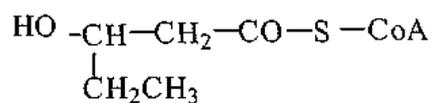


4.4

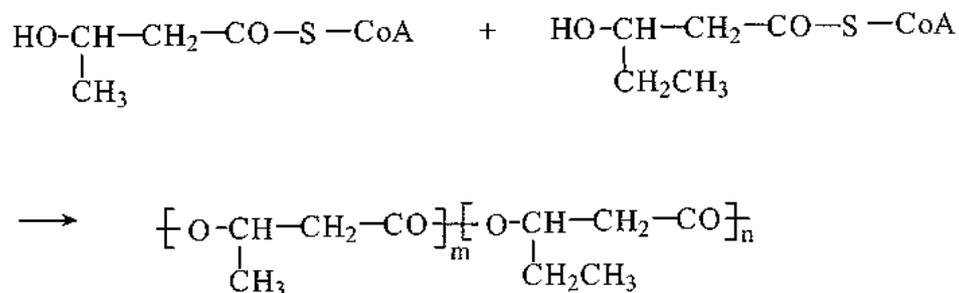


(Coenzyme A activated monomer 3-hydroxypentanoic acid)

This monomer may also be written in the following way:



Polymerization of these two monomers will result in the desired copolymer:



PROBLEM 5

The action of nitric oxide upon human body is dual. The nitric oxide generated in nerve cells will damage the cells, while the nitric oxide generated in endothelial cells of blood vessels can relax the vessels and control blood pressure.

5.1 Indicate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NO molecule using one of symbols π , σ , π^* or σ^* , and indicate the electron(s) residing in the corresponding orbital using symbols \uparrow and/or \downarrow .

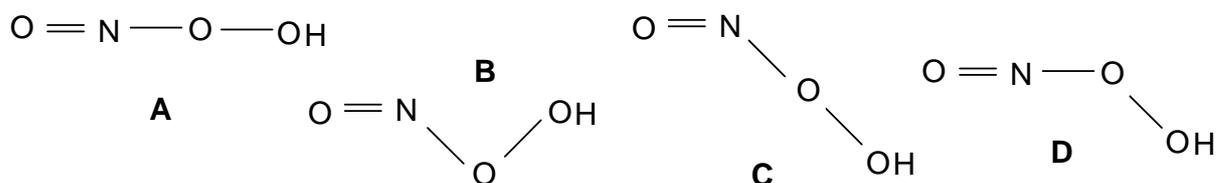
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species really exists in the iron complex?

- a) NO b) NO⁺ c) NO⁻

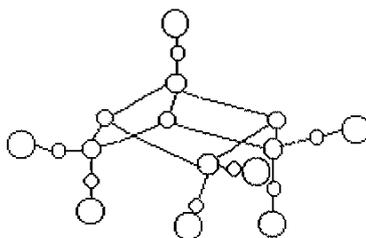
5.3 The cell damage is caused by free radical OH, which is one of the product of reaction between O₂⁻ and NO:



in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.



5.4 For preservation of meat, sodium nitrite is usually added and as a result NO is, then, formed. Consequently, NO reacts with the sulphur and iron atoms from decomposition of proteins, forming [Fe₄S₃(NO)₇]⁻. The complex anion is bacteriostatic and antiseptic. X-ray crystallography shows that the complex anion has a structure as shown below:



- i) Blacken all the circles corresponding to iron atoms and add symbols Fe(A), Fe(B), Fe(C) and Fe(D) beside the circles in the sequence of top → left → right.
- ii) The configuration of 3d electron shell of the iron atoms has been studied with modern structural analysis. Knowing that the mean oxidation number of the four iron atoms is -0.5 , give their configurations of 3d shell, respectively. Assume that each iron atom adopt sp hybridization.

5.5 $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$ anion can be reduced and a new complex $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$ is formed which contains a cyclic structure unit of Fe_2S_2 .

- i) Write the structural formula for the anion $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$.
- ii) Give the oxidation state of each iron atom with Arabic numerals.
- iii) $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$ can be converted into $[\text{Fe}_2(\text{SCH}_3)_2(\text{NO})_4]^n$, a carcinogen. Which of the following three species is added to $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$: CH_3^+ , $\bullet\text{CH}_3$ or CH_3^- ? Assign the value of n.

SOLUTION

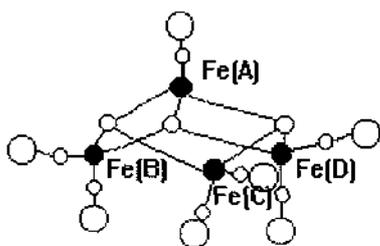
5.1 The HOMO of NO molecule is π^* , its electron arrangement \uparrow ;

The LUMO of NO molecule is π^* .

5.2 (b)

5.3 B

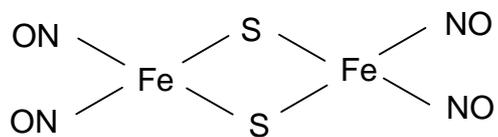
5.4



Fe(A) has $3d^7$ configuration;

Fe(B), Fe(C) , and F(D) have $3d^9$ configuration.

5.5 i)



ii) Fe(-1) Fe(-1)

iii) The species added to S atom is CH_3^+ ; $n = 0$.

PROBLEM 6

A surfactant molecule can generally be modelled as Fig. 1 where a circle presents the polar head (PH), i.e. the hydrophilic part of the molecule, and a rectangle represents the non-polar tail (NT), i. e. the hydrophobic part of the molecule.

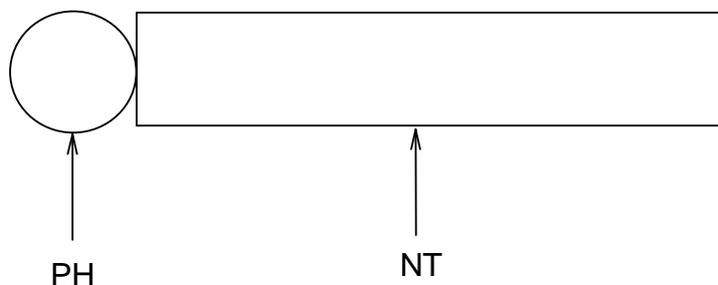


Fig. 1

6.1 AOT is a surfactant. Its systematic name (IUPAC name) is sulfobutanedioic acid 1,4-bis-(2-ethylhexyl) ester sodium salt (formula $C_{20}H_{37}NaO_7S$).

- i) Write the structural formula for AOT and fill its PH and NT in the circle and rectangle on your answer sheet.
- ii) Choose the type of surfactant AOT among the following.
 - a) Non-ionic; b) Anionic; c) Cationic; d) Others.

6.2 Mixing an aqueous solution of 50 mmol AOT with isooctane (volume ratio 1 : 1), a micellar extraction system will be formed in the isooctane phase (organic phase).

- i) Using the model as shown in Fig. 1, draw a micelle with 10 AOT molecules under the given condition.
- ii) What species are in the inner cavity of this micelle? Write their chemical formulas.

6.3 There is an aqueous solution containing the proteins as listed below:

Protein	Molecular mass (M_r) $\times 10^4$	Isoelectric point (PI)
A	1.45	11.1
B	1.37	7.8
C	6.45	4.9
D	6.80	4.9
E	2.40	4.7
F	2.38	0.5

The separation of proteins can be performed by mixing the AOT micellar extraction system with the solution. Adjusting the *pH* value of the solution to 4.5, only three of the above listed six proteins can be extracted into the micelles. Which proteins will be extracted?

- 6.4 The three proteins entered into the micelles will be separated from each other by the following procedure shown as in Fig. 2. Each extracted protein can be sequentially transported into a respective water phase.

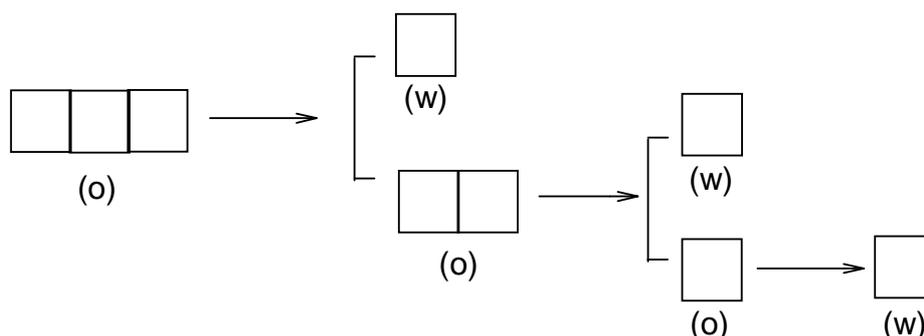


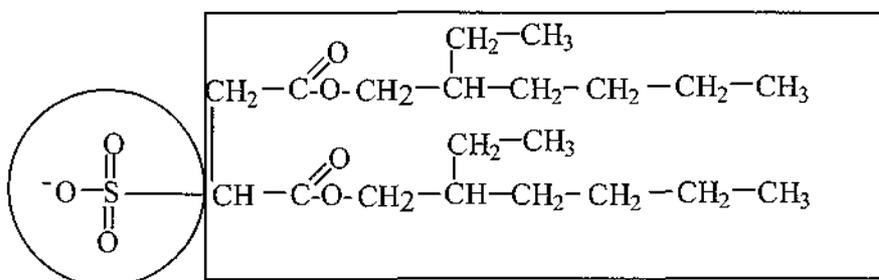
Fig. 2

Note: (w) represents water phase; (o) represents organic phase

Fill the three extracted proteins in the left boxes first and then separate them by the procedure given, and give the separation conditions above each arrow as well.

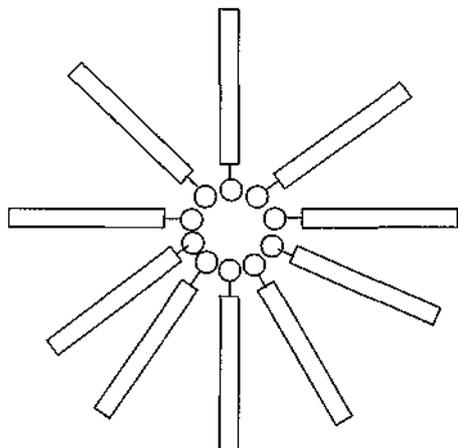
SOLUTION

6.1 i)



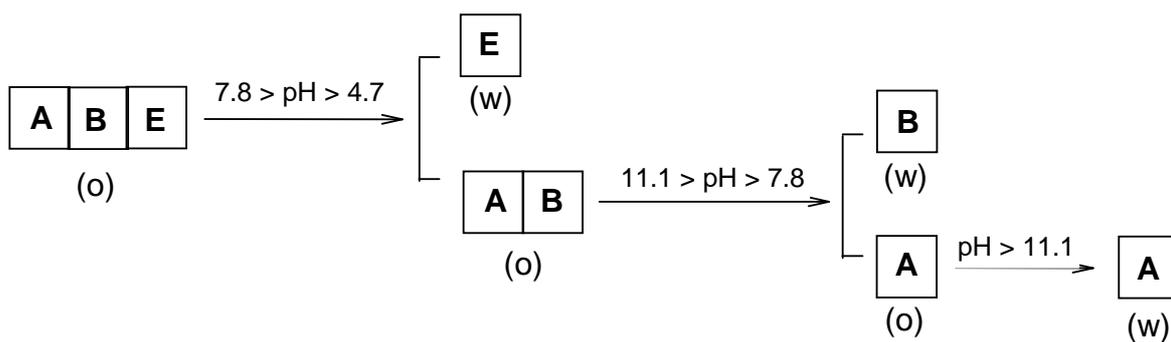
ii) (b)

6.2 i)



6.3 A, B, and E.

6.4



PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Identification of Unknown Solutions**

You are supplied with five different solutions contained in five test tubes labelled as A, B, C, D and E, respectively. The solution in each test tube contains one of the following compounds:



Identify these solutions.

Reagents

H_2SO_4 (conc.)	H_2SO_4 (6 mol dm^{-3})
HNO_3 (conc.)	HNO_3 (6 mol dm^{-3})
HCl (conc.)	HCl (6 mol dm^{-3})
$\text{Ba}(\text{OH})_2$ (satd.)	NaOH (6 mol dm^{-3})
BaCl_2 (0.5 mol dm^{-3})	$\text{Ba}(\text{NO}_3)_2$ (0.5 mol dm^{-3})

NOTES:

- (1) You can only select the provided reagents and use a procedure as simple as possible to complete your task. You are getting a mark not only according to the correct identification, but also to the number of steps you have taken.
- (2) You have to carry out the whole analysis by using the provided amount of these unknown solutions. Supplement of them will be available, but it will reduce the mark you obtain.

PROBLEM 2 (Practical)**Preparation of cis-Copper-bis-Glycinate Hydrate [Cu(gly)₂·xH₂O]**

Copper(II) amino acidate coordination compounds are monomeric units for synthesizing important biopolymers such as metalloenzymes like ceruloplasmin, on which every living organism depends. In laboratory cis-copper-bis-glycinate hydrate can be produced by the reaction of cupric hydroxide with glycine at a temperature of ca. 70 °C.

Reagents:

CuSO₄·5 H₂O(s)

NH₃ (aq) (3 mol dm⁻³)

glycine(s)

95% ethanol,

acetone

NaOH (2 mol dm⁻³)

BaCl₂ (0.5 mol dm⁻³)

1. Preparation of Cu(OH)₂

Procedure:

- (1) Dissolve your pre-weighted sample of CuSO₄·5 H₂O (6.0 g) in 40 cm³ of water with a 250 cm³ beaker as a container.
- (2) Add slowly 3 mol dm⁻³ ammonia solution to the CuSO₄ solution, gently stirring, until the precipitate is completely dissolved and the solution is turning blue-violet.
- (3) Add 2 mol dm⁻³ NaOH solution to the above solution until no more precipitate formed.
- (4) Filter the precipitate over a Büchner funnel under reduced pressure. Wash the precipitate with water until no SO₄²⁻ ion is detected in the filtrate.
- (5) Collect Cu(OH)₂ for the preparation of Cu(gly)₂·x H₂O.

Write the equations for the main chemical reactions having taken place in the above procedure.

2. Preparation of cis-Copper-bis-Glycinate Hydrate

Procedure:

- (1) Dissolve a pre-weighted sample of glycine (3.6 g) in 130 cm³ of water and then warm the solution in a hot water bath (70 °C). Add the Cu(OH)₂ to the solution, stir gently until the precipitate is dissolved. Perform a hot filtration and add 10 cm³ of 95 % ethanol.
- (2) Cool the solution and when needle-like crystals appear, place it in the ice water bath for 10 min.
- (3) Filter the crystals over a Büchner funnel under reduced pressure, wash once with 10 cm³ of ethanol-water mixing solvent and then twice with 10 cm³ acetone, squeeze the crystals as dry as possible on the funnel.
- (4) Collect the crystals to a watch glass and dry it (consult your supervisor).
- (5) Half an hour later weigh the product. Write the mass of product and the percentage of yield on your student's report. Give the expressions for calculation to show how you calculate.

SOLUTION

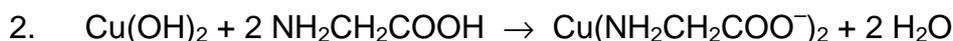
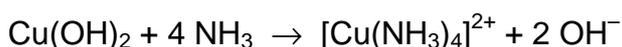
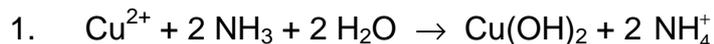
The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield in g.
- The yield obtained as a percentage of the theoretical yield.

Tasks:

Write down the balanced chemical equations used in the preparation.

Solution of the tasks:



PROBLEM 3 (Practical)**Determination of Copper(II) Content in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$**

The Cu(II) content in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$ crystals prepared yourself can be determined by iodometry with starch solution as indicator. Based on the data obtained one can calculate

the moles of hydrate in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$.

Reagents:

Standard KIO_3 (see the label on the bottle to get the accurate concentration)

H_2SO_4 (1.0 mol dm^{-3}) as indicator.

KI (0.6 mol dm^{-3})

KSCN (2 mol dm^{-3})

Starch (0.5 %)

$\text{Na}_2\text{S}_2\text{O}_3$ (to be standardized)

1. Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution

Procedure

- (1) Transfer 25.00 cm^3 of standard KIO_3 solution to an Erlenmeyer flask.
- (2) Add 5 cm^3 of water, 10 cm^3 of KI solution and 5 cm^3 of H_2SO_4 (1.0 mol dm^{-3}) to the flask.
- (3) Titrate immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution.
- (4) Add 2 cm^3 starch solution when the colour of the titrand turns pale yellow.
- (5) Continue titrating until the blue colour of the solution disappears.
- (6) Proceed with step (1) – (5) twice parallel.

2. Determination of Cu(II) content in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$

- (1) Weigh $1.0 - 1.2 \text{ g}$ (precision of $\pm 0.0002 \text{ g}$) of $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$ with a dry 100 cm^3 beaker as the container.
- (2) Dissolve it with 40 cm^3 of water and 8 cm^3 of H_2SO_4 (1.0 mol dm^{-3}).
- (3) Transfer the above solution quantitatively to a 100 cm^3 volumetric flask and dilute to the mark.

- (4) Transfer 25.00 cm³ of the Cu(II) solution to an Erlenmeyer flask, add 50 cm³ of water and 10 cm³ of KI solution to the flask.
- (5) Titrate immediately with standardized Na₂S₂O₃ solution.
- (6) Add 2 cm³ of starch solution and 3 cm³ of KSCN solution to the flask when the colour of the titrand turns from brown to pale yellow.
- (7) Titrate continuously until the blue colour of the solution disappears.
- (8) Proceed with steps (4) – (7) twice parallel.

SOLUTION

The following values were required to be written on the Answer Sheet :

Part 1

- Volumes of Na₂S₂O₃ solution
- Calculation of the concentration of Na₂S₂O₃ solution.

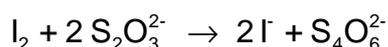
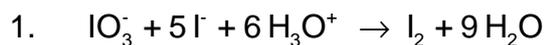
Part 2

- Mass of the product.
- Volumes of Na₂S₂O₃ solution
- Mass % of Cu(II) in Cu(gly⁻)₂ · x H₂O. Calculation.
- The value of x in the formula of the product. Calculation.

Other Tasks:

1. Write two equations for chemical reactions taking place during the standardization of Na₂S₂O₃ solution.
2. Write the equation for the reaction between Cu²⁺ and I⁻.

Solutions of the tasks:



28th



International Chemistry Olympiad

**7 theoretical problems
2 practical problems**

THE TWENTY-EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD 14–23 JULY 1996, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the π -bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like AlCl_4^-) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A = Te(cryst.) and B = $(\text{TeCl}_4 + 4 \text{AlCl}_3)$. The second component B was considered as an analog of Te(IV) chloroaluminate $\text{Te}[\text{AlCl}_4]_4$ which, however, cannot be isolated as an individual compound. It was found out that the interaction of the components A and B can lead to the formation of three new compounds (I, II and III) in the systems containing initially 77.8, 87.5 and 91.7 mol. % of the component A, respectively. It was also noticed that while in the case of compounds II and III no side products were formed, the formation of I was accompanied by the evolution of 1 mole of volatile TeCl_4 per two moles of I.

The compounds I and II attracted a particular interest of investigators. They both have pinkish-purple color and both dissociate into three ions as the conductivity studies in melted NaAlCl_4 showed. The cryoscopic measurements in NaAlCl_4 melt enabled to determine the molecular weights of these compounds being equal to $1126 \pm 43 \text{ g mol}^{-1}$ and $867 \pm 48 \text{ g mol}^{-1}$ for I and II, respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by Te atom. This band lies at 133 cm^{-1} and is therefore so low in energy that this bond undoubtedly is a kind of Te - Te interaction. The ^{27}Al NMR data for the complexes I and II show that in each compound there is only one type of tetrahedrally coordinated

aluminum. However, the observed chemical shifts of aluminium for the compounds **I** and **II** are different, thus manifesting that Al atoms are different in them.

- 1.1 Determine Te : Al : Cl minimal atomic ratio for the complexes **I**, **II** and **III**.
- 1.2 Write the molecular-formulae of the compounds **I** and **II**.
- 1.3 Write the formulae of the anions and cations in compounds **I** and **II**.
- 1.4 Draw stereochemical formulae of cations and anions in the structures of **I** and **II** assuming that the cations in **I** and **II** are examples of inorganic aromatic systems.
- 1.5 Which compound has a higher thermal stability, **I** or **II**, taking into account that AlCl_3 is extremely volatile compound.
- 1.6 If one of the compounds **I** or **II** can be transformed into the other by heating, write the corresponding reaction equation.

SOLUTION

- 1.1 Te : Al : Cl ratios:

Compound I 2 : 2 : 7

Compound II 2 : 1 : 4

Compound III 3 : 1 : 4

solution:

The determination of the Te : Al : Cl ratios can be made using the data on the content of Te(cryst.) thus:

77.8 % of Te(cryst.) corresponds to $\text{Te}(\text{cryst.}) + 2 \text{TeCl}_4 + 8 \text{AlCl}_3$ and the minimum atomic ratio for the composition from which the excess of TeCl_4 is not subtracted is Te : Al : Cl = 9 : 8 : 32, where the contents of Al and Cl are even and can be divided by 4, while that of Te exceeding the analogous even number by 1. Subtracting one mole of TeCl_4 from the obtained ratio and dividing by 2 we obtain $4 \text{Te} + 4 \text{Al} + 14 \text{Cl}$ and the ratio is Te : Al : Cl = 2 : 2 : 7, which can be then verified by comparison with the molecular weight given 87.5 % of Te(cryst.) corresponds to $7 \text{Te}(\text{cryst.}) + \text{TeCl}_4 + 4 \text{AlCl}_3 = 8 \text{Te} + 4 \text{Al} + 16 \text{Cl}$ and the ratio is Te : Al : Cl = 2 : 1 : 4. 91.7 % of Te(cryst.) corresponds to $11 \text{Te}(\text{cryst.}) + \text{TeCl}_4 + 4 \text{AlCl}_3 = 12 \text{Te} + 4 \text{Al} + 16 \text{Cl}$ and the ratio is Te : Al : Cl = 3 : 1 : 4.

- 1.2 The molecular formulae of compounds **I** and **II**:

Compound I: $\text{Te}_4\text{Al}_4\text{Cl}_{14}$

Compound II: $\text{Te}_4\text{Al}_2\text{Cl}_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to double simplest formula.

For compound I: 2 ($\text{Te}_2\text{Al}_2\text{Cl}_7$) gives calculated $M_r = 1114.7$ while experimental value is 1126 ± 43 .

For compound II: 2 (Te_2AlCl_4) gives calculated $M_r = 848$ while experimental value is 867 ± 48 .

1.3 Cations and anions in compounds I and II:

Compound I: $[\text{Te}_4]^{2+} [\text{Al}_2\text{Cl}_7]^-$

Compound II: $[\text{Te}_4]^{2+} [\text{AlCl}_4]^-$

The compositions of the ions included in the structures of **I** and **II** can be determined by taking into consideration that both **I** and **II** are tri-ionic electrolytes, and the fact that all the tellurium atoms should be equivalent according to IR and are bonded only to each other. The Al atoms are in both compounds tetrahedrally coordinated and equivalent. At least in one case this can be AlCl_4^- anion which seems probable for **II**, which therefore can be formulated as $[\text{Te}_4]^{2+}[\text{AlCl}_4]_2^-$. As according to similar colouration the cations are likely to be the same in both cases, the structure of **I** should contain $[\text{Te}_4]^{2+}$ cations and $[\text{Al}_2\text{Cl}_7]^-$ anions, which seems also to be in a good agreement with NMR data, assigning to Al atoms in **I** with a different tetrahedral geometry than that in **II**.

1.4 The geometry of the cation:

$[\text{Te}_4]^{2+}$ is a plane square due to proclaimed aromaticity.

The plane square configuration appears to be more favourable because the cation is mentioned to be aromatic, which means planar and possessing equal bond lengths for the sides of the corresponding aromatic ring.

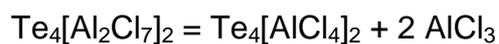
The geometry of anions:

AlCl_4^- is a single tetrahedron;

Al_2Cl_7^- - there are two tetrahedra sharing a common vertex (a chlorine atoms).

1.5 The thermal stability of **II** should be higher than that of **I**. They both are ionic compounds with high melting points, but compound **I** can be transformed into **II** by the elimination of AlCl_3 , which is a volatile solid and can be relatively easily removed on heating.

1.6 The reaction equation:



PROBLEM 2

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

As an example we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate $[\text{C}_9\text{H}_6(\text{OH})\text{NH}][\text{BiI}_4]$ ($M_r = 862.7$).

2.1 a) Draw the structural formulae of the cation and anion of this salt.

b) What is the oxidation state of Bi atom in this compound?

2.2 Evaluate the smallest mass of bismuth (in *mg*), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is 50.0 mg.

For the determination of trace amounts of bismuth R. Belcher and co-workers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1: To a given small amount ($\approx 2 \text{ cm}^3$) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($\text{K}_3[\text{Cr}(\text{SCN})_6]$) is added in the cold, that leads to practically quantitative precipitation of bismuth.

2.3 Write a balanced net ionic equation of this reaction.

Step 2: The precipitate is filtered off, washed by cold water, and treated with 5 cm^3 of 10 % solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth(III) carbonate $(\text{BiO})_2\text{CO}_3$ with liberation of hexathiocyanatochromate(III) ions into solution.

2.4 Write a balanced net ionic equation of this reaction.

Step 3: To the slightly acidified filtrate transferred to a separatory funnel 0.5 cm^3 of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulphate ion.

2.5 Write a balanced net ionic equation of this reaction.

Step 4: Upon 5 minutes 4 cm³ of 2 M H₂SO₄ solution are added to the mixture. The acidification leads to the reaction of coproportionation with the evolution of molecular iodine.

2.6 Write a balanced net ionic equation of the reaction occurred on acidification.

Step 5: Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which 1 cm³ of bromine water is added, and the mixture is mixed for 5 minutes.

2.7 Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidized into IO₃⁻.

Step 6: To eliminate an excess of molecular bromine 3 cm³ of 90 % methanoic (formic) acid is added to the mixture.

2.8 Write a balanced net ionic equation of this reaction.

Step 7: To the slightly acidic solution an excess (1.5 g) of potassium iodide is added.

2.9 Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with BrCN in a similar manner as with ICN to form molecular iodine.

Step 8: The resulting solution is titrated by a standard 0.00200 M Na₂S₂O₃ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

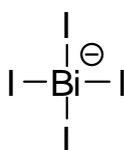
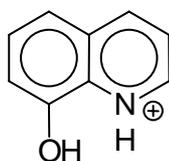
2.10 a) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm³ of standard 0.00200 M Na₂S₂O₃ solution)?

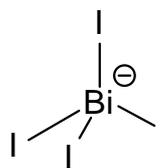
2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

SOLUTION

2.1 a)



or



Cation

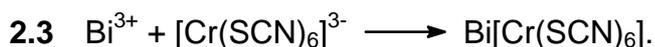
Anion

b)

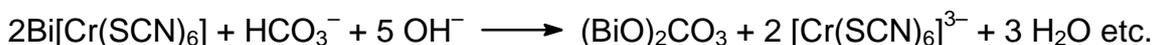
The oxidation number of bismuth in 8-hydroxyquinolinium tetraiodobismuthate: **III**

2.2 The smallest mass of bismuth determined reliably by Berg method, 12.1 mg.

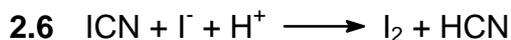
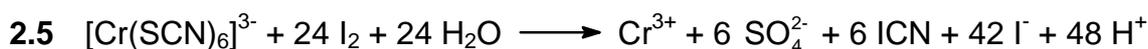
Molar mass of the precipitate is 862.7 g, which contains 209.0 g of bismuth. Thus, 0.0500 g of the precipitate correspond to 1.21×10^{-2} g = 12.1 mg of bismuth.



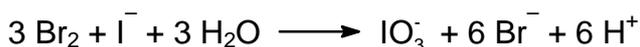
or



(variations are possible)



2.7 a)



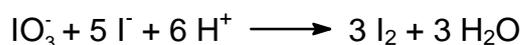
b)



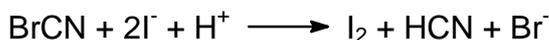
Comment. From reaction 2.5 it is evident that considerably more of ions I^- are formed than of ICN molecules. Therefore, after the completion of reaction 2. 6 an excess of I^- ions will be left.



2.9 a)



b)



2.10 a)

228 moles of thiosulphate correspond to 1 mole of bismuth.

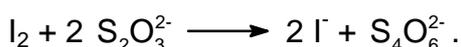
b)

The least mass of bismuth, $1.83 \cdot 10^{-3}$ mg

Solution:

a)

Titration of iodine by thiosulphate involves the reaction:



Assume that the initial solution contained 1 mole of Bi. In the reaction 5 each mole of Bi leads to the formation of 42 moles of iodide (for convenience divide all coefficients of reaction 4 by 2), of which 6 moles of iodide-ion was consumed in reaction 2.6. Thus, 36 moles of iodide was consumed in reaction 2.7a) to give 36 moles of IO_3^- , which in reaction 2.9a) gave $36 \times 3 = 108$ moles of I_2 , which take $108 \times 2 = 216$ moles of thiosulphate for titration. However, that is not all. Indeed, 6 moles of HCN are generated per mole of Bi^{3+} according to reactions 2.5 and 2.6. The oxidation of HCN by bromine in reaction 2.7b) gives 6 moles of BrCN, which in its turn in reaction 2.9b) gives 6 moles of iodine taking 12 more moles of thiosulphate. Thus, total amount of thiosulphate is $216 + 12 = 228$.

b)

1.00 cm^3 of 0.00200 M thiosulphate solution contains 2.00×10^{-6} mole of $\text{Na}_2\text{S}_2\text{O}_3$, which corresponds to $209.0 \times 2.00 \times 10^{-6} / 228 = 1.83 \times 10^{-6} \text{ g} = 1.83 \times 10^{-3} \text{ mg} = 1.83 \text{ } \mu\text{g}$.

2.11 $\frac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplied method}} = 6600$

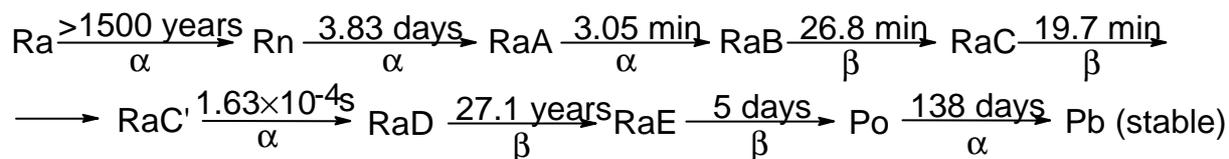
The multiplicative method is more sensitive than the gravimetric method by $12.1 \text{ mg} / 1.83 \times 10^{-3} \text{ mg} = 6600$ times.

PROBLEM 3

In 1908 Rutherford together with H. Geiger measured the rate of emission of α -particles (x) by radium (in the nature this element is represented by a single nuclide ${}^{226}_{88}\text{Ra}$) and found that 1.00 g of radium emits $x = 3.42 \times 10^{10}$ α -particles per second.

In 1911 Rutherford and American physical chemist B. Boltwood measured the rate of formation of helium from radium. This experiment permits to obtain the most accurate value of Avogadro's number available at that time, given that the value of molar volume of ideal gas was well established. To achieve this goal a sample of radium salt purified from decay products and containing $m = 192$ mg of Ra was put into a device and the volume of the evolved helium was measured. After 83 days ($t = 83.0$ days) of the experiment 6.58 mm^3 of He was collected ($V_{\text{He}} = 6.58 \text{ mm}^3$ corrected to 0°C and 1 atm).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).



(RaA -RaE are intermediate products of radon decay).

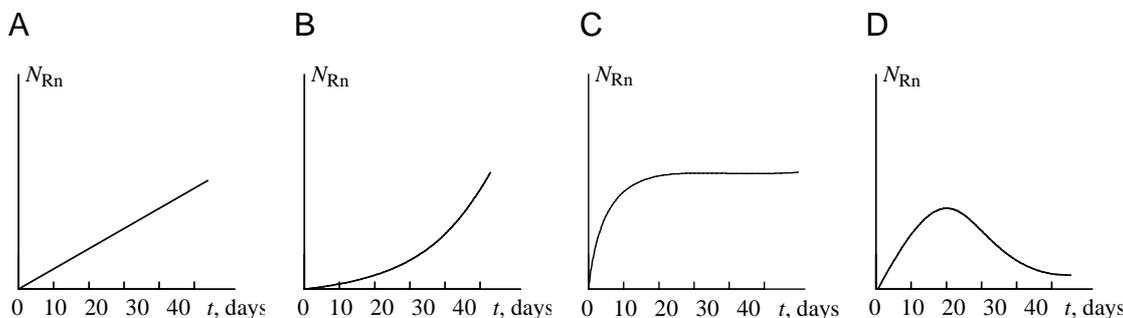
3.1 Write the first six radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement t . Using this approximation perform the following calculations.

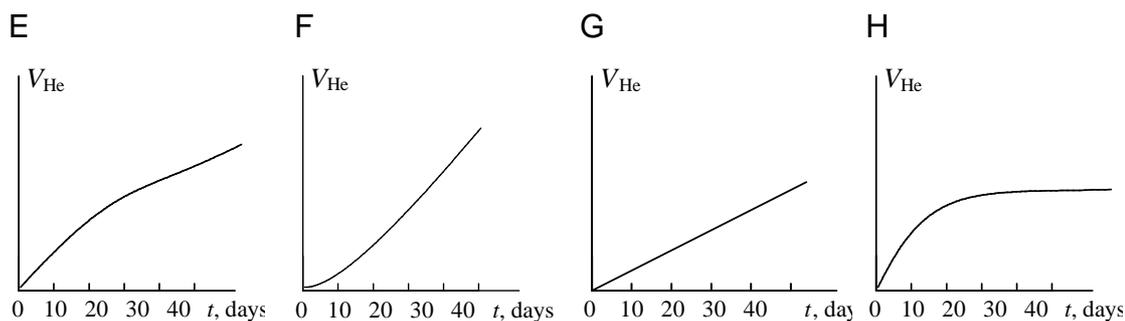
- 3.2** a) How many helium atoms were formed from each decayed radium atom after 83 days?
 b) How many helium atoms were formed in total during the experiment?
- 3.3** Calculate an approximate value of Avogadro's number from the above data.

For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}(\text{Rn}) = 3.83$ days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

3.4 Choose which of the plots given below displays the time dependence of the number N_{Rn} of radon atoms in the course of the experiment.



3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.



3.6 Choose the relation between the decay rate k of any given nuclide and its half-life $T_{1/2}$.

3.7 a) Using a short kinetic scheme



(where k_1 and k_2 are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment N'_{Rn} and the number of radium atoms N_{Ra} .

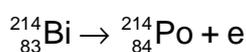
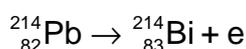
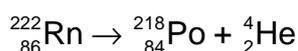
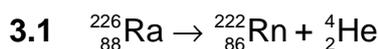
b) Calculate N'_{Rn} using the rate of radium decay given above ($x = 3.42 \times 10^{10}$ α -particles per gram of radium per second).

3.8 How many helium atoms could be formed from radon atoms remaining at the end of experiment N'_{Rn} , if all these atoms had decayed to RaD?

3.9 Using the solutions of the above questions calculate a better approximation to:

- the number of helium atoms formed;
- the Avogadro's number.

SOLUTION



3.2 a) The correct answer: 4

b) Number of helium atoms (rough 1.9×10^{17} estimate)

$$N_{\text{He}} = 4 \times m \times t = 1.9 \times 10^{17}$$

3.3 The first estimate of Avogadro's number: $6.4 \times 10^{23} \text{ mol}^{-1}$

Solution: The Avogadro's number N_A is the number of particles in one mole.

$N_A = N_{\text{He}} / \nu_{\text{He}}$, where N_{He} is number of helium atoms, and ν_{He} is the number of moles of helium formed within time t . If we assume that all radon atoms formed from radium atoms decayed during the time of experiment (this assumption follows from the assumption that radon half-life can be neglected in comparison with 83 days, that introduces an error of about 5 %), then we obtain that during time t the number of helium atom emitted is $N_{\text{He}} = 4xmt$, and

$$N_A = \frac{4 \times m \times t}{\nu_{\text{He}}} = \frac{4 \times 3.42 \times 10^{10} \times 0.192 \times (83 \times 24 \times 3600)}{\frac{6.58 \times 10^{-6}}{22.4}} = 6.4 \times 10^{23} \text{ mol}^{-1}.$$

3.4 Correct answer: **C**.

The number of radon atoms reaches a quasi-stationary state which is sometimes called as the radioactive equilibrium.

3.5 Correct answer: **F**.

In the beginning helium is formed only from α -particles emitted by radium, but to the end of the experiment α -particles are emitted both by radium and by decay products, the amount of which is four times that of radium.

3.6 Underline the correct answer:

$k = 1 / T_{1/2}$	<u>$k = \ln 2 / T_{1/2}$</u>	$k = \ln 2 \cdot T_{1/2}$	$k = \pi / T_{1/2}$
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3.7 a) Underline the correct answer:

<u>$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / k_2$</u>	$N'_{\text{Rn}} = k_2 \cdot N_{\text{Ra}} / k_1$	$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / 2k_2$	$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / 3k_2$
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The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay $k_2 N'_{\text{Rn}} = k_1 N_{\text{Ra}}$, whence $N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / k_2$

b) $N'_{\text{Rn}} = 3.14 \times 10^{15}$

The rate of radium decay is $k_1 N_{\text{Ra}} = xm$, whence

$$N'_{\text{Rn}} = \frac{xm}{\ln 2} = \frac{3.42 \times 10^{10} \times 0.192}{0.693} = 3.14 \times 10^{15}$$

$$T_{1/2(\text{Rn})} \quad 3.83 \times 24 \times 3600$$

3.8 Underline the correct answer:

$4N'_{\text{Rn}}$	$2N'_{\text{Rn}}$	$5N'_{\text{Rn}}$	N'_{Rn}	<u>$3N'_{\text{Rn}}$</u>
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3.9 a) A more accurate estimate of the number of helium atoms: 1.79×10^{17}

$$N_{\text{He}} = 4 xmt - 3N'_{\text{Rn}} = 1.9 \times 10^{17} - 3 \times 3.14 \times 10^{15} = 1.79 \times 10^{17}$$

 b) A more accurate estimate of Avogadro's number (mol^{-1}): 6.09×10^{23}

$$N_A = \frac{N_{\text{He}}}{n(\text{He})} = \frac{1.79 \times 10^{17}}{\frac{6.58 \times 10^{-6}}{22.4}} = 6.09 \times 10^{23}$$

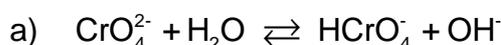
PROBLEM 4

The precipitation is widely used in classical methods of the quantitative and qualitative analysis for the separation of ions. The possibility of separation is determined by the equilibrium concentrations of all species in a solution to be analyzed.

Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).



4.1 Calculate the equilibrium constants



The ionic product of water $K_W = 1.0 \times 10^{-14}$.

4.2 In what direction shall the equilibrium state 1b shift upon the addition of the following reagents to the aqueous solution of potassium dichromate?

- KOH
- HCl
- BaCl₂
- H₂O

The solubility product of BaCrO₄ is 1.2×10^{-10} . BaCr₂O₇ is well soluble in water.

4.3 Calculate the pH value of the following solutions

- 0.010 M K₂CrO₄
- 0.010 M K₂Cr₂O₇
- 0.010 M K₂Cr₂O₇ + 0.100 M CH₃COOH

Dissociation constant of acetic acid $K_a = 1.8 \times 10^{-5}$.

4.4 Calculate the equilibrium concentrations of the following ions in the solution of 0.010 M K₂Cr₂O₇ + 0.100 M CH₃COOH

- CrO₄²⁻
- Cr₂O₇²⁻

Pb²⁺ and Ag⁺ form poorly soluble compounds with chromate and dichromate ions.

The solubility products of these compounds are indicated below.



To the aqueous solution of the mixture of 1.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$ and 2.0×10^{-4} M AgNO_3 an equal volume of 0.020 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.200 M CH_3COOH was added.

- 4.5 a) Shall Pb^{2+} be precipitated?
 b) Shall Ag^+ be precipitated?
 c) Shall a quantitative separation of Pb^{2+} and Ag^+ ions be thus achieved?

The quantitative precipitation is achieved if the residual concentration of the ion being precipitated is not higher than 1×10^{-6} M.

SOLUTION

4.1

a)

Equilibrium constant = 3.2×10^{-8}

$$\frac{[\text{HCrO}_4^-][\text{OH}^-]}{[\text{CrO}_4^{2-}]} = \frac{[\text{HCrO}_4^-][\text{OH}^-][\text{H}^+]}{[\text{CrO}_4^{2-}][\text{H}^+]} = \frac{K_w}{K_1}$$

$$\frac{1.0 \times 10^{-14}}{3.16 \times 10^{-7}} = 3.2 \times 10^{-8}$$

b) Equilibrium constant $> 4.4 \times 10^{13}$

$$\frac{K_1^2}{K_2 K_w^2} = \frac{\left(\frac{[\text{CrO}_4^{2-}][\text{H}^+]}{[\text{HCrO}_4^-]} \right)^2}{\frac{[\text{HCrO}_4^-]^2}{[\text{Cr}_2\text{O}_7^{2-}]} \frac{([\text{H}^+][\text{OH}^-])^2}}{10^{1.36} \times 10^{-2 \times 14.00}} = 10^{13.64} = 4.4 \times 10^{13}$$

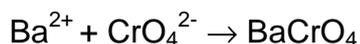
4.2 Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a)		<input checked="" type="checkbox"/>	
b)	<input checked="" type="checkbox"/>		
c)		<input checked="" type="checkbox"/>	
d)		<input checked="" type="checkbox"/>	

Calculations:

In case a) and b) the answer is self-evident.

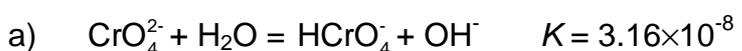
- c) BaCl_2 shifts the equilibrium to the right due to the binding of chromate ion into a poorly soluble compound



- d) This answer may appear as strange, as water is among the products specified in the right part of the equilibrium equation. However, this is too formal. Actually in dilute aqueous solutions the concentration of water may be regarded as fairly constant and the addition of water would not affect it. Nevertheless, the addition of water to dichromate solution leads to the dilution, which in its turn shifts the dichromate ion dissociation equilibrium to the right. Second, in the aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ the value of $\text{pH} < 7$ due to the processes described in the problem statement (cf. also the solution to 3b). With the dilution of any aqueous solution pH is varying towards 7, that in this case means the increase of pH . This also shifts the equilibrium to the right.

- 4.3 a) $\text{pH} = 9.25$
 b) $\text{pH} = 4.20$
 c) $\text{pH} = 2.87$

Calculations:



$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}] \approx [\text{CrO}_4^{2-}],$$

$$[\text{HCrO}_4^-] \approx [\text{OH}^-]$$

$$[\text{OH}^-]^2/c_{\text{Cr}} = K, [\text{OH}^-] = \sqrt{K c_{\text{Cr}}} = \sqrt{3.16 \times 10^{-8} \times 0.01} = 1.78 \times 10^{-5}$$

$$[\text{H}^+] = 5.65 \cdot 10^{-10}, \quad \text{pH} = 9.25$$



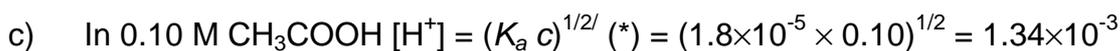
$$[\text{H}^+] \approx [\text{CrO}_4^{2-}] \Rightarrow [\text{H}^+] = \sqrt{K_1[\text{HCrO}_4^-]}$$

$$[\text{HCrO}_4^-] = ?$$

$$c_{\text{Cr}} = 2.0 \cdot 10^{-2} \text{ M (**)} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2 [\text{Cr}_2\text{O}_7^{2-}] \approx [\text{HCrO}_4^-] + 2 [\text{Cr}_2\text{O}_7^{2-}]$$

$$[\text{HCrO}_4^-] = x; \quad K_2 = [\text{Cr}_2\text{O}_7^{2-}] / [\text{HCrO}_4^-]^2 = (c_{\text{Cr}} - x) / 2x^2; \quad 2 K_2 x^2 + x - c_{\text{Cr}} = 0$$

$$\text{hence } [\text{H}^+] = (3.16 \times 10^{-7} \times 1.27 \times 10^{-2})^{1/2} = 6.33 \times 10^{-5}; \quad \text{pH} = 4.20$$



$$\text{pH} = 2.87$$

4.4 Equilibrium concentrations

a)	3.0×10^{-6}
b)	3.7×10^{-3}

Calculations:

The different methods can be used.

Method 1.

a)

$$[\text{HCrO}_4^-] = 1.3 \times 10^{-2} \text{ (*)}$$

$$[\text{CrO}_4^{2-}] = K_1[\text{HCrO}_4^-] / [\text{H}^+] = 3.16 \times 10^{-7} \times 1.3 \times 10^{-2} / 1.34 \times 10^{-3} = 3.0 \times 10^{-6}$$

b)

$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2 [\text{Cr}_2\text{O}_7^{2-}]$$

$$[\text{Cr}_2\text{O}_7^{2-}] = \frac{1}{2}(c_{\text{Cr}} - [\text{CrO}_4^{2-}] - [\text{HCrO}_4^-]) = \frac{1}{2}(2.0 \times 10^{-2} - 3.0 \times 10^{-6} - 1.3 \times 10^{-2}) = 3.7 \times 10^{-3}$$

or otherwise

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-]^2 = 22.9 \times (1.3 \times 10^{-2})^2 = 3.9 \times 10^{-3}$$

Method 2

a)

$$[\text{CrO}_4^{2-}] = x; [\text{HCrO}_4^-] = x[\text{H}^+] / K_1$$

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-] = x^2 K_2 [\text{H}^+]^2 / K_1^2$$

$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}] = 2K_2 [\text{H}^+]^2 / K_1^2 x^2 + (1 + [\text{H}^+] / K_1)x$$

$$K_1 = 3.16 \times 10^{-7}; K_2 = 22.9; [\text{H}^+] = 1.34 \times 10^{-3}$$

$$8.24 \times 10^8 x^2 + 4.24 \times 10^3 x - 2.0 \times 10^{-2} = 0$$

$$x = 3.0 \times 10^{-6}$$

b)

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-] = K_2 [\text{H}^+]^2 / K_1^2 [\text{CrO}_4^{2-}]^2 = 4.12 \times 10^8 \times (3.0 \times 10^{-6})^2 = 3.7 \times 10^{-3}$$

PROBLEM 5

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Solution I contains a mixture of $\text{FeCl}_2(\text{aq})$ and $\text{FeCl}_3(\text{aq})$, and solution II contains a mixture of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. The concentrations of iron-containing species satisfy the relations $[\text{Fe}^{2+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{4-}]_{\text{II}}$ and $[\text{Fe}^{3+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{3-}]_{\text{II}}$. The potential of platinum electrode immersed into the solution I is 0.652 V, while the potential of platinum electrode immersed into solution II is 0.242 V. The transmittance of the solution II measured relative to the solution I at 420 nm is 10.7 % (optical pathlength $l = 5.02$ mm). The complexes $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ do not absorb light at 420 nm.

Molar absorption at this wavelength $\varepsilon([\text{Fe}(\text{CN})_6^{3-}]) = 1100 \text{ M}^{-1} \text{ cm}^{-1}$.

Standard redox potential for $\text{Fe}(\text{H}_2\text{O})_6^{3+} / \text{Fe}(\text{H}_2\text{O})_6^{2+}$ is 0.771 V.

The factor before the logarithm in the Nernst equation is 0.0590.

5.1 Write Nernst equations for redox systems of

- solution I,
- solution II.

5.2 What are the units of the pre-logarithm factor 0.0590 in the Nernst equation?

5.3 Calculate the ratio of the stability constants $\beta[\text{Fe}(\text{CN})_6^{3-}] / \beta[\text{Fe}(\text{CN})_6^{4-}]$.

5.4 What is the absolute range of variation for the following physical values

- transmittance T ;
- absorbance A .

5.5 Sketch the graphs of concentration dependences satisfying the Lambert-Beer law for

- absorbance A ;
- transmittance T ;
- molar absorption ε .

5.6 Calculate the concentrations of

- Fe^{2+} in solution I;
- Fe^{3+} in solution II.

5.7 Mixing solutions I and II gives intense blue colour. What species is characterized by this colour? Write the reaction equation.

SOLUTION

5.1 Nernst equations:

$$\text{a) } E_1 = E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\text{b) } E_1 = E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) + 0.0590 \log \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]}$$

5.2 The units of pre-logarithm factor: V

5.3 The ratio of stability constants

$$\beta_1\{\text{Fe}(\text{CN})_6^{3-}\} / \beta_2\{\text{Fe}(\text{CN})_6^{4-}\} = 8.90 \times 10^6$$

Calculations:

$$\begin{aligned} E_{II} &= E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) + 0.0590 \log[\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}] = \\ &= E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log(\beta_1 / \beta_2) + 0.0590 \log([\text{CN}^-]^6 / [\text{CN}^-]^6) + \\ &\quad + 0.0590 \log[\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}] = 0.242 \end{aligned}$$

(where β_1 and β_2 are stability constants for $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, respectively.)

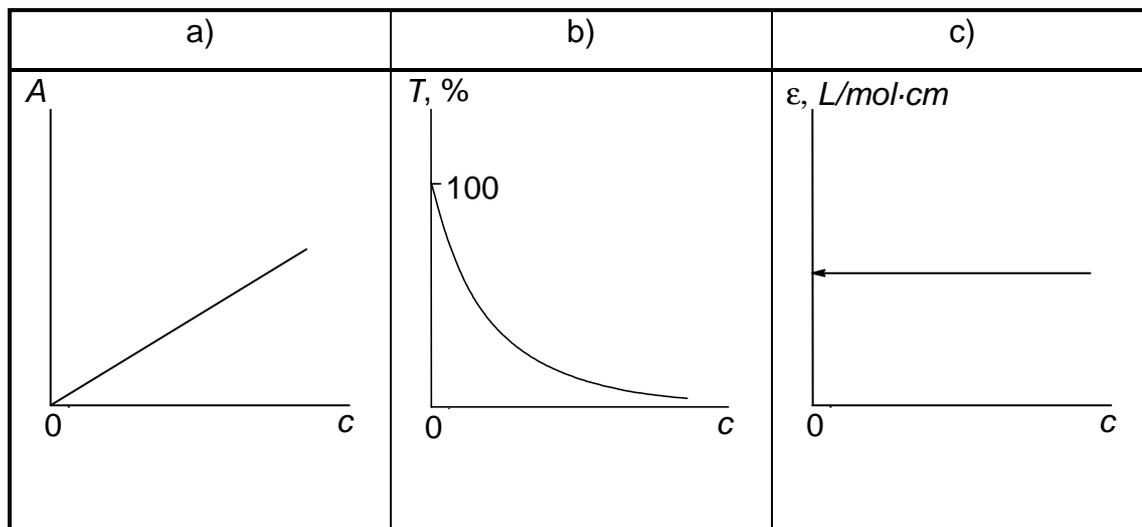
$[\text{Fe}(\text{CN})_6^{3-}] / [\text{Fe}(\text{CN})_6^{4-}] = [\text{Fe}^{3+}] / [\text{Fe}^{2+}]$, therefore

$$\Delta E = E_{II} - E_1 = 0.0590 \cdot \log(\beta_1 / \beta_2), \text{ and } \beta_2 / \beta_1 = 8.90 \times 10^6.$$

5.4 The ranges of variation:

- a) from 0 to 100
- b) from 0 to ∞

5.5



5.6 a) Using Bouguer-Lambert-Beer law

$$A = \varepsilon l c = \varepsilon l c[\text{Fe}(\text{CN})_6^{3-}] = 0.971;$$

$$c[\text{Fe}(\text{CN})_6^{3-}] = 0.971 / (1100 \times 0.502) = 1.76 \times 10^{-3} \text{ M} = c[\text{Fe}^{3+}]$$

b) using Nernst's equation

$$\begin{aligned} E &= E^\circ(\text{Fe}^{3+} / \text{Fe}^{2+}) + 0.0590 \log [\text{Fe}^{3+}]_i / [\text{Fe}^{2+}]_i = \\ &= 0.771 + 0.0590 \log [\text{Fe}^{3+}]_i / [\text{Fe}^{2+}]_i = 0.652 \text{ V.} \end{aligned}$$

hence,

$$[\text{Fe}^{3+}]_i / [\text{Fe}^{2+}]_i = 9.62 \times 10^{-3};$$

$$[\text{Fe}^{2+}]_i = 1.76 \times 10^{-3} / 9.62 \times 10^{-3} = 0.183 \text{ M.}$$

PROBLEM 6

Two isomeric hydrocarbons **A** and **B** contain 85.7 mass % of carbon.

6.1 Write a general formula which satisfies this condition.

The hydrocarbons **A** and **B** possess the following properties. The reaction of each of the compounds with ozone with subsequent treatment of the product with zinc dust in the presence of acid gives a single organic product **C**. The oxidation of compound **C** gives a single product, the carboxylic acid **D**. According to spectral data all hydrogen atoms in this acid except the one in carboxylic group are contained in methyl groups. The density of vapours of **D** corrected to normal conditions (0 °C, 1 atm) is 9.1 g dm⁻³.

Compound **A** is more reactive than compound **B** in the reaction with cold neutral potassium permanganate. A single compound **F** is formed from **A**, and a 1 : 1 mixture of isomers **G1** and **G2** is formed from **B**.

6.2 Draw the structural formulae of the compound **D** both in aqueous solution and in vapour phase.

6.3 Write the formula of compound **C**.

6.4 Draw the structures of isomers **A** and **B**.

6.5 a) Write the reactions of the transformation of **A** or **B** into **C** and **D**.
b) Write the reactions of the transformation of **A** and **B** into **F**, **G1** and **G2**.

6.6 Compounds **G1** and **G2** readily react with acetone in the presence of acids and form compounds **H1** and **H2**. Draw the structures of **H1** and **H2**.

6.7 Compounds **A** and **B** react with bromine. One of the products of these reactions is non-polar (dipole moment of this molecule is practically equal to zero) and optically inactive. Draw the stereochemical formula of this product, and write the reaction of its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to *R,S* nomenclature by *R* or *S* letters.

Alkenes react with peroxyacids with the addition of oxygen to double bond to form a three-member oxygen-containing ring. This epoxidation reaction is highly stereospecific to retain the relative positions of substituents at the bond to which the oxygen atom is attached.

The epoxidation of compound **A** by peroxyacetic acid yields a single compound **K**. Under the same conditions **B** gives a mixture of isomers **L1** and **L2** (the ratio is 1:1).

6.8 Is the compound **K** optically active? Draw the stereochemical formula of **K**. Are the individual compounds **L1** and **L2** optically active? Draw the stereochemical formulae of **L1** and **L2**.

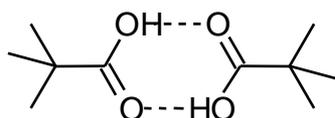
SOLUTION

6.1 The general formula: C_nH_{2n}

6.2 Compound **D**:

In aqueous solution: $(CH_3)_3CCOOH$

In vapours:

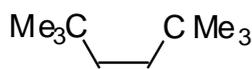


Dimeric structure in vapour phase is guessed using the value of vapour density.

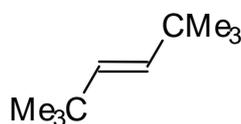
The relative molar weight in vapour phase is $9.1 \times 22.4 = 204$ which is close to double value of the molar weight of $(CH_3)_3CCOOH$. Possibly, as other simple fat acids, this acid is also dimerized in vapours.

6.3 Compound **C**: $(CH_3)_3CCHO$

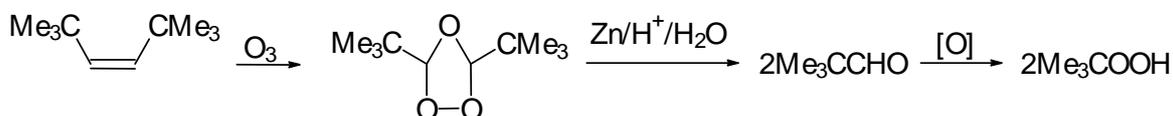
6.4 **A**:



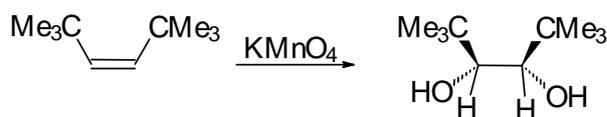
B:



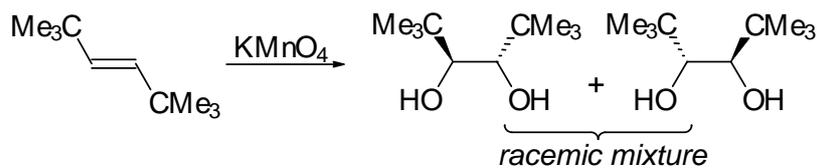
6.5



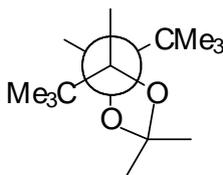
A → F



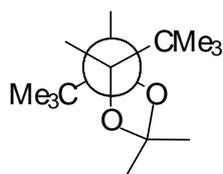
B → G1 + G2



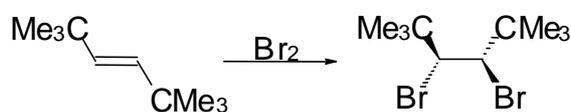
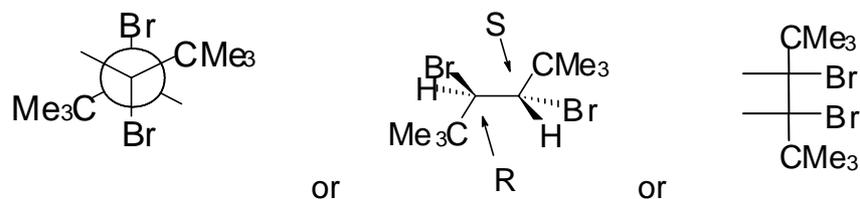
6.6 H1:



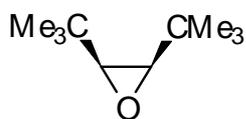
H2:



6.7 Non-polar bromination product (either of three types of structures may be given)

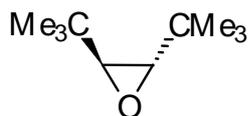


6.8 K:



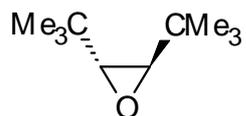
NO; The molecule is not optically active.

L1:



YES; The molecule is optically active.

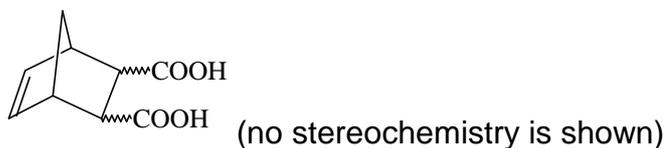
L2:



YES; The molecule is optically active.

PROBLEM 7

Stereochemistry of organic compounds can sometimes be determined by studying their chemical behaviour. The stereochemical configuration of one of the isomers of 5-norbornene-2,3-dicarboxylic acids (compound **X**)



was established by the following experiments.

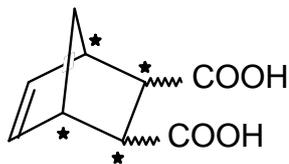
On heating this substance decomposes producing water and a new compound **Y**. Compound **Y** slowly dissolves in excess of aqueous NaOH with the formation of product **X₁** same to that is formed in the reaction of **X** with NaOH. The resulting solution of **X₁** is treated by I₂ to give compounds containing iodine. Acidification of the solution leads to a mixture of two isomeric compounds, **A** and **B** in the 3 : 1 ratio. The titration of 0.3913 g of compound **A** by 0.1000 M aqueous solution of NaOH in the presence of phenolphthalein takes 12.70 cm³ of alkali. The same amount of 0.1000 M solution of NaOH is required for the titration of 0.3913 g of compound **B**. On heating compound **A** slowly transforms into compound **C**, which contains no iodine and is able to react with water. Under the same conditions compound **B** does not undergo this transformation, but on heating with hydrochloric acid slowly transforms into **A**.

All reactions must be written as balance equations. No mechanisms are required.

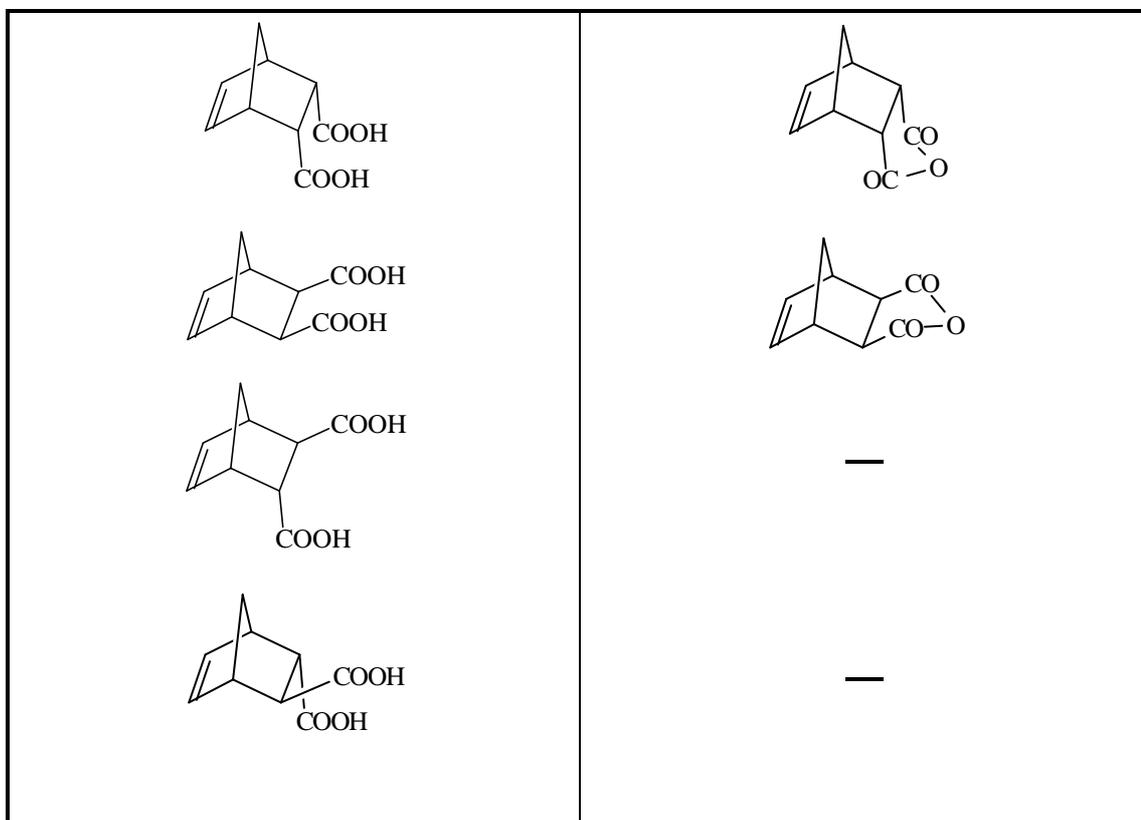
- 7.1 Mark by asterisks (*) the asymmetric carbon atoms in the structure of 5-norbornene-2,3-dicarboxylic acids.
- 7.2 Draw the stereochemical formulas of all stereoisomers of compound **X**, and the structures of products of their dehydration in those cases when it is possible.
- 7.3 Write the reactions of NaOH with a stereoisomer of **X** and a stereoisomer of **Y**.
- 7.4 Calculate the molar mass of compound **A**. Write the reactions leading from **X₁** to **A**.
- 7.5 Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.
- 7.6 Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.
- 7.7 Write the reactions leading from **B** to **A**.
- 7.8 Are the compounds **A** and **B** diastereomers?

SOLUTION

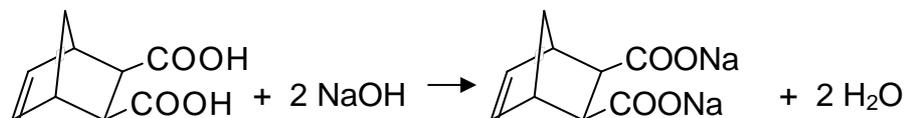
7.1



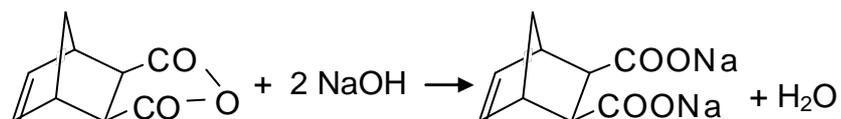
7.2 Fill in left column with the structures of stereoisomers of **X**, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus).



7.3 The reaction of a stereoisomer of **X** with NaOH:

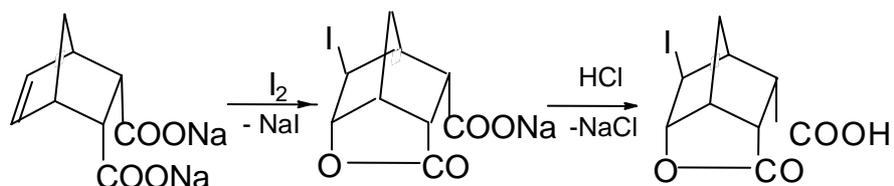


The reaction of a stereoisomer of **Y** with alkali:

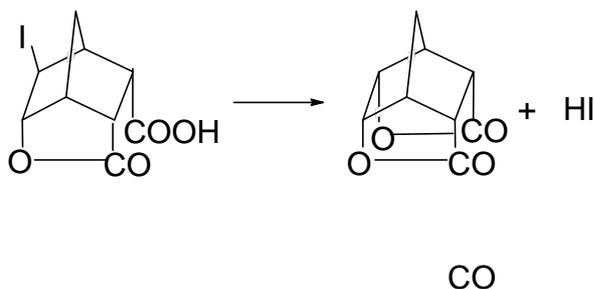


7.4 The molar mass of **A**: 308 g mol^{-1}

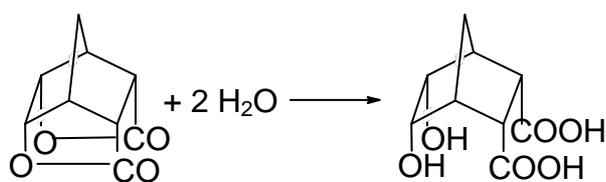
The reactions leading from **X₁** to **A**



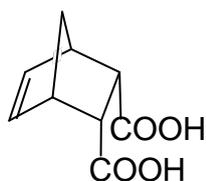
7.5 The transformation of **A** to **C**:



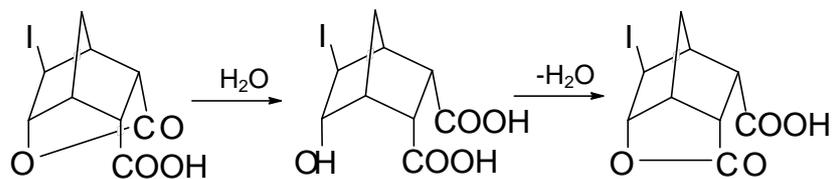
The reaction of **C** with water:



7.6 The structure of compound **X**:



7.7 The transformation of **B** to **A**:



7.8 No, **A** and **B** are not diastereomers.

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Iodometric Determination of the Concentration of Copper(II) and Iron(III) in a Sample of Technological Solution****Reagents**

- $\text{K}_2\text{Cr}_2\text{O}_7$, 0.008333 M
- KI, 20 % by mass.
- HCl, 1 M
- H_2SO_4 , 1 M
- $\text{Na}_4\text{P}_2\text{O}_7$, 5 % by mass.
- Starch, 1 % by mass.
- $\text{Na}_2\text{S}_2\text{O}_3$ (should be standardized)
- The solution to be analyzed in 100 cm³ volumetric flask.

Procedure

1. Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution
 - (1) 10 cm³ of 1 M solution of H_2SO_4 and 2 cm³ of 20 % KI solution are placed into an Erlenmeyer flask (the solution remains colourless).
 - (2) 10.00 cm³ of $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added.
 - (3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.
 - (4) 100 cm³ of water is added to the flask.
 - (5) The mixture is titrated immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the colour of mixture changes to pale yellow. Then 10 drops of starch solution are added. The titration continues until blue colour disappears completely.
 - (6) It is recommended to repeat the titration (steps 1 through 5) two more times.

Do the following and fill in the answer sheet form

- 1.1 Write the reactions involved in the procedure of standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution
- 1.2 Calculate the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution, and write your calculations.

2. The determination of copper

- (1) The solution to be analyzed in a 100 cm³ volumetric flask is diluted with water to the mark and stirred
- (2) A 10.00 cm³ aliquot of the solution is placed into an Erlenmeyer flask.
- (3) 20 cm³ of 5 % solution of Na₄P₂O₇, 7 cm³ of 1 M solution of HCl, and 10 cm³ of 20 % solution of KI are added. A precipitate may form upon the addition of Na₄P₂O₇.
- (4) The Erlenmeyer flask is covered with a watch glass and left in a dark place for 3 - 5 min.
- (5) The mixture is titrated immediately with Na₂S₂O₃ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.
- (6) It is recommended to repeat the titration (steps 2 through 5) two more times.

Do the following and fill in the answer sheet form

- 1.3 Write the reactions involved in the procedure of determination of Cu²⁺ ion.
- 1.4 Calculate the mass of copper in the solution under analysis, and write your calculations.

3. The determination of total amount of copper and iron

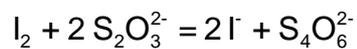
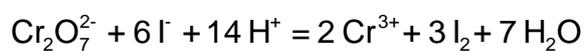
- (1) A 10.00 cm³ aliquot of the solution prepared in the item 2(1) is placed into an Erlenmeyer flask.
- (2) 2 cm³ of 1 M HCl solution and 10 cm³ of 20 % KI solution are added.
- (3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.
- (4) The mixture is titrated immediately with Na₂S₂O₃ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.
- (5) It is recommended to repeat the titration (steps 1 through 4) two more times.

Do the following and fill in the answer sheet form

- 1.5 Write the reactions involved in the procedure of determination of Fe³⁺ ion.
- 1.6 Calculate the mass of iron in the solution under analysis, and write your calculations.

SOLUTION**1.1**

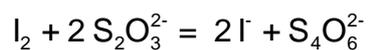
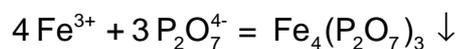
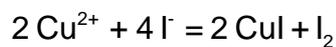
Equations:



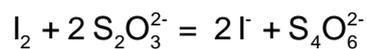
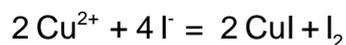
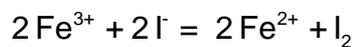
i

1.3

Equations:

**1.5**

Equations:



PROBLEM 2 (Practical)

Qualitative Determination of Paracetamol in a Sample of Unknown Drug

Introduction

Three organic compounds are most widely used as pain relieving drugs: acetylsalicylic acid (ortho-acetoxybenzoic acid), phenacetine (*para*-ethoxyacetanilide), and paracetamol (*para*-hydroxyacetanilide). Paracetamol is now the most popular, being the base of a large number of well known patented pharmaceuticals (panadol, solpadeine, coldrex, calpol, efferalgan etc.), as it is now considered as the safest and highly efficient drug.

You were given a sample of unknown drug which claims to contain paracetamol. Your task is to prove or disprove this claim experimentally. To do this you shall have to prepare an authentic sample of *para*-hydroxyacetanilide, and run a thin layer chromatography test.

Reagents

- *Para*-aminophenol, 3.10 g in a weighing beaker
- Acetic anhydride, 4.00 cm³ in an Erlenmeyer flask
- Ethanol
- Eluent (heptane : ethyl acetate : ethanol = 41 : 47 : 12 by volume)
- Sample of unknown drug in a test tube, 1 % solution in ethanol
- Water (use tap water for all purposes)

Procedure

Preparation of *para*-hydroxyacetanilide

A 50 cm³ round bottom flask is equipped with reflux condenser and installed on a laboratory stand over a hot plate. Note that the space between the top of hot plate and the bottom of flask be about 1-1.5 cm. Use two clamps to properly support the flask and condenser. Remove the hot plate. Do not switch on the hot plate until you finish with adding reagents and reassembling the apparatus. With reflux condenser temporarily removed, 3.10 g of *para*-aminophenol is placed to the flask using a funnel (use a glass rod

to push it through the funnel, if necessary). Water (10 cm³) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 cm³) is carefully poured to the reaction mixture through the condenser (*attention!* acetic anhydride has a strong irritating smell. In case of spill immediately wash hands with water and ask the supervisor to help with the disposal of spilled compound). Carefully stir the contents by slightly relieving clamps and waving the flask 2 - 3 times. Be careful as the mixture and the flask gets very hot due to the reaction heat. Place back the hot plate and switch it on. The reaction mixture is heated for 15 minutes beginning from the time when you switch on the hot plate. Then, the heater is switched off and removed from the apparatus. The mixture is allowed to cool first by immersing the flask into a bath with cold tap water. You may do this immediately after you remove the plate as the flask is made of highly durable glass. After approximately five minutes unattach the condenser and pour the contents into an empty 100 cm³ pyrex glass beaker. Put the beaker into a metal dish filled with ice and water. Accurately rub the walls of beaker with spatula and observe the crystallization of crude product as small white crystals.

Assemble a suction filtration device: put the frit filter onto a rubber ring and a heavy-wall flask. Connect the flask to a suction vacuum pump and turn on water in the pump by turning tap. (*Attention!* Never turn off the water tap if your device is under vacuum. First always disconnect the flask from vacuum pump by carefully pulling off the rubber tubing from the inlet.)

The crystalline precipitate is quantitatively moved onto a filter by spatula. Remaining solid can be washed with small portions of ice cold water (as small as possible, as the compound possesses an essential solubility in water, and the losses of dissolved compound must not outweigh the losses due to incomplete transfer of product to the filter). The product in the filter is carefully washed with 2 - 3 portions of 2 - 3 cm³ of cold water by a) connecting the vacuum suction flask to the atmosphere; b) addition of water and careful mixing it with the precipitate using a spatula; c) reapplying vacuum; d) pressing the precipitate with flat tip of a glass rod to squeeze out as much water as possible.

Several crystals of material are used for chromatography test (see below). All other precipitate is moved to a sheet of filtering paper in a Petri dish, and spread out over the filter in a thin layer, and allowed to dry on a shelf to exclude accidental spill. For rapid drying it is critical to spread it as thin as possible, to break all large pieces, and to stir it

and spread again every 3-5 minutes to expose all wet crystals to air. It is established after a numerous repetition of this procedure, that after 30 min the product contains no more than 5 % of water. Such wetness is considered as insignificant for evaluating the results of the preparation.

Chromatography test

(If for some reason you have failed to obtain *para*-hydroxyacetanilide, you can obtain a sample for chromatography from your supervisor.)

While still wet several crystals of the material obtained by you are dissolved in a tube in 1 - 2 cm³ of ethanol. The unknown drug is already dissolved in ethanol and given to you as 1 % solution. These solutions are used for thin layer chromatography, as follows:

Prepare a sheet of chromatography plate covered with silica. Using a sharp pencil draw a start line and marks for sample spots. A small spot of each solution is placed on a chromatography plate using a capillary. The spots are allowed to dry for 1-2 minutes.

The plate is immersed into a beaker containing the eluent and allowed to be eluted. Use forceps to move the plate in and out of the beaker. After the elution, remove the plate from the flask, mark the front of eluent, and allow it to dry under the hood for 5 minutes. Examine the chromatogram under UV light in a special cabinet. Outline the dark spots (if there are any) with a sharp pencil.

Weighting of sample

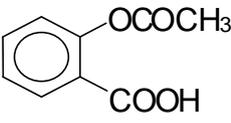
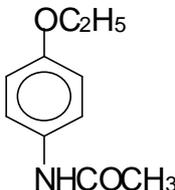
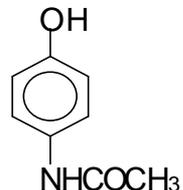
After you complete the chromatography, your product usually is almost dry and is ready for weighting. Ask you supervisor to weight an empty weighing beaker. Put the dry product into a weighted beaker and give it to the supervisor for weighting. Weights are written in your answer sheet by the supervisor. Calculate the weight of the product.

Do the following and fill in the answer sheet form

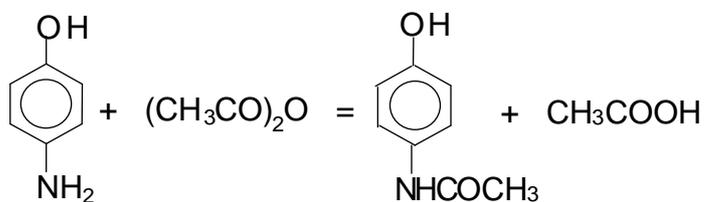
- 2.1 Draw the structures of three main pain relieving drugs mentioned above.
- 2.2 Draw the reaction equation involved in the preparation of *para*-hydroxyacetanilide. Calculate the stoichiometric amounts of reagents needed for the reaction. How much acetic anhydride is taken in excess over the stoichiometry? The density of acetic anhydride is 1.08 g cm⁻³.
- 2.3 Calculate the yield of product obtained by you.
- 2.4 Calculate and compare the values of R_f of unknown drug and your product.
- 2.5 Is it likely that paracetamol is contained in the sample of drug?

SOLUTION

2.1

Acetylsalicylic acid	Phenacetine	Paracetamol
		

2.2



2.5 Yes, the sample is likely to contain paracetamol.

29th



**8 theoretical problems
2 practical problems**

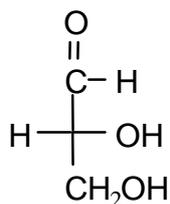
THE TWENTY-NINTH INTERNATIONAL CHEMISTRY OLYMPIAD 13–22 JULY 1997, MONTREAL, CANADA

THEORETICAL PROBLEMS

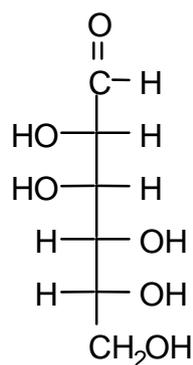
PROBLEM 1

Compound **X** is a trisaccharide which occurs principally in cottonseed meal. Compound **X** does not react with Benedict's or Fehling's solutions nor does it mutarotate. Acid-catalyzed hydrolysis gives three different D-hexoses, **A**, **B**, and **C**. Compounds **A** and **B**, as well as compound **1** (see below), all give the same osazone upon reaction with excess acidic phenylhydrazine. Compound **C** reacts with nitric acid to give an optically inactive compound **D**. The Kiliani-Fischer approach is used to establish the configurational relationship between D-glyceraldehyde and **C**. The intermediate aldotetrose which leads to **C** does not give a meso compound when oxidized by nitric acid. When **A** is treated with nitric acid, the dicarboxylic acid (aldaric acid) produced is optically active. Both **A** and **B** react with 5 moles of HIO_4 ; one mole of **A** gives 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) while one mole of **B** gives 3 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde) and one mole of carbon dioxide. Both **A** and **B** are related to the same aldotetrose which is the diastereoisomer of the one to which **C** is related. Methylation of **X** followed by hydrolysis gives a 2,3,4-tri-O-methyl-D-hexose (**E**) (derived from **A**), a 1,3,4,6-tetra-O-methyl-D-hexose (**F**) (derived from **B**), and a 2,3,4,6-tetra-O-methyl-D-hexose (**G**) (derived from **C**).

- 1.1 On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.
- 1.2 On the answer sheet, complete the appropriate Haworth projection formulas to clearly show the ring size and absolute stereochemistry of **E**, **F**, and **G**. Either of the anomeric forms are acceptable as an answer.
- 1.3 On the answer sheet, underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**.



D-Glyceraldehyde

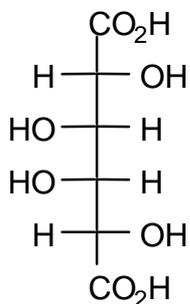


Compound 1

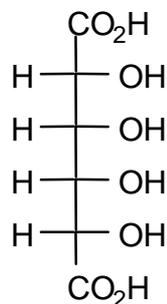
SOLUTION

1.1

Compound **X** is a trisaccharide which does not react with Benedict's solution nor does it mutarotate. This shows that **X** is a non-reducing sugar and therefore only acetal or ketal linkages exist at all of the anomeric carbons. Of the three monosaccharides, **A** and **B** give the same osazone and therefore have identical stereochemistry at C-3, C-4, and C-5 (and C-6). **A** and **B** are also different from compound **1** (i.e. D-mannose) yet give the same osazone, and thus one of them must be the C-2 epimer of D-mannose (i.e. D-glucose) and the other must be the corresponding keto sugar at C-2 (i.e. D-fructose). (This deduction is confirmed later in the oxidative cleavage reactions.) Compound **C**, after reaction with nitric acid, gives an optically inactive aldaric acid **D**. The two possible aldaric acids which could be **D** are thus:

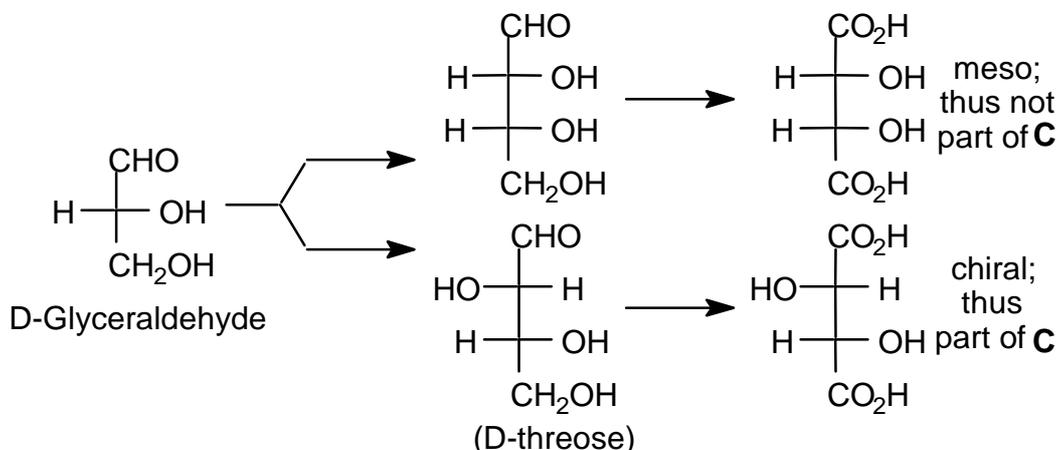


AA1 (=D)



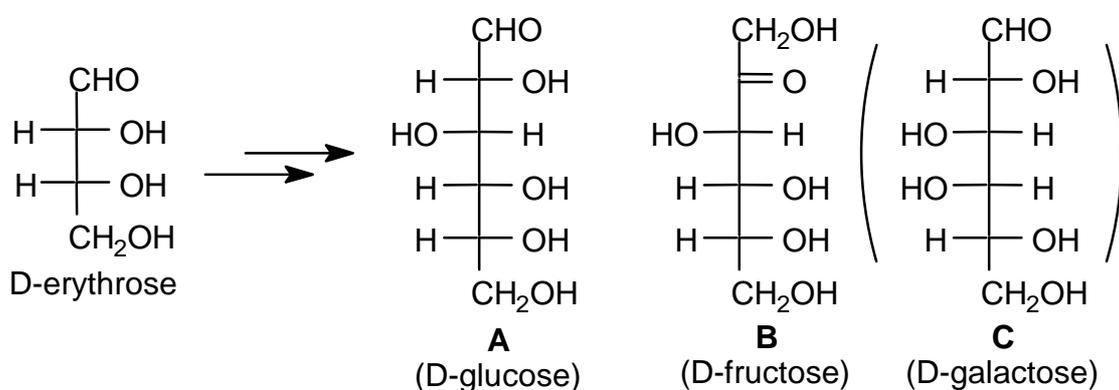
AA2

The aldotetrose which is the precursor of **C** (and thus also of **D**) does not give a meso compound after reaction with nitric acid and therefore must be the D-threose:



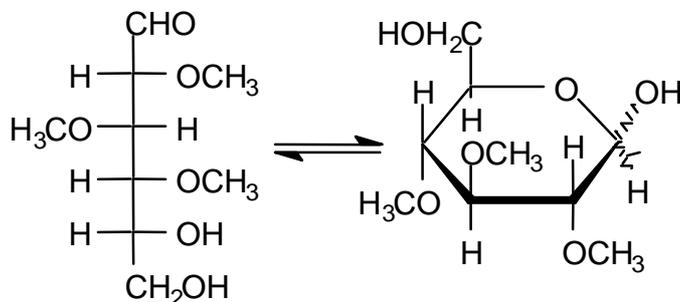
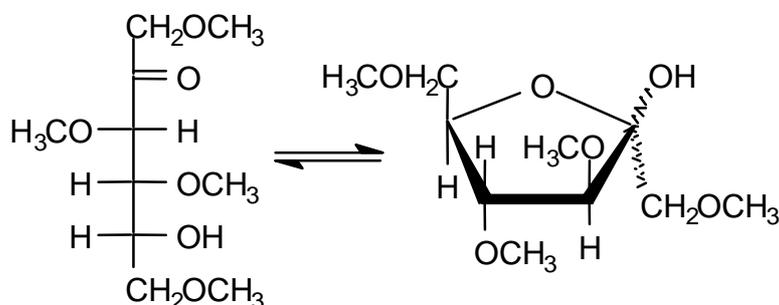
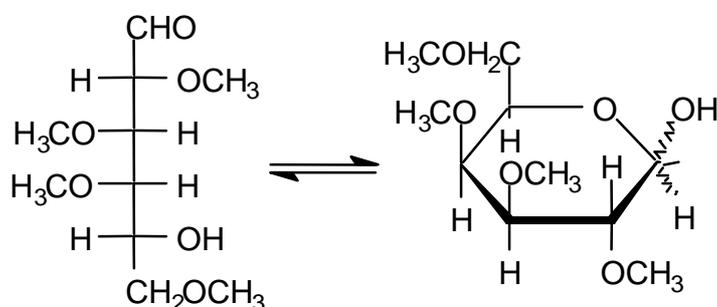
It follows from this that the aldaric acid **D** produced from **C** above is **AA1** and thus that **C** must be D-galactose. Compound **A** reacts with 5 moles of HI to give 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) suggesting that it is an aldohexose while **B** reacts with 5 moles of HI to give 4 moles of methanoic (formic) acid, one mole of methanal (formaldehyde) and one mole of CO₂ suggesting that it is a ketohexose.

Compounds **A** and **B** are related to the same tetrose which is not the same as that of **C** (i.e. are related to D-erythrose). The tetrose which is related to **A** and **B** must therefore have the following structure and accordingly **A** is D-glucose and **B** is D-fructose.



Methylation of **X** followed by hydrolysis yields **E**, **F** and **G** below:

1.2

**E derived from A****F derived from B****G derived from C**

1.3

During methylation, only hydroxyl groups not involved in acetal/ketal formation (either intra- or intermolecular) will be etherified. From the methylation data, only **E** has two free hydroxyl groups with which to link to the other carbohydrates. Thus **A** must be the central carbohydrate.

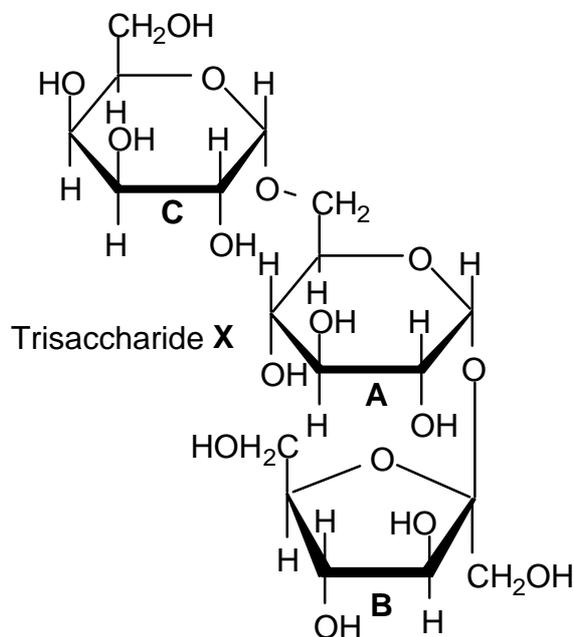
These results indicate that the sequence of monosaccharides in **X** is **C-A-B** (or **B-A-C**).

If: **A5** represents the furanose (5-membered ring) form of carbohydrate **A**.

A6 represents the pyranose (6-membered ring) form of carbohydrate **A**.

B5 represents the furanose (5-membered ring) form of carbohydrate **B**, etc. then the trisaccharide **X** would be represented as: **C**6-**A**6-**B**5

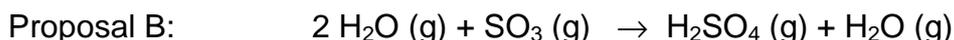
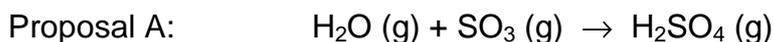
One of the 4 possible variations in the structure of **X** is given below.



Note: The nature of the anomeric linkages was not specified in the problem. The linkage arrangement of **A** to **B** and **C** may also be reversed (i.e. a 1,1' linkage between **C** and **A** and a 1,6 linkage between **A** and **B**).

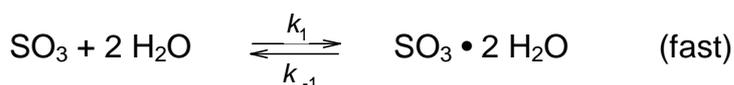
PROBLEM 2

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions:



2.1 Using simple collision theory, what reaction orders would be expected for Proposal A and for Proposal B?

Proposal B is thought to proceed by the following two-step process:



($\text{SO}_3 \cdot 2 \text{H}_2\text{O}$ is a complex which is stabilized by hydrogen bonds and $k_2 \ll k_1$ or k_{-1})

2.2 By applying the principle of stationary (steady) states, derive the appropriate rate law and hence the reaction order of the two-step mechanism for Proposal B.

2.3 Recent quantum chemical calculations have shown that the overall reaction activation energies for the two proposals are:

$$E_A = + 80 \text{ kJ mol}^{-1} \text{ for Proposal A} \quad E_B = - 20 \text{ kJ mol}^{-1} \text{ for Proposal B}$$

State the relationship between the rate constant and the temperature (Arrhenius relationship) for each proposal and predict the temperature dependence of the rate constants for each proposal.

2.4 The formation of H_2SO_4 is faster in the upper atmosphere ($T = 175 \text{ K}$) than at the earth's surface ($T = 300 \text{ K}$). Which proposed pathway must dominate in the upper atmosphere given the activation energies in part (iii) and your understanding of the Arrhenius equation?

SOLUTION

2.1 Proposal A:
$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k[\text{H}_2\text{O}][\text{SO}_3]$$

Summing the exponents gives a second order process

Proposal B:
$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k[\text{SO}_3][\text{H}_2\text{O}]^2$$

Summing the exponents gives a third order process

2.2 The steady state approximation gives:

The rate law here will be similar to that found for an enzymatic process which proceeds through a rapid reversible binding step followed by a slower reaction process.

$$\frac{d[\text{SO}_3 \cdot 2\text{H}_2\text{O}]}{dt} = k_1[\text{SO}_3][\text{H}_2\text{O}]^2 - k_{-1}[\text{SO}_3 \cdot 2\text{H}_2\text{O}] - k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = 0$$

Thus:
$$k_{-1}[\text{SO}_3 \cdot 2\text{H}_2\text{O}] + k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = k_1[\text{SO}_3][\text{H}_2\text{O}]^2$$

and therefore:
$$[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = \frac{k_1[\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1} + k_2}$$

Also:
$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}]$$
 and substituting from above yields

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = \frac{k_1 k_2 [\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1} + k_2}$$

However, since $k_2 \ll k_{-1}$ the above reduces to:

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = \frac{k_1 k_2 [\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1}} = K_{\text{eq}} k_2 [\text{SO}_3][\text{H}_2\text{O}]^2 = k[\text{SO}_3][\text{H}_2\text{O}]^2$$

which is also third order

2.3 Knowing the Arrhenius relationship: $k = A e^{-E/RT}$

For proposal A: $k = A e^{-E_A/RT} = A e^{-83.6/RT}$ which increases with increasing T.

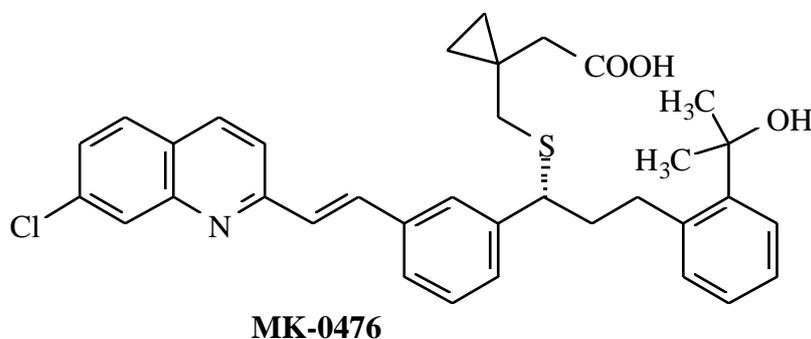
For proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

For proposal B: $k = A e^{-E_B/RT} = A e^{+83.60/RT}$ which decreases with increasing T

2.4 Assuming that the pre-exponential factors are comparable in magnitude as is usually the case, the reaction will be faster at the lower temperatures found in the upper atmosphere due to the temperature dependence deduced above, and thus Proposal B must be operating. The rationale for Proposal B which involves the relative sizes of the rate constants is nonsense and was included to balance the choices. The rationale for Proposal A involving collision probabilities appears plausible but is not a factor — it is the massive negative activation energy which controls the situation.

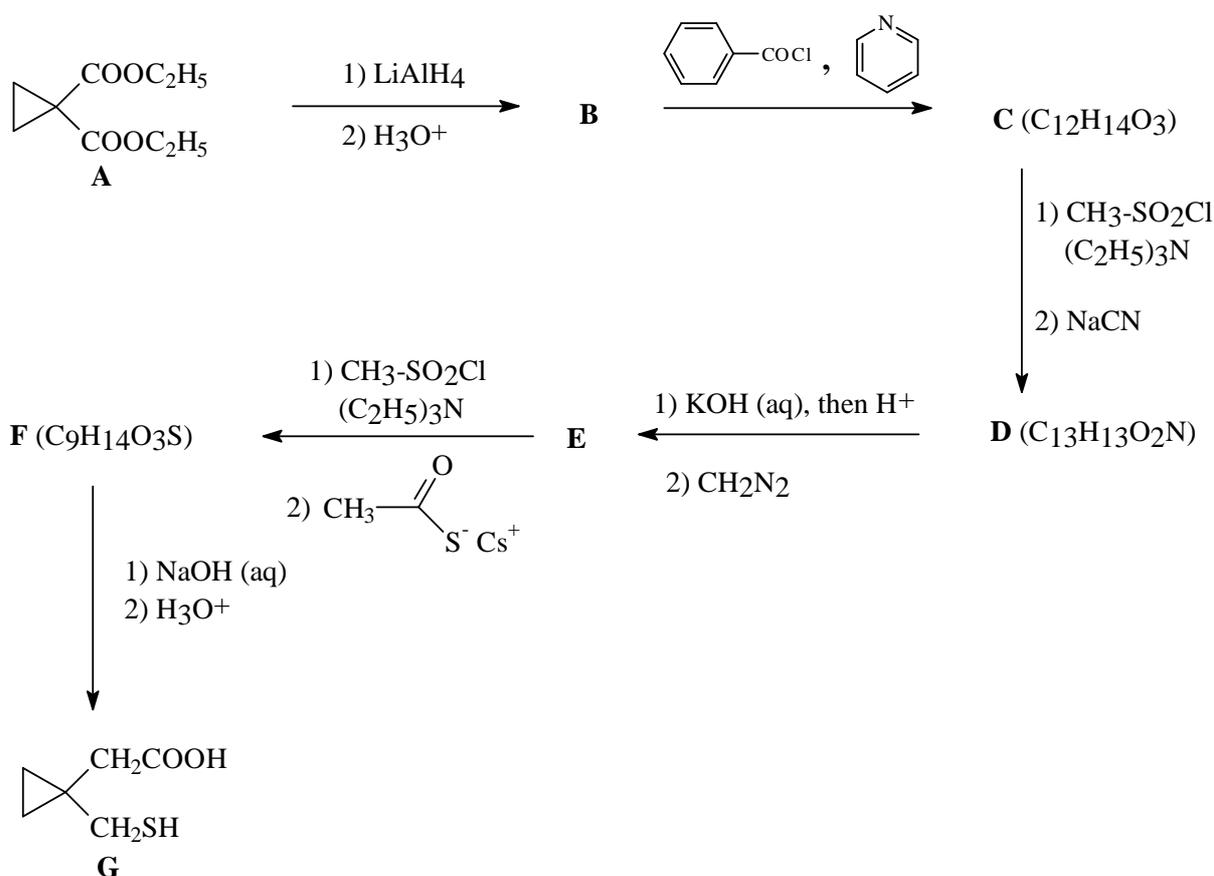
PROBLEM 3

Chemists at Merck Frosst Canada in Montréal have developed a promising drug which is useful against asthma. The structure of MK-0476 is shown below.

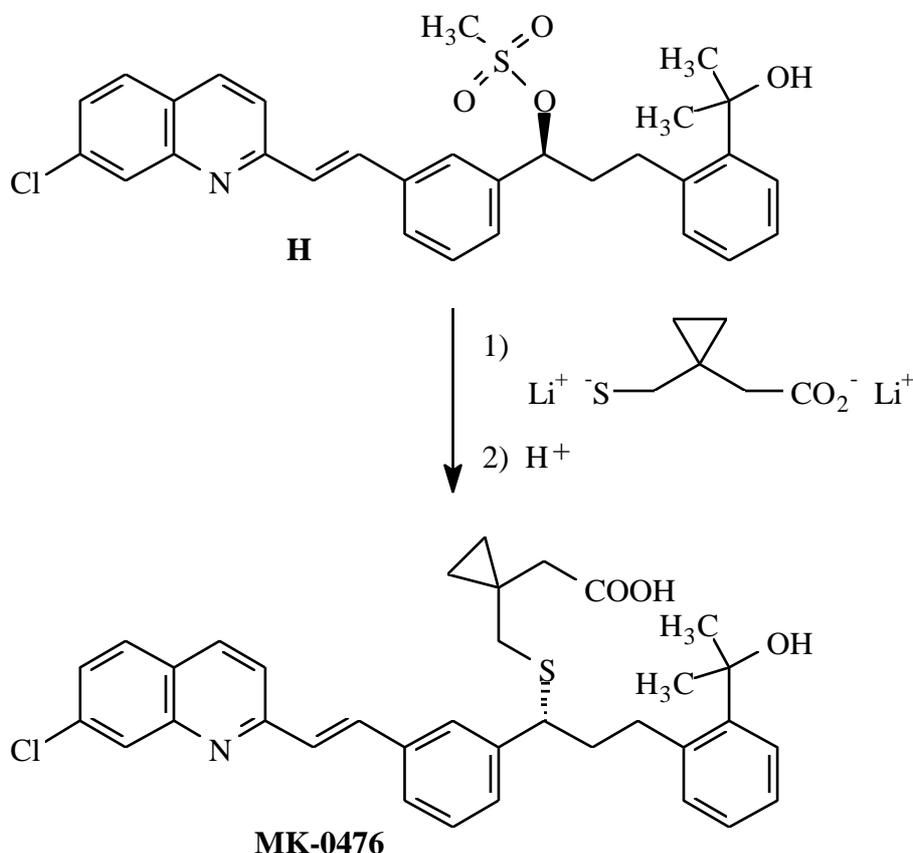


During their investigation, they devised a simple and efficient synthesis, depicted below, for the thiolated portion of MK-0476 starting from diethyl ester **A**.

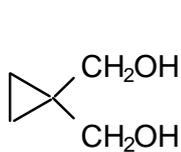
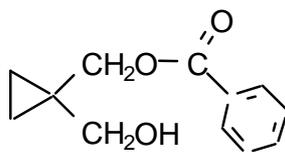
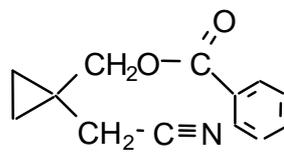
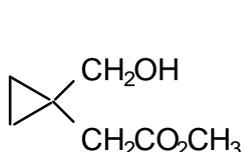
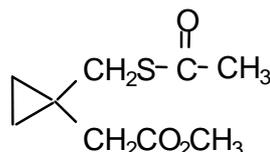
3.1 Give the structures of the intermediate products **B - F** prepared during this synthesis.



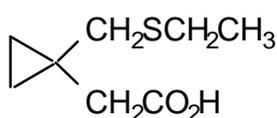
In one of the last steps of the synthesis on MK-0476, the dilithium salt of the above thiol acid (**G**) was coupled with the side chain of the rest of the molecule as shown below.



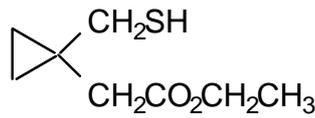
- 3.2** Based on the observed stereochemistry of the above reaction, what is the mechanistic designation of this coupling process?
- 3.3** If the process proceeds by your proposed mechanism, what change would occur to the overall rate of the reaction if the concentration of both the thiolate salt and the substrate **H** were simultaneously tripled?
- 3.4** For the nucleophilic substitution reaction, model studies were carried out using bromoethane as the substrate to perfect the above coupling. Draw only the structure of the major product of the reaction of one molar equivalent of bromoethane with:
- G** plus two molar equivalents of base
 - G** plus one molar equivalent of base
- 3.5** A side reaction of **G** is its oxidative dimerization. Draw the structure of the dimeric product, showing all non-bonded electrons.

SOLUTION**3.1****B****C** (C₁₂H₁₄O₃)**D** (C₁₃H₁₃O₂N)**E****F** (C₉H₁₄O₃S)**3.2** S_N2 Bimolecular Nucleophilic Substitution**3.3** Rate = k[substrate] [nucleophile]

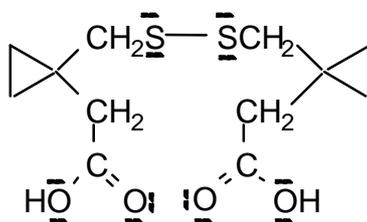
The overall rate is directly dependent on the concentration of both the substrate and the nucleophile. Thus tripling the concentration of both of the reactants will result in a 9-fold increase in the overall reaction rate.

3.4

From 2 equiv base



From 1 equiv base

3.5

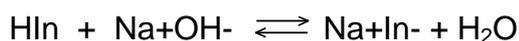
oxidative coupled product

PROBLEM 4

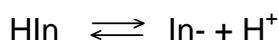
Graph paper is provided for your optional use in this question.

If you choose to use it, print your name and identification code in the upper right corner of the graph paper.

HIn is a weakly acidic indicator.



also written as

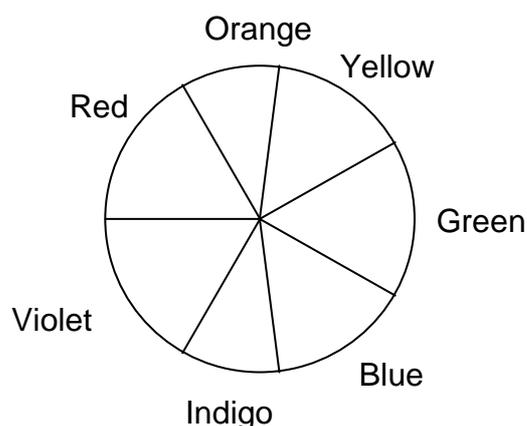


At normal temperatures, the acid dissociation constant for this indicator is $K_a = 2.93 \times 10^{-5}$.

The absorbance data (1.00 cm cells) for 5.00×10^{-4} M (mol dm^{-3}) solutions of this indicator in strongly acidic and strongly alkaline solutions are given in the following table.

Absorbance Data (A)

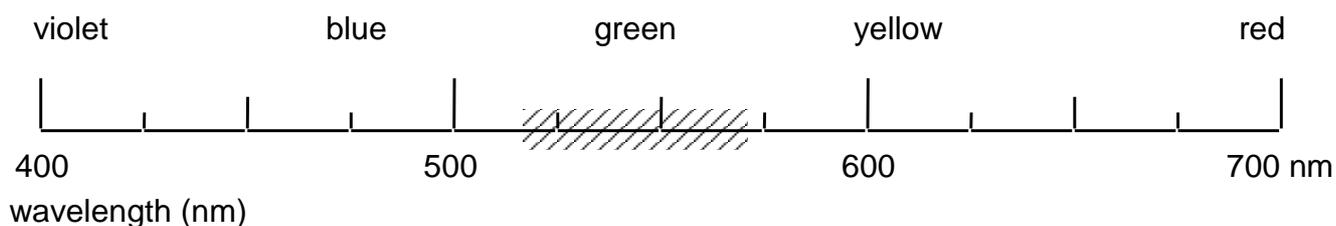
λ , nm	$pH = 1.00$	$pH = 13.00$
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



4.1 Predict the observed colour of the a) acidic and b) basic forms of the indicator.

Using a “50 nm wide bar”, shade the appropriate area of the wavelength scale on the answer sheet which would correspond to the colour of the indicator at the *pH* values given in the table.

For example, if observed colour is green, your answer would appear as:



4.2 A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

4.3 What wavelength range would be most suitable for the photometric analysis of the indicator in a strongly basic medium?

4.4 What would be the absorbance of a 1.00×10^{-4} M (mol dm⁻³) solution of the indicator in alkaline form if measured at 545 nm in a 2.50 cm cell?

4.5 Solutions of the indicator were prepared in a strongly acidic solution (HCl, *pH* = 1) and in a strongly basic solution (NaOH, *pH* = 13). Perfectly linear relationships between absorbance and concentration were observed in both media at 490 nm and 625 nm, respectively.

The molar absorptivities at the two wavelengths are:

	$\lambda = 490$ nm	$\lambda = 625$ nm
HIn (HCl)	$9.04 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$	$3.52 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$
In ⁻ (NaOH)	$1.08 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$	$1.65 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$

(M = mol dm⁻³)

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous 1.80×10^{-3} M (mol dm⁻³) solution of the indicator HIn.

SOLUTION

4.1 The observed colour will be the complementary colour to that of the absorption maximum.

a) Acidic conditions (*pH* 1):

The sample absorbs at 490 ± 25 (blue-green) and thus will transmit the complementary colour and will appear to be yellow-orange (625 ± 25 nm).

b) Basic conditions (*pH* 13):

The sample absorbs at 625 ± 25 (yellow-orange) and thus will transmit the complementary colour and will appear to be blue-green (490 ± 25 nm).

4.2 The filter should transmit the colour that the sample will absorb most efficiently. The acidic sample absorbs most strongly in the blue range (490 ± 25 nm) and thus a similar colour filter would be most suitable for the photometric analysis of the sample.

4.3 The wavelength range to be used for maximum sensitivity should correspond to that at which the sample absorbs most strongly. The maximum absorbance for the basic form of the indicator in solution occurs at 625 ± 25 nm and this is the most suitable wavelength for the analysis.

4.4 From a graph of *A* versus wavelength, the absorbance of a 5.00×10^{-4} M basic solution at 545 nm is 0.256. From the plot, it is clear that this region of the graph is linear and thus the above value can also be interpolated from the data table.

$$A = \epsilon l c \quad (\text{Beer's Law})$$

where *l* = length of cell, *c* = concentration of analyte, ϵ = molar absorptivity.

$$\text{Therefore } \epsilon = \frac{A}{lc} = \frac{0.256}{1.0 \times 5.00 \times 10^{-4}} = 5.12 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$$

$$lc = 1.0 \times 5.00 \times 10^{-4}$$

Absorbance of a 1.00×10^{-4} M basic solution of the indicator using a 2.50 cm cell is:

$$A = 5.12 \times 10^2 \times 2.50 \times 1.0 \times 10^{-4} = 0.128$$

4.5 The dissociation reaction of the indicator is:



accordingly,

$$[\text{H}^+] = [\text{In}^-] \quad (1)$$

and

$$[\text{HIn}] + [\text{In}^-] = 1.80 \times 10^{-3} \text{ M} \quad (2)$$

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad (3)$$

Substitute (1) and (2) into (3)

$$K_a = \frac{[\text{In}^-]^2}{1.8 \times 10^{-3} - [\text{In}^-]} = 2.93 \times 10^{-5}$$

Rearrangement yields the quadratic expression

$$[\text{In}^-]^2 + 2.93 \times 10^{-5} [\text{In}^-] - 5.27 \times 10^{-8} = 0$$

which results in

$$[\text{In}^-] = 2.15 \times 10^{-4} \text{ M}$$

$$[\text{HIn}] = 1.80 \times 10^{-3} \text{ M} - 2.15 \times 10^{-4} \text{ M} = 1.58 \times 10^{-3} \text{ M}$$

The absorbance at the two wavelengths are then:

$$A_{490} = (9.04 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.08 \times 10^2 \times 1 \times 2.15 \times 10^{-4}) = 1.45$$

$$A_{625} = (3.52 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.65 \times 10^3 \times 1 \times 2.15 \times 10^{-4}) = 0.911$$

PROBLEM 5

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centred cubic (bcc) lattice known as α -iron. From 1185 K to 1667 K, the structure becomes face-centred cubic (fcc) and is called γ -iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α -iron. The latter phase is called δ -iron.

Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K:

5.1 Calculate the atomic radius of iron (expressed in cm).

5.2 Calculate its density (expressed in g cm^{-3}) at 1250 K.

Notes: Ignore the small effects due to the thermal expansion of the metal.

Clearly define any symbols which you use, e.g. r = atomic radius of Fe.

Steel is an alloy of iron and carbon in which some of the interstitial spaces (“holes”) of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1 % to 4.0 %. In a blast-furnace, the melting of iron is facilitated when it contains 4.3 % of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α -iron phase. This new solid, called martensite, is extremely hard and brittle. Although it is slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α -iron (bcc).

Assuming that the carbon atoms are evenly distributed in the iron structure:

5.3 Calculate the average number of carbon atoms per unit cell of α -iron in martensite containing 4.3 % C by mass.

5.4 Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants:

$$M(\text{Fe}) = 55.847 \text{ g mol}^{-1}$$

$$M(\text{C}) = 12.011 \text{ g mol}^{-1}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

SOLUTION

5.1 Calculation of the atomic radius of iron (expressed in cm).

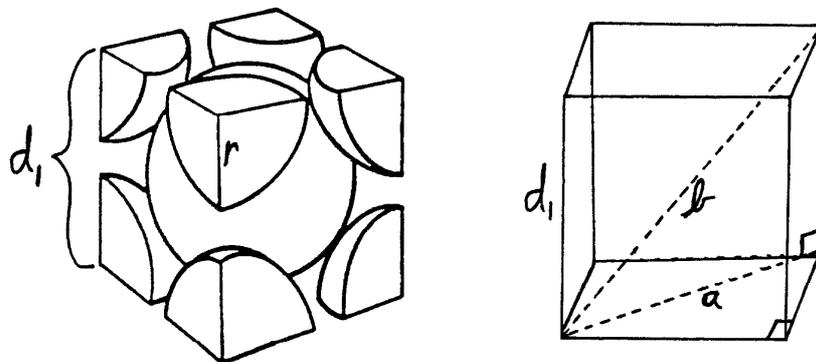
5.2 Calculation of its density (expressed in g cm^{-3}) at 1250 K.

Expected steps of the calculation:

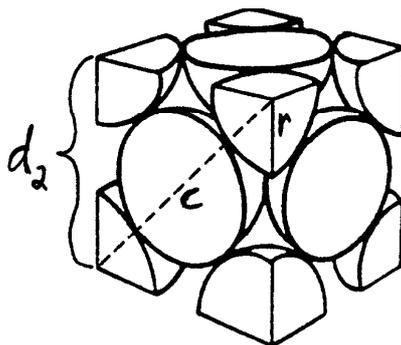
1. Define the length a , b , c , d_1 , d_2 , and r and volume V_1 and V_2 parameters for both bcc and fcc structures of iron (*cf.* Details below).
2. Calculate the volume V_1 of the unit cell of α -iron from its density ρ_{bcc} at 293 K, the molar weight $M(\text{Fe})$ of iron, and Avogadro's number N_A .
3. Calculate the length d_1 of the edge of the bcc unit cell from its volume V_1 .
4. Calculate the atomic radius r of iron from the length " d_1 ".
5. Calculate the length d_2 of the edge of the fcc unit cell at 1250 K from the atomic radius r of iron.
6. Calculate the volume V_2 of the fcc unit cell of γ -iron from the length d_2 of its edge.
7. Calculate the mass m of the number of iron atoms in a unit cell of γ -iron from the molar weight $M(\text{Fe})$ of iron and Avogadro's number N_A .
8. Calculate the density ρ_{fcc} of γ -iron from the values of " m " and " V_2 ".

An alternative route to ρ_{fcc} of γ -iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

- 5'. Calculate the percent space filling ratio of the bcc unit cell.
- 6'. Calculate the percent space filling ratio of the fcc unit cell.
- 7'. Calculate the $\rho_{\text{fcc}}/\rho_{\text{bcc}}$ density ratio from the fcc/bcc space filling ratios.
- 8'. Calculate the density ρ_{fcc} of γ -iron from the value found in step 7'.



Body centered cubic structure (bcc)



Face-centered cubic structure (fcc)

Calculations in details

At 293 K, α -iron has a bcc crystal structure.

Each unit cell possesses 2 atoms and one of them is in the center of the cell.

At 1250 K, γ -iron has a fcc crystal structure.

Each unit cell possesses 4 atoms and each side has one-half an atom at its center.

r = atomic radius of iron.

a = length of the diagonal on one side of the bcc unit cell.

b = length of the diagonal passing through the center of the bcc unit cell.

c = length of the diagonal on one side of the fcc unit cell.

d_1 = length of the edge of the bcc unit cell of α -iron.

d_2 = length of the edge of the fcc unit cell of γ -iron.

V_1 = Volume of the bcc unit cell of α -iron.

V_2 = Volume of the fcc unit cell of γ -iron.

V_a = Volume of one atom.

V_{a1} = Volume occupied by 2 atoms in one bcc unit cell.

V_{a2} = Volume occupied by 4 atoms in one fcc unit cell.

R_1 = Percent space filling ratio in a bcc unit cell.

R_2 = Percent space filling ratio in a fcc unit cell.

$$V_a = \left(\frac{4}{3}\right) \pi r^3$$

$$V_{a1} = 2 V_a$$

$$V_{a2} = 4 V_a$$

$$b = 4 r;$$

$$a^2 = 2 d_1^2;$$

$$b^2 = d_1^2 + a^2 = 3 d_1^2$$

$$d_1 = (b^2/3)^{1/2} = (16 r^2/3)^{1/2};$$

$$V_1 = d_1^3 = [(16 r^2/3)^{1/2}]^3$$

$$c = 4 r; \quad c^2 = 2 d_2^2$$

$$d_2 = (c^2/2)^{1/2} = (16 r^2/2)^{1/2};$$

$$V_2 = d_2^3 = [(16 r^2/2)^{1/2}]^3$$

2. 1.000 cm^3 of iron weights 7.874 g at 293 K (ρ_{bcc}).

1 mole of iron weights 55.847 g (M_{Fe}).

Thus, 0.1410 mol (7.874 g / 55.847 g mol⁻¹) of iron occupy a volume of 1.000 cm³ or
1 mole of iron will occupy a volume of 7.093 cm³

1 mole corresponds to 6.02214×10²³ atoms

$$V_1 = (7.093 \text{ cm}^3 \text{ mol}^{-1}) \times (2 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$$

$$V_1 = 2.356 \times 10^{-23} \text{ cm}^3 \text{ per unit cell}$$

$$3. \quad d_1 = (V_1)^{1/3} = (2.356 \times 10^{-23} \text{ cm}^3)^{1/3}$$

$$d_1 = 2.867 \times 10^{-8} \text{ cm}$$

$$4. \quad \text{For a bcc structure, the value of } d_1 \text{ can be expressed as: } d_1 = [(16 r^2)/3]^{1/2}$$

so the value of "r" will be: $r = (3 d_1^2/16)^{1/2}$

$$r = [3 (2.867 \times 10^{-8} \text{ cm})^2/16]^{1/2}$$

$$r = 1.241 \times 10^{-8} \text{ cm}$$

$$5. \quad \text{At 1250 K, in the fcc structure, the value of "d}_2\text{" is given by: } d_2 = (16 r^2/2)^{1/2}$$

$$d_2 = [16 (1.241 \times 10^{-8} \text{ cm})^2/2]^{1/2}$$

$$d_2 = 3.511 \times 10^{-8} \text{ cm}$$

$$6. \quad V_2 = d_2^3 = (3.511 \times 10^{-8} \text{ cm})^3$$

$$V_2 = 4.327 \times 10^{-23} \text{ cm}^3$$

7. The mass "m" of the 4 iron atoms in the fcc unit cell will be:

$$m = (55.847 \text{ g mol}^{-1}) \times (4 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$$

$$m = 3.709 \times 10^{-22} \text{ g per unit cell}$$

$$8. \quad \rho_{\text{fcc}} = m / V_2 = (3.709 \times 10^{-22} \text{ g}) / (4.327 \times 10^{-23} \text{ cm}^3)$$

$$\rho_{\text{fcc}} = 8.572 \text{ g/cm}^3$$

Alternative route to ρ_{fcc} of γ -iron:

$$5'. \quad R_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2 V_a) / (V_1)] \times 100\%$$

$$R_1 = ([2 \times (4/3) \pi r^3] / [(16 r^2/3)^{1/2}]^3) \times 100\%$$

$$R_1 = ([8/3 \pi r^3] / [(16/3)^{3/2} r^3]) \times 100\%$$

$$R_1 = ([8/3 \pi] / [(16/3)^{3/2}]) \times 100\%$$

$$R_1 = [(8.378) / (12.32)] \times 100\%$$

$$R_1 = 68.02 \%$$

$$6'. \quad R_2 = [(V_{a2}) / (V_2)] \times 100\% = [(4 V_a) / (V_2)] \times 100\%$$

$$R_2 = ([4 \times (4/3) \pi r^3] / [(16 r^2/2)^{1/2}]^3) \times 100\%$$

$$R_2 = ([16/3 \pi r^3] / [8^{3/2} r^3]) \times 100\%$$

$$R_2 = \left(\frac{[(16/3) \pi]}{[8^{3/2}]} \right) \times 100\%$$

$$R_2 = [(16.76) / (22.63)] \times 100\%$$

$$R_2 = 74.05\%$$

$$7'. \quad \rho_{\text{fcc}} / \rho_{\text{bcc}} = (74.05\%) / (68.02\%)$$

$$\rho_{\text{fcc}} / \rho_{\text{bcc}} = 1.089$$

$$8'. \quad \rho_{\text{fcc}} = 1.089 \times \rho_{\text{bcc}}$$

$$\rho_{\text{fcc}} = 1.089 \times 7.874 \text{ g cm}^{-3}$$

$$\rho_{\text{fcc}} = 8.572 \text{ g cm}^{-3}$$

5.3 Calculation of the average number of carbon atoms per unit cell of α -iron in martensite containing 4.3 % C by mass.

5.4 Calculation of the density (expressed in g cm^{-3}) of this material.

Expected Steps of the Calculation:

1. From the percent composition of martensite (by mass), calculate the relative amounts of moles of carbon and iron.
2. Bring the C/Fe molar ratio to one (1) unit cell (Note: 2 Fe atoms per unit cell).
3. Find the smallest whole number of C atoms for the smallest whole number of unit cell (facultative).
4. Calculate the mass of iron per unit cell.
5. Calculate the mass of carbon per unit cell.
6. Calculate the total mass of carbon and iron in one unit cell.
7. Calculate the density of martensite [$\rho(\text{martensite at 4.3 \%C})$] from the total mass of C and Fe and volume (V_1) of α -iron bcc unit cell.

Details:

$$1. \quad \text{In 100.0 g of martensite at 4.3 \% C: } (4.3 \text{ g C}) / (12.011 \text{ g mol}^{-1}) = 0.36 \text{ mol C}$$

$$(95.7 \text{ g Fe}) / (55.847 \text{ g mol}^{-1}) = 1.71 \text{ mol Fe}$$

So we have 1 carbon atom for 4.8 iron atoms or

0.21 carbon atoms per iron atom.

2. Martensite has a "bcc" crystal structure (2 iron atoms per unit cell).

$$[(1 \text{ C atom}) / (4.8 \text{ Fe atoms})] \times (2 \text{ Fe atoms} / \text{unit cell})$$

or: 0.42 carbon atoms per unit cell

3. 5 carbon atoms $[(0.42 \text{ C atom} / 0.42) \times 5]$ in 12 unit cells $[(1 \text{ unit cell}/0.42) \times 5]$.
5 carbon atoms dispersed in 12 unit cells
4. $[(55.847 \text{ g/mol}) / (6.02214 \times 10^{23} \text{ atoms/mol})] \times (2 \text{ atoms/unit cell of } \alpha\text{-iron})$
 $1.8547 \times 10^{-22} \text{ g Fe per unit cell of } \alpha\text{-iron}$
5. $(12.011 \text{ g/mol}) / (6.02214 \times 10^{23} \text{ atoms/mol})$
 $1.9945 \times 10^{-23} \text{ g C per atom}$
6. $[1.8547 \times 10^{-22} \text{ g Fe} + (0.42 \text{ C at.} \times 1.9945 \times 10^{-23} \text{ g / C at.})]$ per unit cell
 $1.938 \times 10^{-22} \text{ g C and Fe per unit cell}$
7. Each unit cell of α -iron occupies a volume, $V_1 = 2.356 \times 10^{-23} \text{ cm}^3$
(*cf.* Question i)
 $\rho(\text{martensite at 4.3 \% C}) = (1.938 \times 10^{-22} \text{ g C and Fe}) / (2.356 \times 10^{-23} \text{ cm}^3)$
 $\rho(\text{martensite at 4.3 \% C}) = 8.228 \text{ g cm}^{-3}$
-
-

PROBLEM 6

6.1 Much of the world's supply of platinum group metals is derived from the residues recovered from the electrolytic refining of copper and nickel. A flow chart for the recovery of platinum and palladium is shown on the following page.

- i) Clearly draw the shape (geometry) of both the PtCl_6^{2-} and the PdCl_4^{2-} anions.
- ii) Clearly draw all possible stereoisomeric structures of monomeric $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. Label the structures that you have drawn with their correct stereochemical descriptors.
- iii) What is the role of the FeSO_4 in the second step of the flow chart? Write a balanced equation for the reaction of FeSO_4 in this step.
- iv) Write a complete balanced equation for the ignition of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in air to give Pd metal. In this reaction, what is being oxidized and what is being reduced?

6.2 Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH_4Cl (25.68 g), a solid element **A** (2.57 g) and a yellow crystalline nitride of this element (7.37 g) according to the equation below.



(where n, m, p, q, r, w, x, y and z are coefficients to be determined)

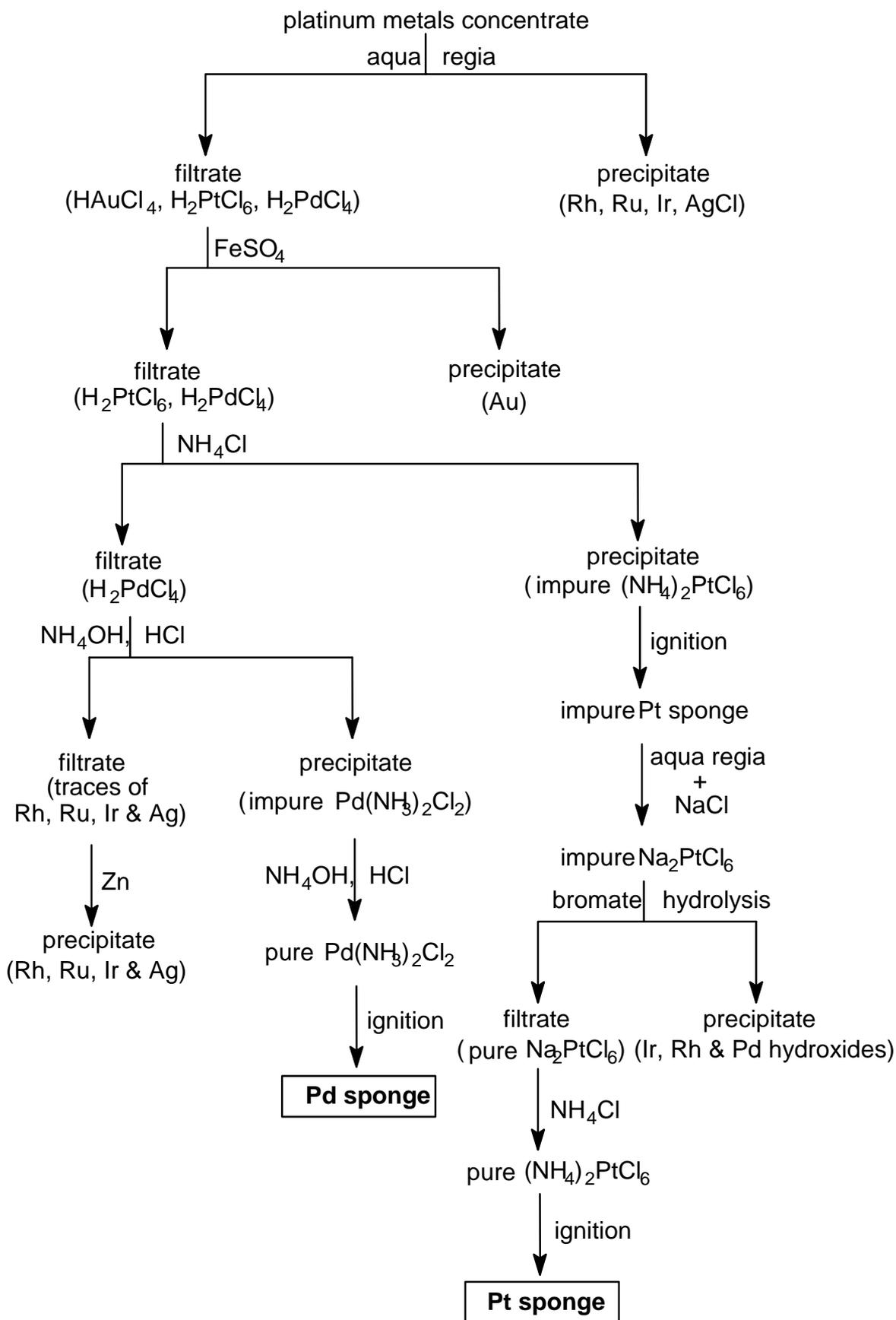
A sample of the nitride exploded violently when struck with a hammer, but it underwent controlled polymerization on heating to give a bronze-coloured, fibrous solid which exhibits metallic conductivity. Element **A** also undergoes polymerization to a high molecular weight linear polymer upon heating.

Molar masses:

$$M(\text{Cl}) = 35.453 \text{ g mol}^{-1} \quad M(\text{N}) = 14.007 \text{ g mol}^{-1} \quad M(\text{H}) = 1.008 \text{ g mol}^{-1}$$

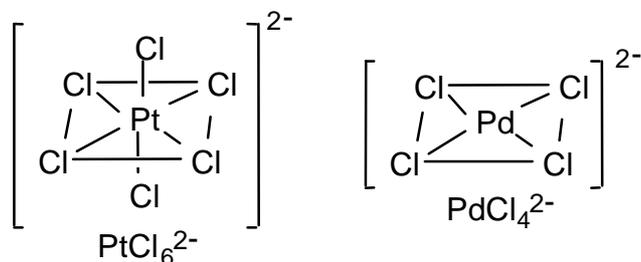
- i) Identify element **A**.
- ii) Write a complete balanced equation for the reaction of the chloride with ammonia.
- iii) Assuming conventional oxidation states, write the balanced redox half-reaction equations involved in this reaction.

Method of Purification of Platinum and Palladium

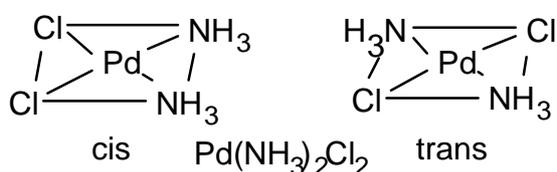


SOLUTION**6.1**

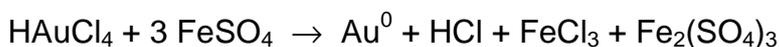
- i) The PtCl_6^{2-} anion consists of a Pt(IV) centred in a regular octahedron of Cl^- ions. The PdCl_4^{2-} anion consists of a Pd(II) centred in a square of Cl^- ions.



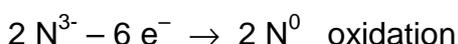
- ii) Like PdCl_4^{2-} , $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is also square planar. However, in this case there are two distinct ways in which the two different substituent groups (ligands) can be arranged. One places the two Cl^- on adjacent corners of the square (and axiomatically, the two NH_3 on the other two adjacent corners). This arrangement is called the *cis* isomer. The second arrangement has the pairs of the same ligand placed on diagonally opposite corners of the square. This arrangement is called the *trans* isomer. There are only these two stereoisomers possible for a monomeric form of the complex.



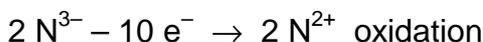
- iii) The FeSO_4 [i.e. Fe(II)] acts as a reducing agent. Under the conditions used in the process, the Fe(II) is a strong enough reducing agent to reduce Au(III) to Au(0), but not to reduce Pd(II) or Pt(IV).



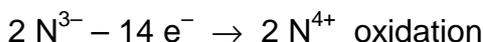
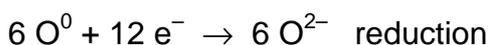
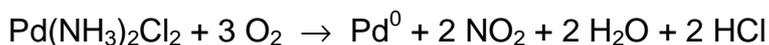
- iv) $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + \text{O}_2 \rightarrow \text{Pd}^0 + \text{N}_2 + 2 \text{H}_2\text{O} + 2 \text{HCl}$



or



or



In this reaction the ammonia is oxidized to water and dinitrogen (or nitrogen oxides) and the Pd(II) and dioxygen are being reduced.

Part of the oxidation is due to the Pd(II) acquiring two electrons to go to Pd(0), and part by dioxygen which is reduced to water. In the presence of noble metal catalysts, NH_3 can also be oxidized to $(\text{NO})_x$. Thus other nitrogen species are also in principle possible in the above ignition.

6.2

i) A = sulphur

All Cl is located in the NH_4Cl , and thus the weight of Cl is found by:



$$? = 25.68 \times 35.453 / 53.492 = 17.02 \text{ g Cl}$$

Total amount of A in the reaction is $24.71 \text{ g Cl} - 17.02 \text{ g Cl} = 7.69 \text{ g A}$ There is 2.57 g free A and $(7.69 - 2.57) = 5.12 \text{ g A}$ in the nitride.

The amount of N bound in nitride is therefore

$$7.37 \text{ g nitride} - 5.12 \text{ g A bound in nitride} = 2.25 \text{ g N bound in nitride}$$

The amount of nitrogen bound in NH_4Cl is $25.68 - 17.02 = 8.66 \text{ g}$

The rule of multiple proportions is applied:

Proportions of 1 : 1

Chloride:



? g A binds \rightarrow 35.453 g Cl

? = $35.453 \times 7.69/17.02 = 16.02$ g

A could be oxygen, but it is a main group element and it is a gas and thus it can be excluded.

Nitride:

5.12 g A binds \rightarrow 2.25 g N

? g A binds \rightarrow 14.007 g N

? = $14.007 \times 5.12/2.25 = 31.87^*$ g

A could be sulphur, fits the physical description and $M_r(\text{S}) = 32.064$

(*Phosphorus, $M_r(\text{P}) = 30.97$, is also possible, but the highest degree of "polymerization" known is 4, in the P_4 molecule and thus P must also be excluded.)

Proportions of 1 : 2

Chloride:

7.69 g A binds \rightarrow 17.02 g Cl

? g A binds $\rightarrow 2 \times 35.453$ g Cl

? = $2 \times 35.453 \times 7.69 / 17.02 = 32.03$ g. Again A could be sulphur.

Nitride:

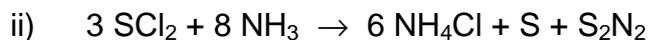
5.12 g A binds \rightarrow 2.25 g N

? g A binds $\rightarrow 2 \times 14.007$ g N

? = $2 \times 14.007 \times 5.12 / 2.25 = 63.75$ g

A could be Cu but it is a Group B element and thus can be excluded.

Therefore element A must be sulphur.



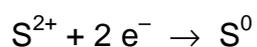
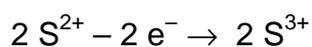
or



In fact the elemental S is in the form of S_8 and so the equation should be multiplied by a factor of 8. Although S_2N_2 roughly fits the description of colour and explosive instability, it is actually S_4N_4 that is produced in this reaction. Both of these ring compounds under carefully controlled heating polymerize to give the high molecular weight linear polymer $(\text{SN})_n$, which is one of the rare examples of a metal containing only lighter p-group elements. The tendency of these ring compounds to polymerize

is due to the relatively weak S-N bonds and the large amount of strain energy in the ring. The S-S bond is also quite weak and can be broken by heating. For this reason the S₈ ring also undergoes polymerization at high temperature. However, there is hardly any energy stored in the form of ring strain in this ring and so the polymerization is not highly exothermic or explosive. Other sulphur chlorides (S₂Cl₂ and SCl₄) do not fit the stoichiometry of the reaction.)

iii) A disproportionation reaction involving sulphur occurs:



PROBLEM 7

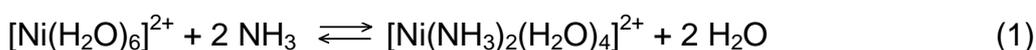
7.1 One mole of Cl_2 (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325×10^7 Pa, is expanded against a constant external pressure of 1.01325×10^5 Pa to a final pressure of 1.01325×10^5 Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl_2), and 0.100 mol of Cl_2 condensed.

The enthalpy of vaporization of Cl_2 (l) is $20.42 \text{ kJ mol}^{-1}$ at the normal boiling point, the molar heat capacity of Cl_2 (g) at constant volume is $C_V = 28.66 \text{ J K}^{-1} \text{ mol}^{-1}$ and the density of Cl_2 (l) is 1.56 g cm^{-3} (at 239 K). Assume that the molar heat capacity at constant pressure for Cl_2 (g) is $C_p = C_V + R$.

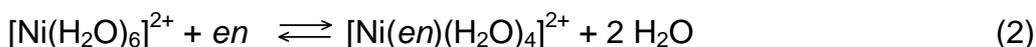
(1 atm = 1.01325×10^5 Pa, $R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

- Either draw a complete molecular orbital energy diagram or write the complete electronic configuration of Cl_2 . Predict the bond order of Cl_2 and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.
- For the changes described above, calculate the change in the internal energy (ΔE) and the change in the entropy (ΔS_{sys}) of the system.

7.2 For the following reactions occurring in dilute aqueous solution at 298 K:



$$\ln K_c = 11.60 \text{ and } \Delta H^0 = -33.5 \text{ kJ mol}^{-1}$$

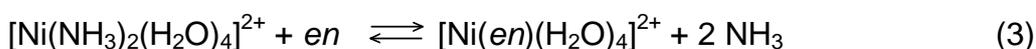


$$\ln K_c = 17.78 \text{ and } \Delta H^0 = -37.2 \text{ kJ mol}^{-1}$$

Note: *en* is ethylenediamine (a neutral bidentate ligand)

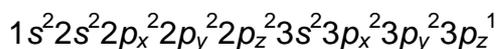
$$(R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1})$$

Calculate ΔG^0 , ΔS^0 , and K_c at 298 K for reaction [3] occurring in a dilute aqueous solution:



SOLUTION**7.1**

i) Electronic configuration of a Cl atom:



Significant atomic orbitals (AO) = 1(K) + 4(L) + 4(M) = 9 AO

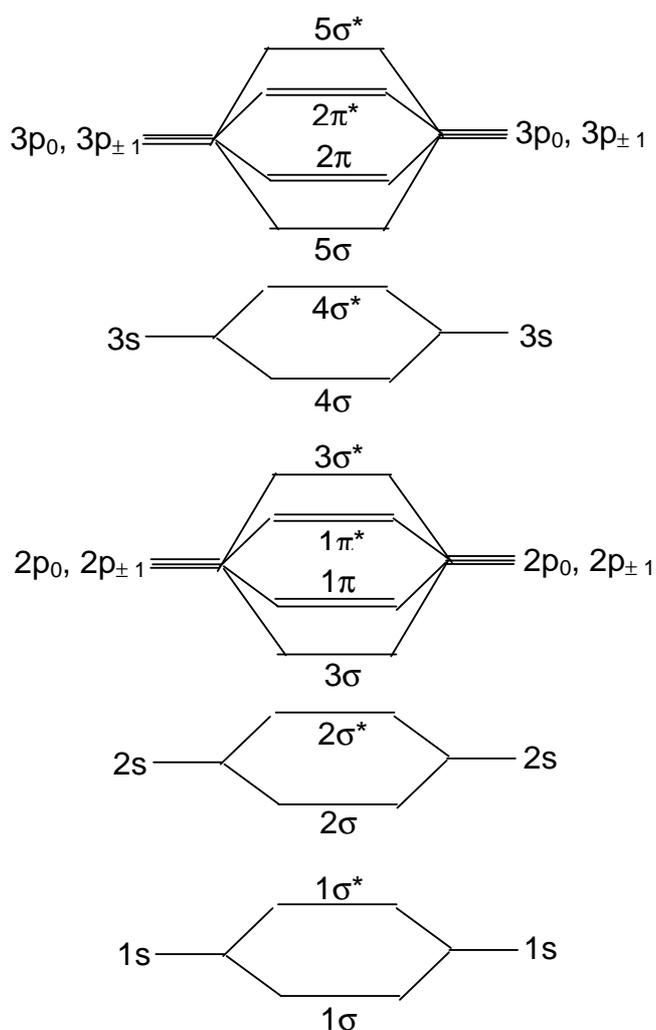
Number of electrons in these AOs: 17

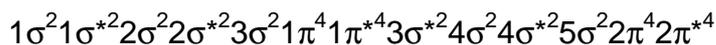
Number of molecular orbitals (MO) equals number of AOs:

Thus $2 \times [1(K) + 4(L) + 4(M)] = 18$ MOs are present in a Cl_2 molecule

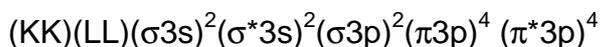
In the formation of Cl_2 : $2 \times 17 = 34$ electrons to go into the 18 MOs.

MO description of Cl_2 :

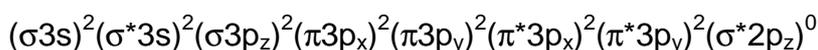
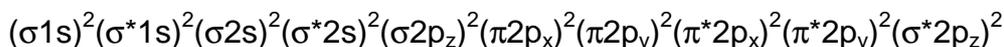




or



or



or



*assumption: - bond formation is along the z-axis

(equivalent formulae for x or y axes are accepted)

Bond order is given by $(n-n^*)/2$:

$$n = 18; \quad n^* = 16$$

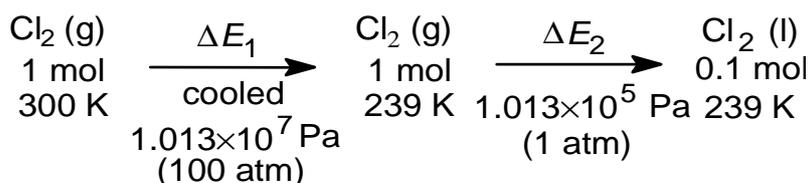
$$(18 - 16) / 2 = 1$$

(1 σ bond, no π bond)

The Cl_2 molecule has a bond order of 1.

The Cl_2 molecule is diamagnetic since there are no unpaired electrons.

ii) Summary of the changes involved:



The total process is an expansion plus an isobaric change of phase (gas to liquid) and since the internal energy (E) is a function of state, the total change in the internal energy is $\Delta E = \Delta E_1 + \Delta E_2$.

Process 1:

$$\Delta E_1 = \int n C_v dT = 1 \times 28.66 \times 239 - 300 = -1748.3 \text{ J}$$

- Note:
- ΔE for a perfect gas is a function only of T
 - C_v is constant
 - “-” sign means a loss of energy due to the work needed for expansion of 1 mole of gas

Process 2: For convenience, the data were manipulated in atm; equivalent procedure in Pa will require the appropriate conversion factor

From an energetic point of view, the liquid formation Process 2 can be split into two separate steps :

- the vaporization heat loss (decreased internal energy, -) from the system into surroundings (since the process takes place at constant pressure, the heat is equal to the change in the enthalpy)
- the work done by the surroundings in compressing the system to a smaller volume (increased internal energy, +).

Volume of gas which condensed is

$$V = n R T / P = (0.1 \times 0.0820584 \times 239) / 1 = 1.96 \text{ dm}^3$$

$$\text{Volume of liquid Cl}_2: (0.1 \times 2 \times 35.454) / 1.56 = 4.54 \text{ cm}^3$$

$$\Delta E_2 = \Delta H_2 - \int P_{\text{ext}} \Delta V(\text{phase change}) = \Delta H_2 - P_{\text{ext}}(V_l - V_g)$$

but V_l is approximately 0 and can be neglected

(ca. 4.5 cm³ liquid volume vs. ca. 17.6 dm³; ca. 0.03 % error)

$$\Delta E_2 = (0.1) (-\Delta H_{\text{vap}}) + P_{\text{ext}} V_g$$

$$= 0.1 \times (-20420) + (1 \times 1.96 \text{ L}) \times 101.325 \text{ J dm}^{-3} \text{ atm}^{-1} = -2042.0 + 198.5 = -1843.5$$

$$\Delta E = \Delta E_1 + \Delta E_2 = -1748.3 + (-1843.5) = -3591.8$$

Entropy S is a function of two variables of state. Since in Process 1 the known variables are T and P , expression of S is chosen as $S(T, P)$.

$$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2 \text{ and}$$

$$\bar{C}_p = \bar{C}_v + R = 28.66 + 8.314 = 36.97 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta S_1 &= n C_p \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} = 1.0 \times 36.97 \ln \frac{239}{300} - 8.314 \ln \frac{1}{100} = -8.40 + 38.29 = \\ &= 29.89 \text{ J K}^{-1} \end{aligned}$$

For the phase transition (constant temperature), by definition $\Delta S_2 = Q / T$

Since the pressure is constant in this case, $Q / T = Q_p / T = \Delta H / T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{0.1 \times (-20420)}{239} = -8.54 \text{ J K}^{-1}$$

$$\Delta S_{\text{sys}} = 29.89 - 8.54 = 21.35 \text{ J K}^{-1}$$

7.2 Beware of round-off errors in the variations to the solution to this problem: One can get small differences due to conversion into and out of the \ln relationships. It is the approach which matters.

One reverses the signs of $\ln K_c$ and ΔH^0 for Reaction 1 when it is reversed.

Equilibrium constants are multiplied when equations are added, thus $\ln K$'s will add.

Reaction 3 = Reaction 2 - Reaction 1

Thus $\Delta S_3 = \Delta S_2 - \Delta S_1$ and $\Delta G_3 = \Delta G_2 - \Delta G_1$

$$\Delta G_1^0 = -RT \ln K_{c1} = -8.314 \times 298 \times 11.60 = -28740 \text{ J mol}^{-1} = -28.74 \text{ kJ mol}^{-1}$$

$$\Delta H_1^0 = -33.5 \text{ kJ mol}^{-1}$$

$$\Delta S_1^0 = (\Delta H_1^0 - \Delta G_1^0) / T$$

$$= (-33.5) - (-28.74) / 298 = -0.0161 \text{ kJ K}^{-1} \text{ mol}^{-1} = -16.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Similarly:

$$\Delta G_2^0 = -44.05 \text{ kJ mol}^{-1}$$

$$\Delta H_2^0 = -37.2 \text{ kJ mol}^{-1}$$

$$\Delta S_2^0 = -22.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

Reaction 3 = Reaction 2 - Reaction 1, thus

$$\Delta H_3^0 = \Delta H_2^0 - \Delta H_1^0 = -3.7 \text{ kJ}$$

$$\Delta S_3^0 = \Delta S_2^0 - \Delta S_1^0 = 39.08 \text{ J K}^{-1}$$

$$\Delta G_3^0 = \Delta H_3^0 - T \Delta S_3^0 = -15.35 \text{ kJ mol}^{-1}$$

$$\text{Thus } K_{c3} = e^{\frac{15.35}{RT}} = 4.90 \times 10^2$$

Alternatively:

$$\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0 = -44.05 - (-28.74) = -15.31 \text{ kJ mol}^{-1} \text{ thus } K = 4.82 \times 10^2$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T = (-3700 - (-15311)) / 298 = 38.96 \text{ J K}^{-1}$$

PROBLEM 8

An electrolyte is prepared from H_2SO_4 , CuSO_4 and distilled water and its volume is 100.0 cm^3 . The concentrations of H^+ and Cu^{2+} in the electrolyte are $c(\text{H}^+) = 1.000 \text{ M}$ (mol dm^{-3}) and $c(\text{Cu}^{2+}) = 1.000 \times 10^{-2} \text{ M}$ (mol dm^{-3}), respectively. Two cubic platinum electrodes are immersed in the electrolyte. Both of the electrodes are single crystals with only one face (100) exposed to the electrolyte (the other five faces are blocked physically by an insulator which is stable in the electrolyte). The exposed surface area of each electrode is equal to 1.000 cm^2 . During an electrolysis a total charge of 2.0000 C is passed between the cathode and the anode. At the cathode, two simultaneous processes are occurring: deposition of an epitaxial (layer-by-layer) Cu layer and H_2 gas generation. At the anode, O_2 gas is generated. The H_2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

$T = 273.15 \text{ K}$ and $P(\text{H}_2) = 1.01325 \times 10^4 \text{ Pa}$; the volume of H_2 is equal to 2.0000 cm^3

- 8.1** Write equations of the processes taking place at the electrodes.
- 8.2** Calculate the number of moles of H_2 gas generated at the cathode and the number of moles of Cu deposited on the electrode.
- 8.3** Calculate the number of Cu monolayers formed on the Pt (100) cathode.

Note that the lattice constant of Pt is $a(\text{Pt}) = 3.9236 \times 10^{-8} \text{ cm}$.

Both Pt and Cu have the *fcc* (face centred cubic) crystallographic structure.

Molar masses and constants:

$$M(\text{H}) = 1.00795 \text{ g mol}^{-1}$$

$$M(\text{Cu}) = 63.546 \text{ g mol}^{-1}$$

$$e = 1.60218 \times 10^{-19} \text{ C}$$

$$F = 96485.3 \text{ C mol}^{-1}$$

$$R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

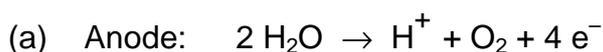
$$V_m = 22.4141 \text{ dm}^3$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

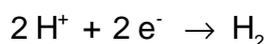
SOLUTION*Approach*

- Determine the number of H₂ moles generated by the electrolysis.
- Calculate the charge required for the H₂ production and the charge of the formation of the Cu deposit and thus the number of moles of Cu in the deposit.
- Calculate the surface concentration of atoms in the Pt (100) face thus the number of Pt atoms per 1 cm²; during an epitaxial growth the number of Cu atoms per 1 cm² equals the number of Pt atoms
- Determine the charge necessary to form one monolayer of Cu and subsequently the number of Cu monolayers on Pt (100)

*Calculations***8.1** Balanced electrode equations

(b) Cathode:

Two reactions occur simultaneously at the cathode:

**8.2** Determination of the charge necessary to generate 2.0000 cm³ of H₂ gas $(T = 273.15 \text{ K}, p = 10.1325 \text{ kPa})$ Two approaches to determination of the number of H₂ gas moles(a) *Determination of $n(\text{H}_2)$: $pV = n(\text{H}_2)RT$*

$$n(\text{H}_2) = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6} \text{ mol}$$

$$n(\text{H}_2) = \frac{V(\text{H}_2)}{V_m}$$

$V_m = 22.4141 \text{ dm}^3 \text{ mol}^{-1}$ (V_m refers to the pressure of 1 atm or at $p(\text{H}_2) = 101.325 \text{ kPa}$ and because the pressure of H₂ is ten times smaller, one knows right away that the volume occupied under 1 atm would be 0.2000 cm³)

$$n(\text{H}_2) = \frac{0.20000 \times 10^{-3}}{22.4141} = 8.9230 \times 10^{-6} \text{ mol}$$

Determination of the charge necessary to generate 8.9230×10^{-6} moles of H_2 gas

Two approaches to determination of the charge:

- (a) the number of H atoms, N_H , equals twice the number of H_2 molecules; if one multiplies N_H by e , then one gets the sought charge, Q_H

$$Q_H = 2 \times 8.9230 \times 10^{-6} \times N_A \times 1.60218 \times 10^{-19}$$

$$Q_H = 1.7219 \text{ C}$$

- (b) one may use the Faraday law

$$m_H = k_H Q_H$$

where k_H is the electrochemical equivalent of H thus the mass of H generated by 1 C; to use this formula one has to calculate k_H ; knowing that the charge of 1 F = 96485.3 C results in formation of 1 mole of H (1/2 mole of H_2), one may easily determine k_H

$$\frac{96485.3}{1.00795} = \frac{1.0000}{k_H}$$

$$k_H = 1.04467 \times 10^{-5} \text{ g C}^{-1}$$

Subsequently

$$Q_H = \frac{m_H}{k_H} = \frac{2 \times 8.9230 \times 10^{-6} \times 1.00795}{1.04467 \times 10^{-5}}$$

$$Q_H = 1.7219 \text{ C}$$

Determination of the Cu deposition charge

$$Q_{Cu} = 2.0000 - Q_H$$

$$Q_{Cu} = 2.0000 - 1.7219 = 0.2781 \text{ C}$$

The moles of Cu is thus $0.2781 / 2 F = 1.4412 \times 10^{-6}$

8.3 Determination of the charge of formation of 1 monolayer (ML) of the Cu deposit and the number of Cu monolayers on the Pt (100) substrate

Calculate the number of surface Pt atoms in the (100) face

Surface area of the fundamental unit:

$$A_u = a_{Pt}^2 = 1.5395 \times 10^{-15} \text{ cm}^2$$

Number of atoms per fundamental (100) unit: $n_u = 2$

Surface atom concentration:

$$s_{\text{Pt}(100)} = \frac{n_u}{A_u} = \frac{2}{1.5395 \times 10^{-15} \text{ cm}^2} = 1.2991 \times 10^{15} \text{ cm}^{-2}$$

The number of Cu atoms per 1 cm^2 equals the number of Pt atoms - epitaxial growth

$$\sigma_{\text{Cu}(100)} = \sigma_{\text{Pt}(100)} = 1.2991 \times 10^{15} \text{ cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{\text{ML}} = 2 \times e \times 1.2991 \times 10^{15}$$

$$q_{\text{ML}} = 4.1628 \times 10^{-4} \text{ C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{\text{ML}} = \frac{0.2780 \text{ C}}{4.1628 \times 10^{-4} \text{ C}}$$

$$n_{\text{ML}} = 668 \text{ ML}$$

One can also calculate the number of Cu atoms (8.6802×10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991×10^{15}) on the exposed Pt surface to also arrive at 668 monolayers.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Mg^{2+} and Ca^{2+} in Bottled Water

- The K_{sp} for calcium oxalate is 2.3×10^{-9} and the K_{sp} for magnesium oxalate is 8.6×10^{-5} .
- In a solution buffered to maintain pH 10, Calmagite indicator is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Calcium ions are not bound by Calmagite.
- EDTA binds to Mg^{2+} and Ca^{2+} even in the presence of Calmagite. The stoichiometry of the EDTA-metal complex formed with both Mg^{2+} and Ca^{2+} is 1:1.
- Molar masses: $M(\text{Ca}) = 40.08 \text{ g mol}^{-1}$ $M(\text{Mg}) = 24.31 \text{ g mol}^{-1}$

Chemicals Available

500 cm^3 sample of "Bottled Water"

aqueous buffer (pH 10)

Calmagite indicator

aqueous saturated ammonium oxalate

aqueous ethylenediaminetetraacetic acid

aqueous standardized* Mg^{2+}

distilled water

*0.928 $\text{mg Mg}^{2+}/\text{cm}^3$ solution, 0.0382 moles $\text{Mg}^{2+}/\text{dm}^3$

Procedure

A. Precipitation of calcium ions

Precipitate the calcium ions in a 25.00 cm^3 aliquot of the "Bottled Water" sample by accurately adding approximately 0.50 cm^3 of saturated ammonium oxalate solution (from the common burettes in each lab room). Carefully swirl the solution to ensure uniform mixing. Allow at least 45 minutes for complete precipitation to occur.

B. Standardization of the EDTA solution

Using distilled water, dilute 5.00 cm³ of the standardized magnesium solution to a final volume of 100.0 cm³. Add 40 cm³ of distilled water, 5 cm³ of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm³ of diluted magnesium solution. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

C. Titration of Mg²⁺ and Ca²⁺

Add 40 cm³ of distilled water, 5 cm³ of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm³ of the “Bottled Water” sample. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

D. Titration of Mg²⁺

Add 40 cm³ of distilled water, 5 cm³ of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm³ of the calcium-free “Bottled Water” sample prepared in part **A**. The presence of a small amount of calcium oxalate will not interfere with your titration. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

Calculations

Calculate the concentration of Mg²⁺ (in mg dm⁻³) in the “Bottled Water” sample.

Calculate the concentration of Ca²⁺ (in mg dm⁻³) in the “Bottled Water” sample.

PROBLEM 2 (Practical)**Organic qualitative analysis**

You have six bottles containing six different organic compounds. From the list of eight compounds given below, identify the contents of each bottle using the reagents available.

Many of these compounds have strong odours. To prevent the laboratory from becoming too odorous, you must keep each bottle tightly capped when it is not in use. Dispose of any waste produced in the bottle labelled "ORGANIC WASTE" at your station. Also place used litmus paper in this bottle. Keep the waste bottle capped when not in use.

Chemicals Available

litmus paper, red and blue

aqueous ceric ammonium nitrate

aqueous chromic-sulfuric acid

aqueous 2,4-dinitrophenylhydrazine

aqueous 0.2% KMnO₄

acetone (2-propanone)

Possible Unknowns*

2-butanone

1-decene

2,3-diamino-2,3-dimethylbutane

hexane

3-methyl-1-butanol

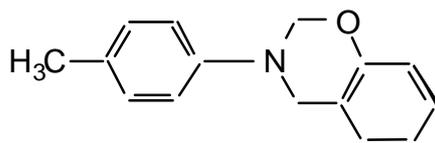
2-methyl-2-butanol

nonanal

propanoic acid

*Several of the unknowns are present as dilute aqueous solutions.

This will not interfere with the test results.

PROBLEM 3 (Practical)**Synthesis of the Substituted Dihydro-1,3-benzoxazine (C)****C**

Benzoxazines have long been recognized as useful biologically-active compounds. One such compound (**C**) will be prepared using the three-step synthesis described below. All of the product obtained in Step I should be used in Step II and similarly all of the product from Step II should be used in Step III. You will be evaluated on both the yield and purity of the final product.

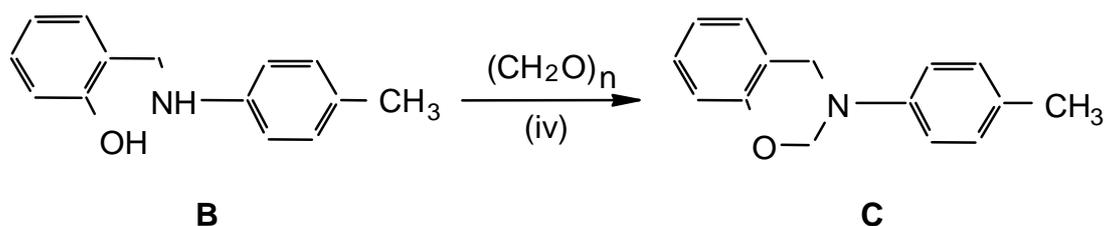
Chemicals available

5 cm³ reaction vial containing 2.5 cm³ of ethanolic 1-amino-4-methylbenzene (0.22 g),
 vial containing 0.25 g of 2-hydroxybenzaldehyde,
 vial containing 0.1 g of sodium borohydride,
 vial containing 0.042 g of paraformaldehyde,
 test tube containing dilute ethanolic KOH,
 (50 mg of KOH dissolved in 10 cm³ of ethanol),
 wash bottle containing dry ethanol,
 Ice is available in each laboratory room.

Molar masses:

$$\begin{array}{lll}
 M(\text{H}) = 1.008 \text{ g mol}^{-1} & M(\text{C}) = 12.011 \text{ g mol}^{-1} & M(\text{N}) = 14.007 \text{ g mol}^{-1} \\
 M(\text{O}) = 15.999 \text{ g mol}^{-1} & M(\text{Na}) = 22.990 \text{ g mol}^{-1} & M(\text{B}) = 10.811 \text{ g mol}^{-1}
 \end{array}$$

STEP III



1. Dissolve all of the paraformaldehyde (iv) in approximately 2.5 cm³ of ethanolic potassium hydroxide (v) in a 5 cm³ vial. Stir to dissolve all of the solid.
2. Add all of product **B** from Step II to the vial. Stir and gently reflux the mixture for 15 minutes. A clear solution should be obtained.
3. Concentrate the solution by carefully boiling off some of the ethanol leaving approximately 1 cm³ in the vial and allow the vial to cool. The crystals which form are the required product **C**.
4. Isolate the crude product **C** by vacuum (suction) filtration and air dry the crystals.
5. Recrystallize the crude product from ethanol. Air dry the crystals for 15 minutes.
6. Determine the melting point* and then mass of the final product.
7. Place all of your remaining product in the numbered vial labelled "PRODUCT C" and hand it in for evaluation.

* Note: A melting point is always recorded as a range -- from when the crystals first begin to melt until the last crystal has melted. The melting point apparatus should be allowed to cool to approximately 50 degrees before you use it. The supervisors will be rechecking both your reported melting point and mass for product C.

30th



International Chemistry Olympiad

**7 theoretical problems
2 practical problems**

THE THIRTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 5–14 JULY 1998, MELBOURNE, AUSTRALIA

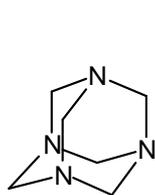
THEORETICAL PROBLEMS

PROBLEM 1

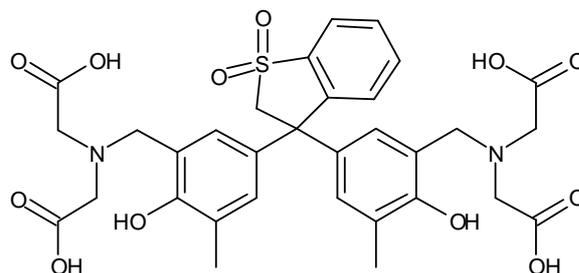
The following 8 steps describe the procedure for analysing a sample of alloy that contains both tin and lead.

1. A 0.4062 g sample of alloy was dissolved by heating it in a small beaker with a mixture of 11 M hydrochloric and 16 M nitric acid. The beaker was heated until the entire alloy dissolved. In this procedure, lead is oxidised to Pb(II) and tin becomes Sn(IV).
2. After 5 minutes of heating to expel oxides of nitrogen and chlorine, some acid remained. When the solution was cooled, a precipitate of some tin compounds and a lead compound appeared.
3. A 25.00 cm³ aliquot of 0.2000 M Na₂H₂EDTA solution was added. The precipitate dissolved and a clear, colourless solution was obtained.
4. This solution was quantitatively transferred to a 250.0 cm³ volumetric flask and made up to the mark with distilled water.
5. A 25.00 cm³ aliquot of this solution was treated with 15 cm³ of a 30 % w/v solution of hexamine (hexamethylenetetramine), some water and two drops of Xylenol Orange solution. The pH of each aliquot was 6.
6. The clear, yellow solution from Step 5 was titrated with standard 0.009970 M lead nitrate solution until the colour just changed from yellow to red. The titre at this endpoint was 24.05 cm³.
7. 2.0 g of solid NaF was added to the titration flask. The solution turned back to yellow.
8. The solution was titrated with more standard 0.009970 M lead nitrate solution until the colour changed to red again. The titre at this endpoint was 15.00 cm³.

Hexamine and Xylenol Orange have the structures shown below. The pK_b of hexamine is 9.5. Xylenol Orange is red below pH 4, yellow above pH 5.



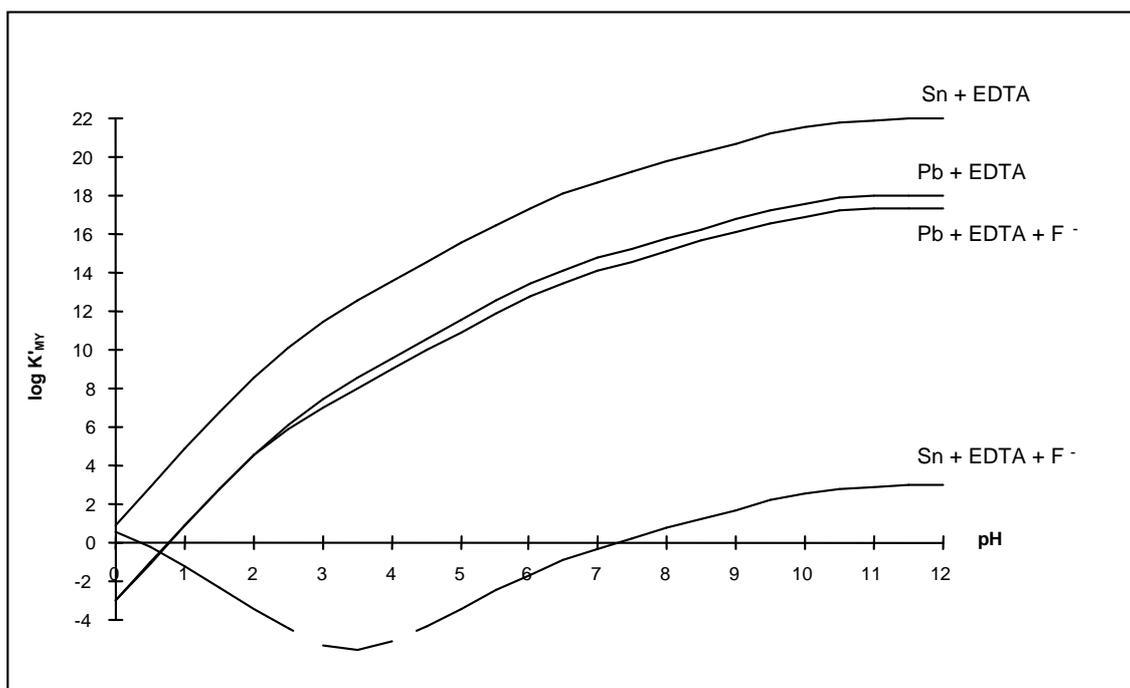
Hexamine



Xylenol Orange (XO)

K_{MY} is the conditional formation constant = αK_{MY} .

K_{MY} for the formation of the EDTA complexes of Pb(II) and Sn(IV), in the presence and absence of fluoride, are shown in the following Figure.



- 1.1 What is the lead compound that precipitates in Step 2?
- 1.2 Write a balanced ionic equation that explains the disappearance of the precipitate in Step 3 (at pH 6).
- 1.3 What is the purpose of hexamine in Step 5 of the analysis?
- 1.4 What is the purpose of Xylenol Orange in the analysis?

- 1.5 Write balanced ionic equations for the reactions occurring during the titration and responsible for the colour change at the endpoint in Step 6 of the analysis
- 1.6 What is the purpose of NaF in Step 7 of the analysis?
- 1.7 Write a balanced ionic equation for the reaction that occurs in Step 7.
- 1.8 Write a balanced ionic equation that explains why the colour changed from red to yellow in Step 7 of the analysis.
- 1.9 Write a balanced ionic equation that explains why the lines on the graph below of $\log K_{MY}$ vs pH for Pb + EDTA and Pb + EDTA + F⁻ are coincident below pH 2.
- 1.10 Calculate the percentage by weight of Sn and Pb in the alloy.

SOLUTION

- 1.1 PbCl₂ or any hydroxo species etc.
- 1.2 $PbCl_2(s) + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+ + 2 Cl^-$ or similar
- 1.3 It forms a pH buffer.
- 1.4 It is a metallochromic indicator.
- 1.5 (i) The reaction that occurs during the titration:
 $Pb^{2+} + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+$
- (ii) At the endpoint, a slight excess of Pb²⁺ forms a red complex with the xylenol orange indicator:
 $Pb^{2+} + XO \text{ (yellow)} \rightarrow PbXO^{2+} \text{ (red)}$
- 1.6 The role of the NaF: It forms a complex with tin.
- 1.7 From the graph of $\log K_{MY}$ vs pH , it can be seen that the fluoride forms a stable complex with Sn⁴⁺ but not with Pb²⁺ at pH 6, displacing EDTA:
 $SnY + nF^- + 2 H^+ \rightarrow SnF_n^{(n-4)-} + H_2Y^{2-}$ where n is typically 4 - 6.
- 1.8 The released EDTA destroys the small amount of red PbXO complex, producing free (yellow) XO. (Charge on XO ignored)
 $H_2Y^{2-} + PbXO^{2+} \rightarrow PbY^{2-} + XO \text{ (yellow)} + 2 H^+$
- 1.9 Below pH 2, F⁻ is protonated and does not compete effectively with Y for Pb²⁺
 $H^+ + F^- \rightarrow HF$.
- 1.10 The percentage by mass of Sn and Pb in the alloy:
 The amount of EDTA in excess from the amount of standard Pb²⁺ titrant:
 $n(EDTA) = n(Pb^{2+}) = 0.02405 \text{ dm}^3 \times 0.009970 \text{ mol dm}^{-3} = 2.398 \times 10^{-4} \text{ mol}$.

The original amount of EDTA:

$$n(\text{EDTA})_{\text{init.}} = 0.1 \times 25.00 \text{ dm}^3 \times 0.2000 \text{ mol dm}^{-3} = 5.000 \times 10^{-4} \text{ mol}$$

EDTA consumed by the Pb^{2+} and Sn^{4+} in a 25 cm^3 aliquot:

$$n(\text{EDTA})_{\text{consumed}} = 5.000 \times 10^{-4} - 2.398 \times 10^{-4} \text{ mol} = 2.602 \times 10^{-4} \text{ mol} = n(\text{Pb}^{2+} + \text{Sn}^{4+}) \text{ in a } 25 \text{ cm}^3 \text{ aliquot.}$$

The amount of EDTA released from SnY by reaction with fluoride:

$$n(\text{EDTA})_{\text{released}} = n(\text{Pb}^{2+})_{\text{stand.}} = 15.00 \text{ cm}^3 \times 0.009970 \text{ mol dm}^{-3} = 1.496 \times 10^{-4} \text{ mol} = n(\text{Sn}^{4+}) \text{ in the } 25 \text{ cm}^3 \text{ aliquot}$$

$$\text{in a } 25 \text{ cm}^3 \text{ aliquot } n(\text{Pb}^{2+}) = (2.602 \times 10^{-4} - 1.496 \times 10^{-4}) \text{ mol} = 1.106 \times 10^{-4} \text{ mol}$$

In the original 0.4062 g sample of alloy:

$$m(\text{Sn}) = 10 \times 1.496 \times 10^{-4} \text{ mol} \times 118.69 \text{ g mol}^{-1} = 0.1776 \text{ g}$$

$$m(\text{Pb}) = 10 \times 1.106 \times 10^{-4} \text{ mol} \times 207.19 \text{ g mol}^{-1} = 0.2292 \text{ g}$$

The percentages of tin and lead:

$$\text{Sn: } 100 \times (0.1776 / 0.4062) = 43.7 \%$$

$$\text{Pb: } 100 \times (0.2292 / 0.4062) = 56.4 \%$$

PROBLEM 2

Part A: Dating Historical Events Using Pb-210

Nathan Thompson, one of the first inhabitants of Lord Howe Island, decided to plant some European deciduous trees in his garden. Unfortunately the exact timing of the planting of the seeds is not known. Over the years, pollen produced by the European oak and elm accumulated at the bottom of the lake near Nathan's house. Very small quantities of radioactive Pb-210 (half-life = 22.0 years) were deposited at the same time. Note that the European oak and elm trees pollinate in their first year of growth.

In 1995, a team of researchers sampled a sediment core from the bottom of the lake. The sediment core was cut into 1 cm slices and examined for pollen and radioactive Pb-210.

The examination of the sediment core found that:

- Pollen of European oak and elm first occur at a depth of 50 cm.
- The activity of Pb-210 at the top of the sediment core is 356 Bq/kg and at 50 cm depth 1.40 Bq/kg.

2.1 In what year did Nathan Thompson plant the seeds?

Radioactive Pb-210 is one of the daughters of U-238. U-238 is present in the earth's crust and for some reason a certain amount of Pb-210 rains out of the atmosphere and attaches itself to sediment particles that accumulate at the bottom of lakes.

- The U-238 decay chain is:
- U-238 – U-234 – Th-230 – Ra-226 – Rn-222 – (Po-218 – Bi-214)* – Pb-210 – Pb-206 (stable)

* Very short half-lives: minutes and days

2.2 Which step in the decay scheme explains how Pb-210 ends up in rainwater while its parent U-238 is only present in the earth's crust?

Part B: Separation of Radionuclides for Nuclear Medicine Applications.

The Ga-67 is used to image lymphoma. It is preferentially produced by bombarding a target enriched in Zn-68 (> 98%) with high energy protons for 11 hrs. Zn-68 has a natural abundance of 18.8%. Due to the target design other radionuclides may be produced (see Table 1). Twelve hours after the end of bombardment, Ga-67 is bound on a cation exchange. Then the other radionuclides and the Zn-68 are eluted in the wash solution leaving Ga-67 bound to the column.

Table 1

Radionuclide	Half-life
Co-55	18.2 hr
Ni-57	36.0 hr
Co-57(daughter of Ni-57)	270 days
Cu-64	12.7 hr
Cu-67	61.7 hr
Zn-65	244 days
Ga-67	78.35 hr
Ga-66	9.4 hr

Cu-64 and Co-55 have ideal half-lives for use in nuclear medicine applications and it would be useful to isolate them from the wash solution.

The distribution coefficient D is a measure of the partition of a metal ion between the ion-exchange resin and the eluant.

For a given ion-exchange resin and eluant, D is given by

$$D = \frac{\text{radioactivity per mg of resin}}{\text{radioactivity per cm}^3 \text{ of eluant}}$$

For a reasonable separation of two metal ions their D values should differ by at least 10 units.

2.3 The wash solution is evaporated to dryness and the residue resuspended in a small amount of 0.2 M HCl 96 % methanol and loaded onto an anion exchange column. Use the distribution coefficients D given in Figures 1 and 2 and rank the best solvent systems (from given alternatives) for eluting Cu-64 and Co-55.

2.4 Having isolated relevant radionuclides, the presence of some long-lived radionuclides could interfere with medical use of Cu-64 or Co-55 or Ga-67. Indicate which of the following statements is either true or false (one or more may be true).

- a) Ni-57 may be present as a contaminant of Co-55.
- b) Co-57 will interfere with the medical use of Co-55.
- c) Cu-67 will interfere with the medical use of Cu-64.
- d) Ga-66 will interfere with the use of Ga-67.
- e) Ga-67 will interfere with the medical use of Cu-64.

2.5 If radionuclide contamination of Cu-64 or Co-55 or Ga-67 occurred, which method would reduce the amount of radionuclide contaminant/s? Indicate which of the following statements is either true or false. (one or more may be true).

- a) Remove Ni-57 before isolating Co-55.
- b) Separate the Ni-57 from the bombarded target material before isolating the Ga-67.
- c) Separate the radionuclides closer to the end of bombardment.
- d) Allow the Ni-57 to decay before isolation of Co-55.

2.6 If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with high energy protons, indicate which of the following statements is either true or false. (one or more may be true).

- a) Ga-67 would be produced at 5 fold higher yields.
- b) Ga-67 would be produced at 5 fold lower yields.
- c) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would increase.
- d) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would remain the same.

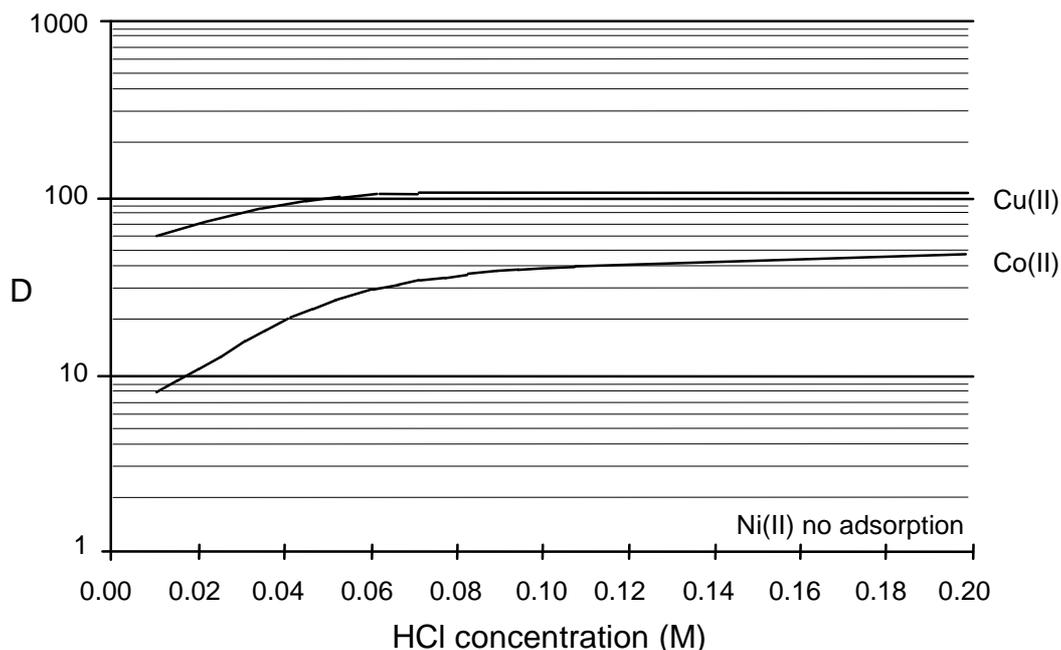


Figure 1. Distribution coefficients, D of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note D value for Zn > 1000)

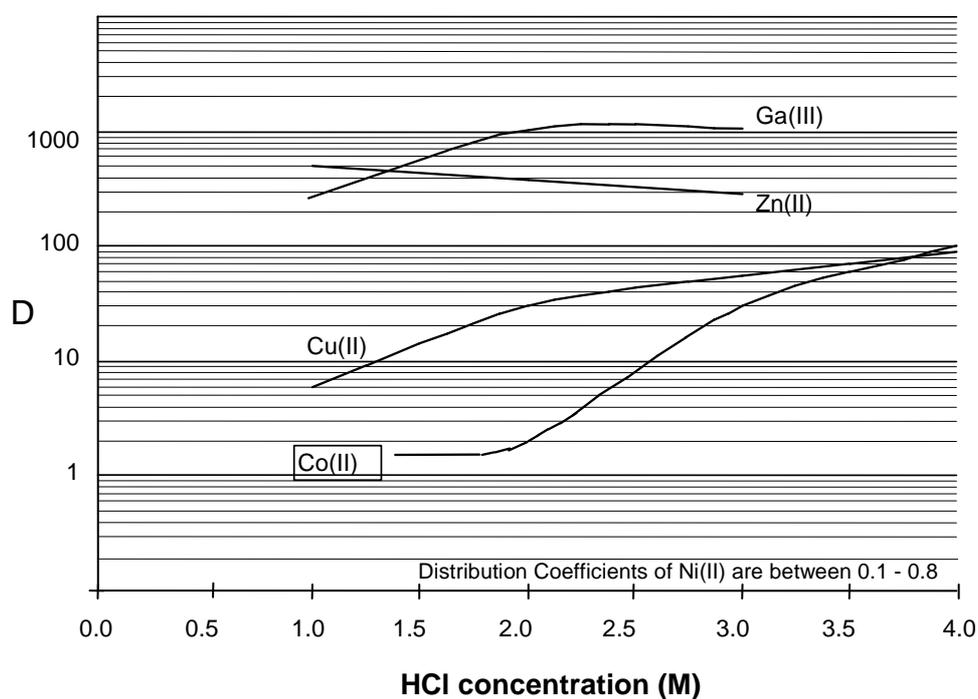


Figure 2. Distribution coefficients, D of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

SOLUTION

2.1 In what year did Nathan Thompson plant the seeds?

Calculations:

Over a depth of 50 cm the apparent decay of Pb-210 was equal to $356 - 178 - 89 - 44.5 - 22.5 - 11.25 - 5.63 - 2.81 - 1.39 = 8$ half-lives = 8×22 years = 176 years

If 1995 was the year of coring then the year of arrival was $1995 - 176 = 1819 (\pm 2)$

2.2 Correct answer: Ra-226 - Rn-222

2.3 Use the distribution coefficients D given in Figures 1 and 2 and rank the following solvent systems for isolating Cu-64 and Co-55 by writing the numbers 1 to 4 in the boxes (1 is best).

- | | | |
|---|---------------------------------|-----------------------------|
| A | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 2.0 M HCl 55% isopropyl alcohol | to remove Cu-64 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Co-55 |
| | | |
| B | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 2.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |
| | | |
| C | 2.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |
| | | |
| D | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 3.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 4.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |

The best sequence: B, C, D, A

The other sequences: B, C, A, D or C, B, D, A or C, B, A, D were also accepted but evaluated by less points.

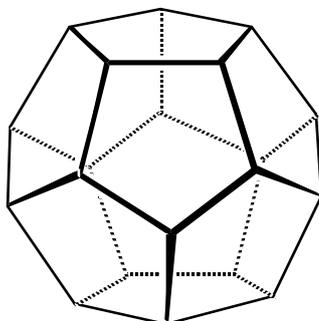
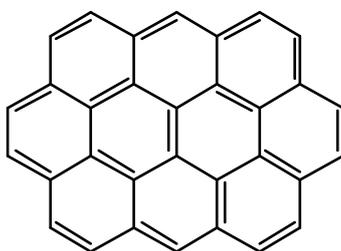
- 2.4 a) False;
 b) True;
 c) True
 d) False
 e) False

- 2.5** a) True
b) True
c) True
d) False

- 2.6** a) False
b) True
c) False
d) True
-
-

PROBLEM 3

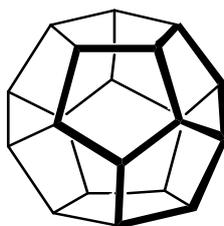
The three-dimensional structures of polycyclic molecules can often be explained in terms of the minimisation of angle strain. Consider the following molecules:

Dodecahedrane, C₂₀H₂₀and Ovalene, C₃₂H₁₄.

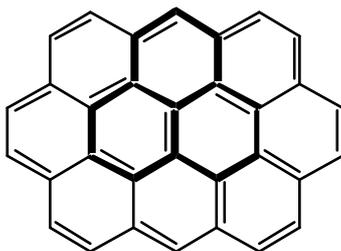
Each C₅ ring of dodecahedrane is a regular pentagon, while each C₆ ring of ovalene can be regarded as a regular hexagon.

- 3.1 What are the $\angle(\text{CCC})$ angles for each of these rings?
- 3.2 Which configuration (trigonal planar, 120°; tetrahedral, 109.5°; or octahedral, 90°) do the above $\angle(\text{CCC})$ angles most closely match?
- 3.3 What is the hybridization (sp , sp^2 , or sp^3) which most closely conforms to the geometric structure of dodecahedrane, and of ovalene?

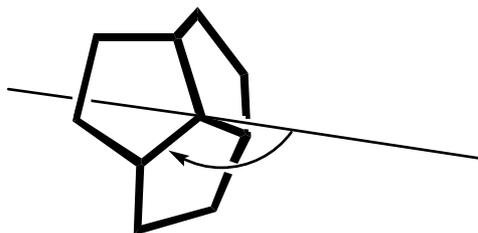
A “junction” is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctions (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:

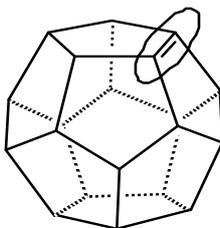


Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.

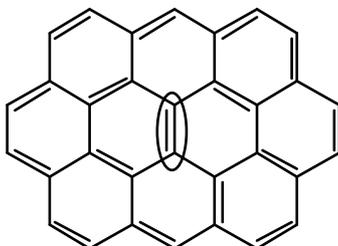


- 3.4** What is the value of this angle for dodecahedrane (make an “educated guess”, to the nearest three degrees), and for ovalene?
- 3.5** Subtracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar ?

Now consider two polycyclic 'alkenes', dodecahedrene ($C_{20}H_{18}$):



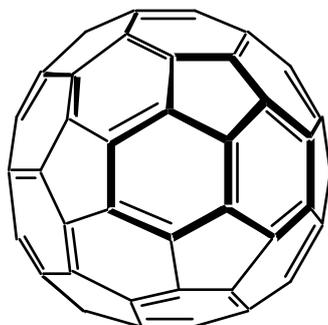
and ovalene:



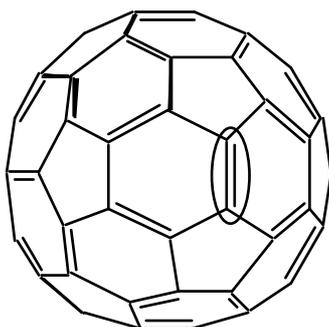
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

3.6 Compare the indicated pairs of carbon atoms (encircled above). For which C=C pair is H₂ addition expected to be more exothermic?

And now, on to fullerenes. For all known fullerenes, the deviation from planarity at any juncture is less than is the case for dodecahedrane.



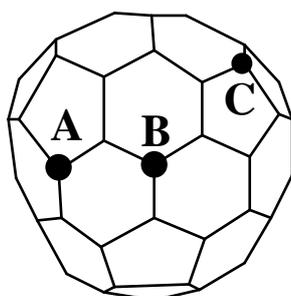
For C₆₀, all junctures are entirely equivalent. Now consider H₂ addition at a C=C bond of C₆₀:



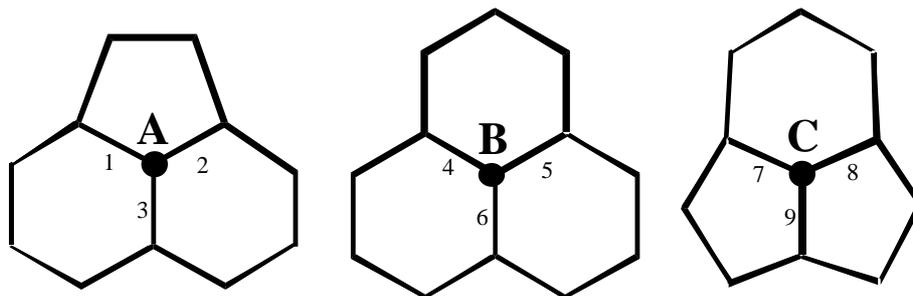
3.7 For which of C₆₀, dodecahedrene, or ovalene is H₂ addition most exothermic? (Again, assume localization of double bonds.)

3.8 For which of C₆₀, dodecahedrene, or ovalene is H₂ addition least exothermic?

There is evidence for fullerenes smaller than C₆₀, such as C₅₈. The C₅₈ structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:

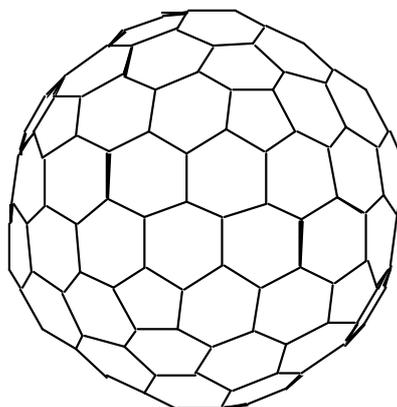


The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:



- 3.9 Which juncture has the least deviation from planarity ?
- 3.10 Which juncture has the greatest deviation from planarity ?
- 3.11 Of the above carbon-carbon bonds, numbered from 1 to 9, which represents the most favourable site for H₂ addition?

Finally, consider a larger fullerene, C₁₈₀:



To a first approximation, both C₆₀ and C₁₈₀ are "perfect" spheres.

- 3.12 Which has the larger average deviation from planarity at each juncture? C₆₀ or C₁₈₀?
- 3.13 Compare the geometries of C₆₀ and C₁₈₀, and graphite. Which of the statements shown on the answer sheet (concerning enthalpies of formation, in kJ g⁻¹ units) is correct?
- Fullerenes are generated on a very rapid timescale, typically milliseconds. In all techniques, C₆₀ is produced in much greater quantities than C₁₈₀.
- 3.14 Which of the graphs shown on the answer template best represents the dependence of potential energy upon reaction progress for the two processes:



and



SOLUTION

3.1 Dodecahedrane: 108 °
Ovalene 120 °

3.2 Dodecahedrane: tetrahedral
Ovalene: trigonal planar

The $\angle(\text{CCC})$ angle for dodecahedrane is only slightly lower than the tetrahedral angle, but is much higher than the 90° required for octahedral coordination and is obviously too low for a trigonal planar arrangement. The corresponding angle for ovalene is identical to that for trigonal planar.

3.3 Dodecahedrane: sp^3
Ovalene: sp^2

Reasoning: As above, dodecahedrane conforms quite closely to a tetrahedral arrangement at each C atom, thus sp^3 . Ovalene corresponds exactly to a trigonal planar arrangement, so sp^2 .

3.4 Dodecahedrane, $\text{C}_{20}\text{H}_{20}$ 109 -115 degrees
ovalene, $\text{C}_{32}\text{H}_{14}$ 90 degrees

Reasoning: For dodecahedrane, the three rings are not coplanar. Determination of the exact axis angle is complicated; but note that the $\angle(\text{CCC})$ angle for a C_5 ring is very close to the tetrahedral angle. Therefore distortion from a tetrahedral configuration at each carbon in dodecahedrane is slight: therefore the axis angle is about 109.5° (more probably ~112°). For ovalene, all rings are coplanar. The axis angle is clearly 90°.

3.5 Correct: Ovalene, $\text{C}_{32}\text{H}_{14}$

3.6 H_2 addition is more exothermic dodecahedrene.

Reasoning: The C=C pair within the dodecahedrene skeleton is more suited to sp^3 -hybridization than sp^2 -hybridization: this favours dihydrogenation to yield dodecahedrane. For ovalene, sp^3 -hybridization is disfavoured relative to sp^2 -

hybridization, so dihydrogenation at the indicated site is disfavoured on the grounds of angle strain.

(This is quite apart from any reduction in ovalene's aromaticity, which is also likely to disfavour hydrogenation!)

3.7 H₂ addition from among C₆₀, dodecahedrene, ovalene is most exothermic for dodecahedrene.

Reasoning: The deviation from planarity, in a C₆₀ juncture, is less than in dodecahedrene (which has very close to tetrahedral, i.e. sp^3 , coordination at each carbon) but is clearly more than in ovalene (which is flat, i.e. ideal for sp^2 hybridization). Thus C₆₀ is intermediate between dodecahedrene and ovalene in its preference for hydrogenated versus dehydrogenated structures. The junctures in dodecahedrene are all pentagons [C₅,C₅,C₅]. The junctures in ovalene are all [C₆,C₆,C₆]. Those in C₆₀ are [C₅,C₆,C₆]. The implication is that, the more pentagons are found in a juncture, the greater the deviation from planarity and hence the greater the relative stability of sp^3 hybridization, rather than sp^2 , at the central carbon atom.

3.8 H₂ addition from among C₆₀, dodecahedrene and ovalene is the least exothermic for ovalene.

3.9 The least deviation from planarity is in **B**.

3.10 The greatest deviation from planarity is in **C**.

Reasoning: The juncture centred on atom 'A' features two hexagons and a pentagon: this is the same pattern as that seen in the Ceo junctures. For 'B', the three surrounding rings are all hexagons, while for 'C', the juncture contains two pentagons and a hexagon. The trend for increasing deviation from planarity with increasing number of pentagons in the juncture indicates that the deviation from planarity will be most severe at 'C', and least severe at 'B'.

3.11 The most favourable site for H₂ addition is at bond number 9.

Reasoning: Bonds 1,2,7, and 8 are each flanked by a pentagon and a hexagon. Bonds 3-6 are each 'sandwiched' between two hexagons. Bond 9 is between two adjacent pentagons. Of these configurations, bond 9 represents the geometry which is most distorted from planarity (preferred by sp² hybridization) and is closest to the dodecahedrane skeleton (for which the bond angles are almost ideal for sp³ hybridization). Thus, bond 9 is the most favourable site for dihydrogenation.

3.12 The larger average deviation from planarity at each juncture is in C₆₀.

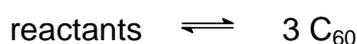
Reasoning: C₁₈₀ obviously has a larger diameter than C₆₀, so its average deviation from planarity at a given juncture is less than that found for C₆₀. [To visualize this, it may help to note that the 'equator' of C₁₈₀ will be defined by more atoms than are found along C₆₀'s 'equator'.]

3.13 The correct statement:

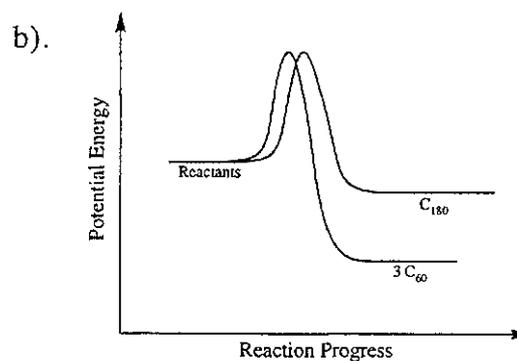
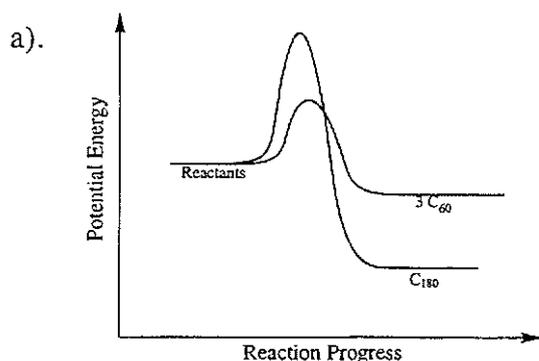
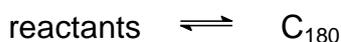
$$\Delta_f H^\circ (\text{C}_{60}) > \Delta_f H^\circ (\text{C}_{180}) > \Delta_f H^\circ (\text{graphite})$$

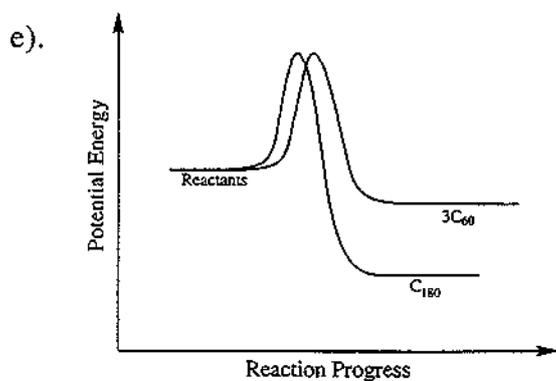
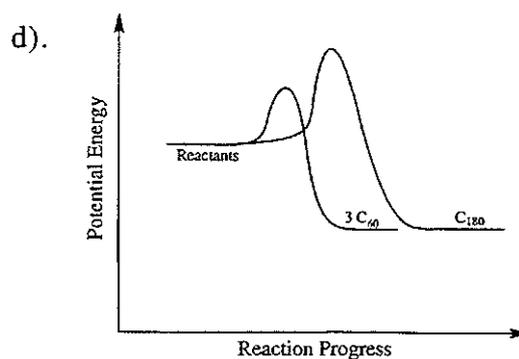
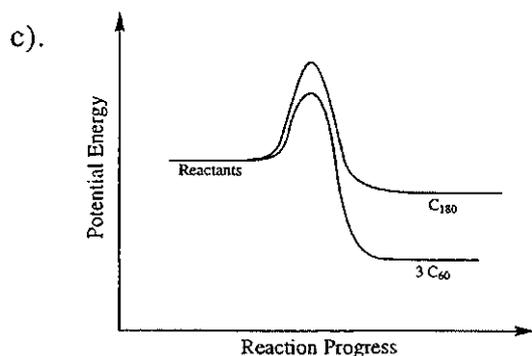
Reasoning: C₆₀ has a larger average deviation from planarity than C₁₈₀, so sp² hybridization is less favourable for the smaller fullerene. However, both fullerenes are non-planar and therefore less amenable to sp² hybridization than graphite (which additionally gets stabilization from inter-layer electronic effects, although this last point does not have to be considered to attain the correct answer).

3.14 Which of graphs best represents the dependence of potential energy upon reaction progress for the two processes:



and





The best graph is: a)

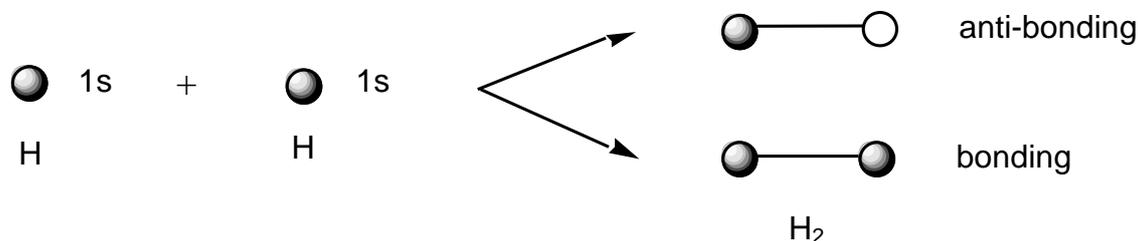
Reasoning: The equilibrium reaction



is characterized by a large positive energy change in going from left to middle, and a negative energy change of smaller magnitude in going from middle to right. Formation of C_{180} is thermodynamically favoured over three C_{60} molecules. However, C_{60} is found to predominate, implying that the reaction is under kinetic control and does not have sufficient time to reach equilibrium.

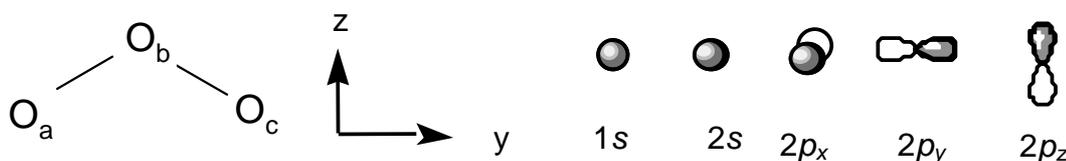
PROBLEM 4

When two hydrogen atoms come together, the 1s atomic orbitals combine to form bonding and anti-bonding molecular orbitals:



In a similar way, we may combine the atomic orbitals of more complicated atoms to form molecular orbitals, taking into account the symmetry of the molecule.

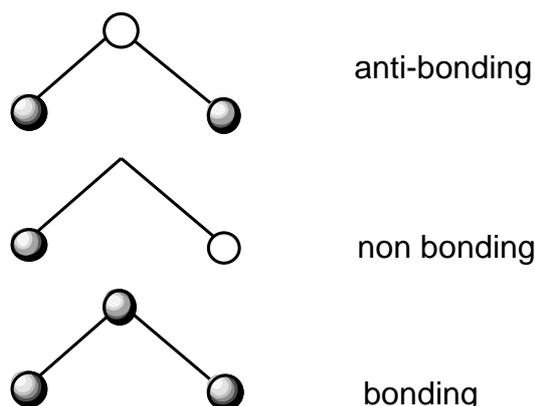
Consider the ozone molecule, O_3 , which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the yz plane) and assume that there are 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on each atom.



The atoms O_a and O_c are "related by symmetry" and the 1s orbitals on these atoms form symmetric and anti-symmetric combinations:



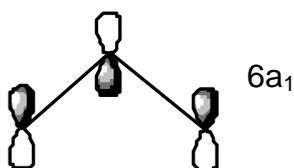
In this molecule the 1s atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final three molecular orbitals are:



- 4.1** On the answer sheet, use a similar approach to construct the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. (Remember to form the symmetric and anti-symmetric combinations of O_a and O_c first.)

We may now rearrange these molecular orbitals in order of increasing energy. This can be generalised to other triatomic molecules. The energy of these orbitals is different in a bent triatomic molecule (like ozone) compared to a linear molecule (like carbon dioxide). The variation in orbital energy may be represented in a "Walsh diagram" for XY_2 molecules as shown on the answer sheet. It shows a plot of the energy of each orbital versus the $Y-X-Y$ bond angle. The orbitals have been given labels which we call "symmetry labels".

The $6a_1$ orbital referred to in the Walsh diagram is shown below.



- 4.2** Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ?

Only occupied molecular orbitals affect the geometry, and a doubly occupied orbital has more influence than a singly occupied orbital. For example, O_3 has 24 electrons and so at a bond angle of 135° the orbitals are doubly occupied up to $6a_1$. Thus, the lowest-energy geometry of ozone (taking into account steric repulsion and the contrasting energy

behaviour of the $4b_2$, $1a_2$ and $6a_1$ orbitals) is probably towards the left of the Walsh diagram, which is consistent with the observed bond angle of 116° .

4.3 At a bond angle of 135° , what are the highest occupied orbitals for the molecules BO_2 , CO_2 , NO_2 and FO_2 ?

4.4 The bond angles of BO_2 , CO_2 and O_3 are known experimentally to be 180° , 180° and 116° , respectively. Use the Walsh diagram on the answer sheet to predict whether NO_2 and FO_2 are more or less bent than O_3 .

SOLUTION

4.1 Construction of the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals is shown on the next page.

4.2 Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ? (Choose one)

- Because the bonding character decreases.
- Because the anti-bonding character increases.
- Both (a) and (b).
- Because the overlap decreases.

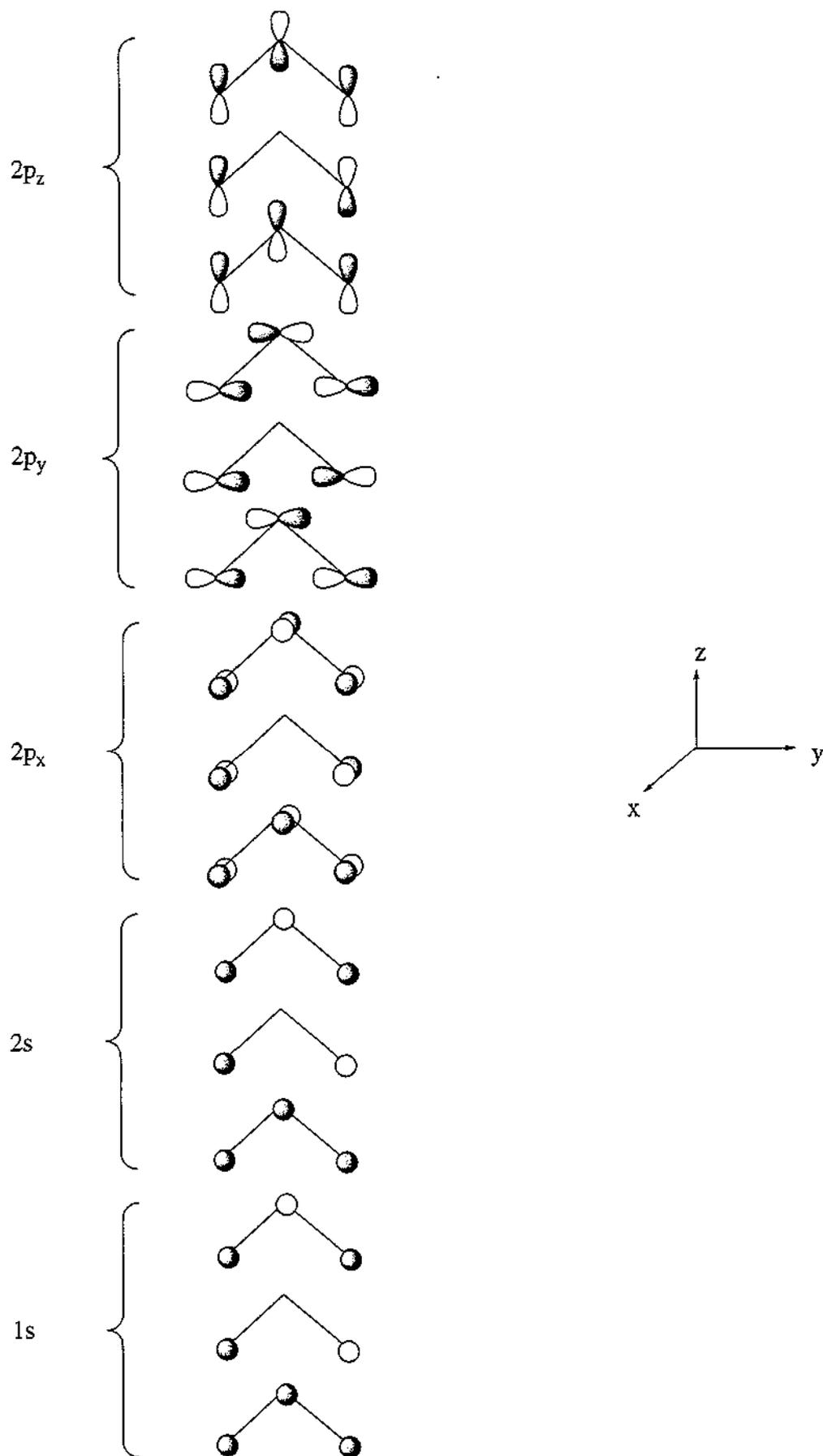
The correct answer is c).

Reasoning: The energy changes so rapidly because the overlap is bonding between all three atoms in the bent molecule, but becomes more and more anti-bonding as the molecule approaches linearity:

4.3	O_3	BO_2	CO_2	NO_2	FO_2
	$6a_x (24e^-)$	$4b_2 (21e^-)$	$4b_2 (22e^-)$	$6a_1 (23e^-)$	$2b_x (25e^-)$

4.4 The correct answer is (d): NO_2 is less bent than O_3 , and FO_2 is more bent than O_3 .

Atomic orbitals Molecular orbitals



PROBLEM 5

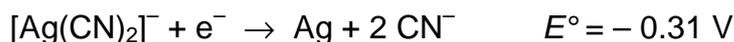
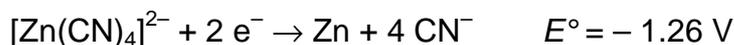
Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[\text{Au}(\text{CN})_2]^-$, which is soluble in water (reaction 1).

After equilibrium has been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc, which is converted to $[\text{Zn}(\text{CN})_4]^{2-}$ (reaction 2).

5.1 Write balanced ionic equations for reactions (1) and (2).

Gold in nature is frequently alloyed with silver which is also oxidized by aerated sodium cyanide solution.

5.2 Five hundred litres (500 L) of a solution 0.0100 M in $[\text{Au}(\text{CN})_2]^-$ and 0.0030 M in $[\text{Ag}(\text{CN})_2]^-$ was evaporated to one third of the original volume and was treated with zinc (40 g). Assuming that deviation from standard conditions is unimportant and that all these redox reactions go essentially to completion, calculate the concentrations of $[\text{Au}(\text{CN})_2]^-$ and of $[\text{Ag}(\text{CN})_2]^-$ after reaction has ceased.



5.3 $[\text{Au}(\text{CN})_2]^-$ is a very stable complex under certain conditions. What concentration of sodium cyanide is required to keep 99 mol% of the gold in solution in the form of the cyanide complex? $\{[\text{Au}(\text{CN})_2]^- : K_f = 4 \times 10^{28}\}$

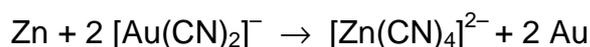
5.4 There have been several efforts to develop alternative gold extraction processes which could replace this one. Why? Choose one of the options on the answer sheet.

SOLUTION

5.1 Reaction 1:



reaction 2:



$$5.2 \quad E^{\circ}(\text{Ag}/\text{Zn}) = -0.31 - (-1.26) = 0.95 \text{ V}$$

$$E^{\circ}(\text{Au}/\text{Zn}) = -0.60 - (-1.26) = 0.66 \text{ V}$$

$$E^{\circ}(\text{Ag}/\text{Zn}) > E^{\circ}(\text{Au}/\text{Zn})$$

Therefore the Ag(I) complex will be reduced first.

$$(i) \quad \text{mol Ag(I) in } 500 \text{ dm}^3 = 500 \times 0.0030 = 1.5 \text{ mol}$$

$$(ii) \quad \text{mol Au(I) in } 500 \text{ dm}^3 = 500 \times 0.010 = 5.0 \text{ mol}$$

$$(iii) \quad \text{mol Zn in } 40 \text{ g} = 40 / 65.38 = 0.61 \text{ mol}$$

1 mol zinc reacts with 2 mol of Ag(I) or Au(I)

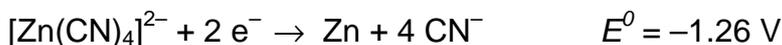
Therefore 0.61 mol Zn will consume 1.2 mol $[\text{Ag}(\text{CN})_2]^-$

$$[\text{Ag}(\text{CN})_2]^- \text{ remaining} = 1.5 - 1.2 = 0.3 \text{ mol}$$

$[\text{Au}(\text{CN})_2]^-$ will not be reduced.

$$\text{Concentration of } [\text{Au}(\text{CN})_2]^- \text{ when reaction has ceased} = 0.010 \times 3 = 0.030 \text{ M}$$

$$\text{Concentration of } [\text{Ag}(\text{CN})_2]^- \text{ when reaction has ceased} = 0.3 \times (3 / 500) = 0.002 \text{ M}$$



$$5.3 \quad \text{Au}^+ + 2 \text{CN}^- \rightarrow [\text{Au}(\text{CN})_2]^- \quad K_f = 4 \times 10^{28}$$

99 mol % $[\text{Au}(\text{CN})_2]^-$

$$K_f = \frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+][\text{CN}^-]^2}$$

$$\frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+] + [\text{Au}(\text{CN})_2]^-} = 99 / 100$$

$$\text{Thus: } 100 \times [\text{Au}(\text{CN})_2]^- = 99 \times [\text{Au}^+] + 99 \times [\text{Au}(\text{CN})_2]^-$$

$$\text{Therefore } [\text{Au}^+] = [\text{Au}(\text{CN})_2]^- / 99$$

Substituting into K_f :

$$4 \times 10^{-28} = 99 / [\text{CN}^-]^2$$

$$[\text{CN}^-] = 5 \times 10^{-14}$$

- 5.4** Sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.
-
-

PROBLEM 6

Unlike carbon, tin can increase its coordination number beyond four. Like carbon, tin forms a chloride, SnCl_4 .

6.1 Draw two alternative geometries for SnCl_4 .

Lewis acids such as SnCl_4 react with Lewis bases such as chloride ion or amines. In the case of chloride the following two reactions are observed.



and



6.2 Draw three alternative geometries for SnCl_5^- .

6.3 Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for SnCl_5^- .

6.4 Draw three alternative geometries for SnCl_6^{2-} .

6.5 Use VSEPR theory to predict which of these geometries is likely to be preferred for SnCl_6^{2-} .

A solution containing SnCl_6^{2-} (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z = 295$.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{35}Cl .

6.6 Write the empirical formula for the tin-containing species detected by this technique.

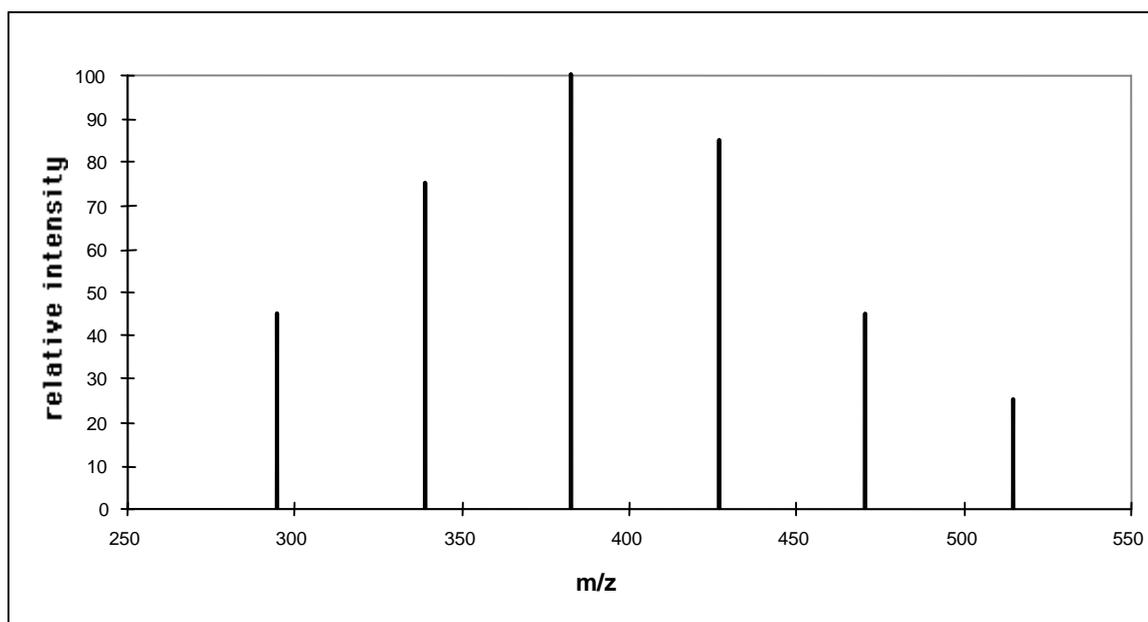
A solution containing SnBr_6^{2-} (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z=515$.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{79}Br .

6.7 Write the formula for the tin-containing species detected by this technique.

The ESMS spectrum of a solution made by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} (as tetrabutylammonium salts) shows six major species (Fig. 1).

Fig. 1



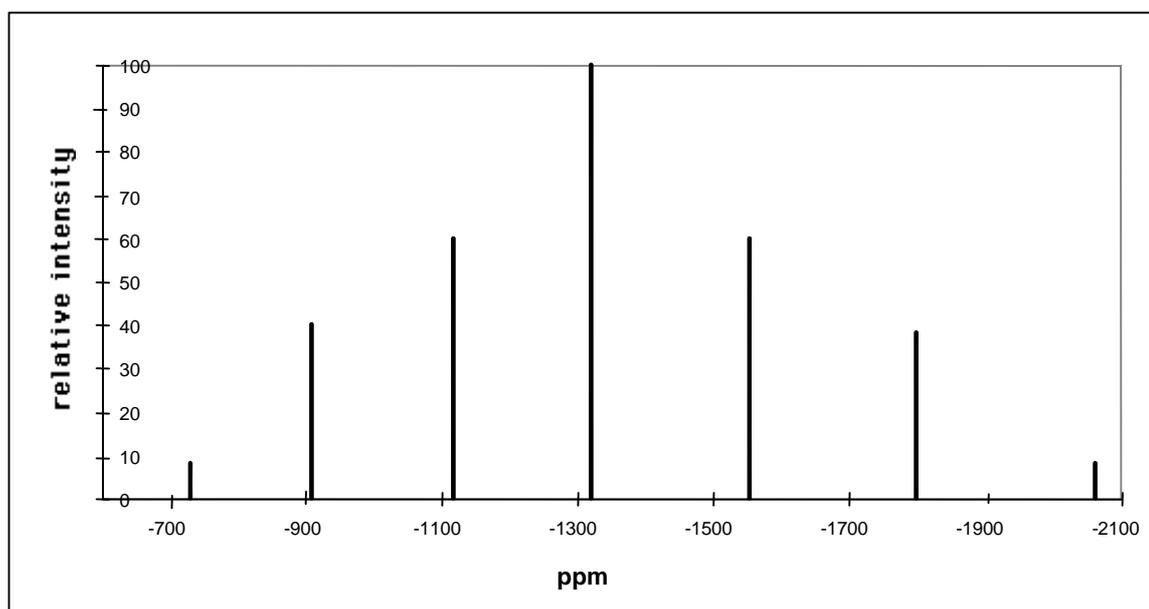
6.8 Write the empirical formula for each of the four new species.

^1H and ^{13}C NMR spectroscopy of molecules enable detection of a separate signal for each proton and ^{13}C nucleus which is in a different environment. These signals are recorded on dimensionless parts per million (ppm) scale relative to some agreed standard reference compound. Similarly, ^{119}Sn NMR gives a signal for each tin atom which is in a different environment.

The ^{119}Sn NMR spectrum of a solution of SnCl_6^{2-} (as the tetrabutylammonium salt) contains only one signal which occurs at -732 ppm (relative to tetramethyltin, Me_4Sn). The ^{119}Sn NMR spectrum of a solution of SnBr_6^{2-} (as the tetrabutylammonium salt) occurs at 2064 ppm. The ^{119}Sn NMR spectrum at 60°C of a solution formed by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} contains seven peaks (Fig. 2).

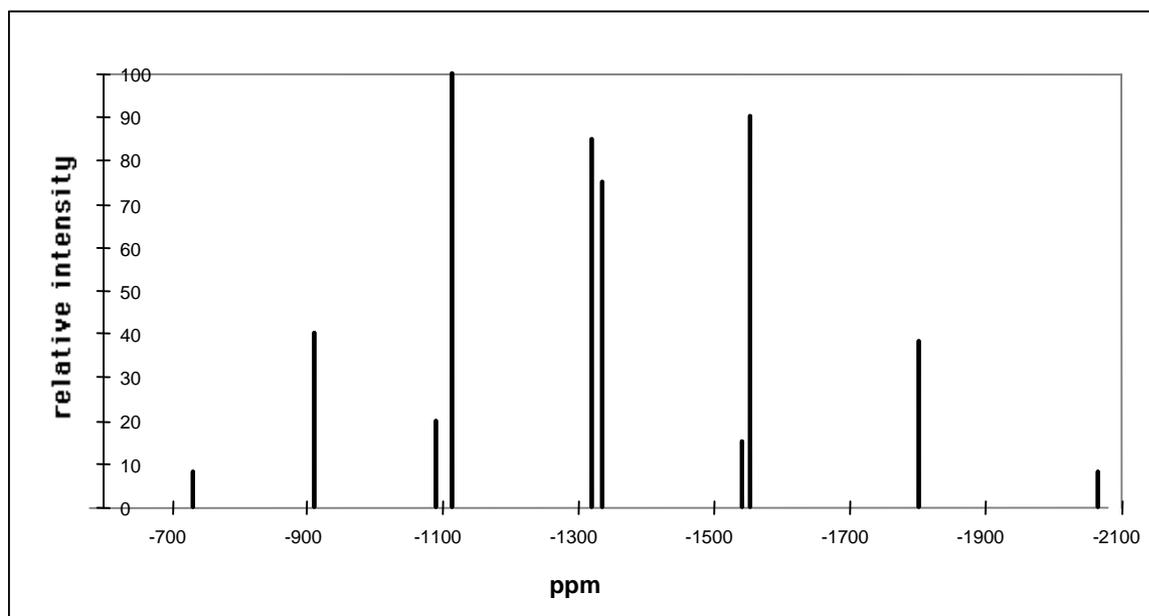
6.9 Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed on the answer template.

Fig. 2



Cooling the solution causes a change to this ^{119}Sn NMR spectrum and at $-30\text{ }^\circ\text{C}$ ten peaks are observed (Fig. 3).

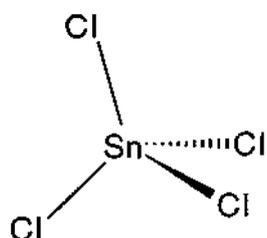
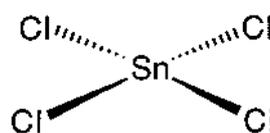
Fig. 3



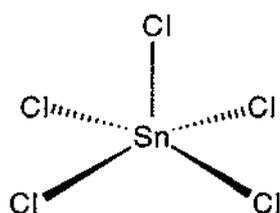
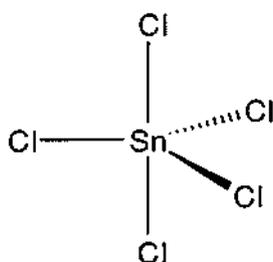
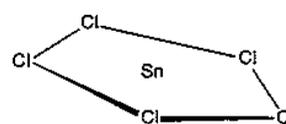
6.10 Draw the geometry for the four tin-containing species present in this solution at $-30\text{ }^\circ\text{C}$ that give rise to the peaks at -1092 and -1115 , -1322 and -1336 ppm.

SOLUTION

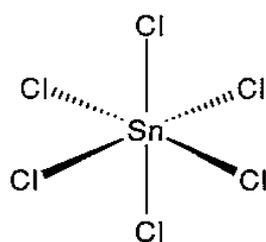
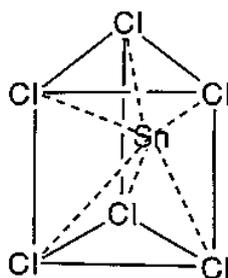
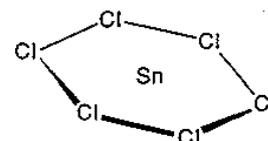
6.1

A

B


6.2

C

D

E

 6.3 In accordance with VSEPR theory geometry D is likely to be preferred for SnCl_5^- .

6.4

F

G

H

 6.5 In accordance with VSEPR theory geometry of F is likely to be preferred for SnCl_5^-

 6.6 SnCl_5^-

 6.7 SnBr_5^-

 6.8 $m/z = 339$: SnCl_4Br^- $m/z = 427$: $\text{SnCl}_2\text{Br}_3^-$
 $m/z = 383$: $\text{SnCl}_3\text{Br}_2^-$ $m/z = 471$: SnClBr_4^-

6.9	- 912 ppm:	$\text{SnCl}_5\text{Br}^{2-}$
	-1117 ppm:	$\text{SnCl}_4\text{Br}_2^{2-}$
	-1322 ppm:	$\text{SnCl}_3\text{Br}_3^{2-}$
	-1554 ppm:	$\text{SnCl}_2\text{Br}_4^{2-}$
	-1800 ppm:	SnClBr_5^{2-}

6.10

-1092 ppm and -1115 ppm (2 compounds)



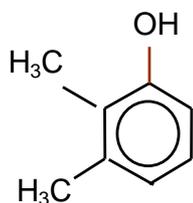
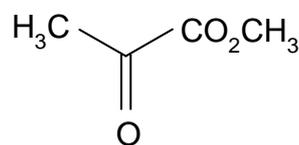
-1322 ppm and -1336 ppm (2 compounds)



PROBLEM 7

The structures needed to read this question are shown in the answer template.

The fungus *Aspergillus nidulans* produces two isomeric aromatic lactones (cyclic esters) **A** and **B** ($C_{10}H_{10}O_4$) each of which dissolved in cold aqueous NaOH but not in aqueous $NaHCO_3$. Both **A** and **B** gave a violet colour with aqueous $FeCl_3$. Reaction of **A** with CH_3I in the presence of K_2CO_3 gave **C** ($C_{11}H_{12}O_4$) which was shown by 1H NMR spectroscopy to contain three non-identical methyl groups one of which was bonded directly to an aromatic ring. Selective demethylation of **C** with BCl_3 followed by aqueous work up gave **D** a new isomer of **A**. The 1H NMR spectrum of compound **D** clearly showed the presence of an intramolecularly hydrogen bonded hydroxyl group at δ 11.8 ppm.

**E****I**

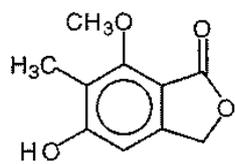
Compound **D** was synthesised as follows: The phenol **E** was methylated (MeI/K_2CO_3) to afford **F** ($C_9H_{12}O_2$) which in turn was reduced with lithium metal in liquid ammonia and 2-methyl-propan-2-ol to give the symmetrical unconjugated diene **G**. Conjugation of this diene was achieved by reaction with KNH_2 in liquid ammonia followed by aqueous work up, a process which afforded only one product **H**. Ozonolysis of **H** followed by non reductive work up afforded amongst other products the ketoester **I**. Compound **H** underwent a Diels-Alder reaction with dimethyl but-2-ynedioate **J** to give the adduct **K** ($C_{15}H_{20}O_6$) which upon heating expelled ethene to afford an aromatic ester **L**. Basic hydrolysis of **L** followed by acidification of the solution gave **M** ($C_{11}H_{12}O_6$) which when heated under vacuum yielded **N** ($C_{11}H_{10}O_5$). Reduction of **N** with $NaBH_4$ in dimethylformamide gave **C** and an isomeric lactone **O** which could also be obtained by the methylation of **B**.

7.1 Using the answer template provided fill in the structures **A** to **O**.

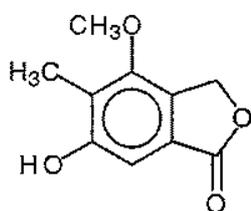
7.2 Using the last space on the answer template provide a second structure for **B**.

SOLUTION

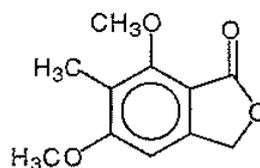
7.1 and 7.2



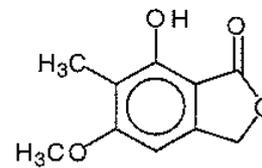
A



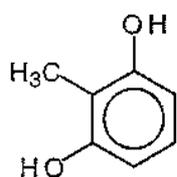
B



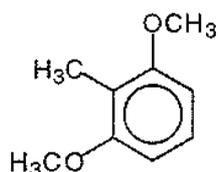
C



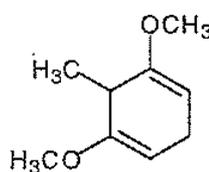
D



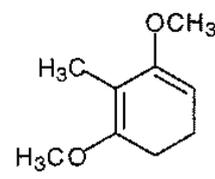
E



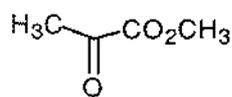
F



G



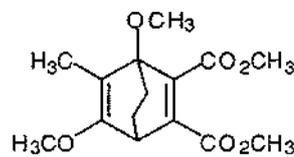
H



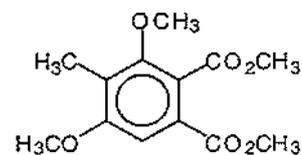
I



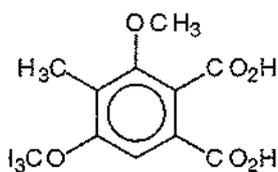
J



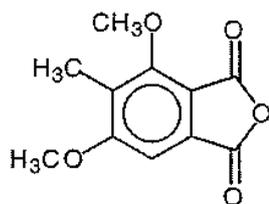
K



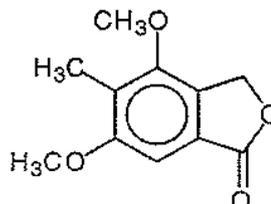
L



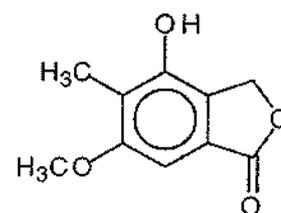
M



N



O



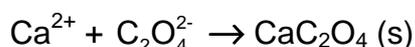
Other structure for **B**

PRACTICAL PROBLEMS

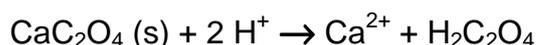
PROBLEM 1 (Practical)

Determination of Calcium by Precipitation with Oxalate Followed by Titration with Permanganate.

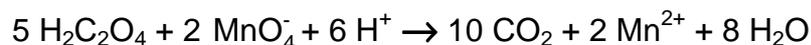
In this exercise, you must determine the amount of calcium ion in a solution that contains both calcium and magnesium, by selectively precipitating only the calcium as calcium oxalate, then quantitatively removing the precipitate from the solution by filtration.



The precipitate must then be re-dissolved in acid:



The liberated oxalic acid is titrated with standard permanganate solution:



Formation of the calcium oxalate precipitate

1. Use a 25.00 cm³ pipette and 250.0 cm³ volumetric flask to accurately dilute (by a factor of 10), the calcium/magnesium solution that has been provided for you.

Analyse two samples of the dilute calcium/magnesium solution. You have sufficient reagents for three analyses, but you must plan your time and use of equipment carefully. Take each of your samples through the following procedure:

2. Transfer a 25.00 cm³ aliquot of the dilute calcium/magnesium solution into a 250 cm³ beaker, add approximately 10 cm³ of 3 M H₂SO₄ and about 50 cm³ of water.

CARE! 3 M H₂SO₄ is very corrosive! The following steps involve hot (nearly boiling) solutions. Be careful and beware of steam!

3. Cover the beaker with a watch glass and gently heat on a hotplate until the solution is very hot, but not boiling.
4. Remove the beaker from the heat, then carefully add solid ammonium oxalate (1.5 g) and swirl the beaker until most of the ammonium oxalate dissolves.

CARE! Oxalate solutions are toxic. Do not wash solutions that contain oxalate down the sink. Place them in the "Permanganate/Oxalate residues" bottle at the end of your bench.

5. Add 5 –10 drops of methyl red indicator to the beaker, then while the solution is hot, increase the *pH* of the solution by slowly adding 1 : 1 ammonia solution with constant stirring, until the colour just changes from pink to orange. If you add too much ammonia, the solution will turn yellow. To correct this problem, add 1 drop of 3 M H₂SO₄ to lower the *pH* again, then repeat the *pH* adjustment with ammonia solution.

CARE! 1 : 1 ammonia solution is corrosive and has a very strong smell! Keep the bottle stoppered when not in use.

6. Allow the solution to stand for at least 60 minutes to quantitatively precipitate the calcium oxalate. Do not stir the solution during this time.

You should complete Laboratory Task 2 during this waiting period.

Do not proceed to the next step until you are confident that precipitation is complete.

Filtration of the calcium oxalate precipitate

7. Prepare a filter paper in a filter funnel supported in the neck of a 250 cm³ conical flask. Rinse the paper with a few cm³ of water then decant most of the supernatant solution from step 6. into the filter funnel. Collect the filtrate in the conical flask. Use a wash bottle to rinse the watch glass into the filter funnel.
8. Test the filtrate for the presence of calcium ion by adding a drop of ammonium oxalate test solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, the calcium oxalate precipitation in step 6 was unfortunately not complete. Perhaps the *pH* was not adjusted correctly or insufficient time was allowed for precipitation. Depending on the time you have left, you may start the analysis again or you may continue with the present experiment.
9. If there is no detectable calcium ion in the filtrate, use a wash bottle to carefully wash the calcium oxalate precipitate into the filter. Use the rubber “policeman” on the end of a glass rod to remove the last traces of precipitate from the beaker, and rinse these into the filter.
10. Wash the precipitate 4 times with approximately 10 cm³ portions of water, collecting the washings in the conical flask.

11. Discard the combined filtrates from the previous steps into the residue bottle labeled "Permanganate/Oxalate residues" then carefully rinse the conical flask with water into the residue bottle.
12. Wash the precipitate one more time with 10 cm³ of water. Collect this filtrate in the conical flask and test it for the presence of oxalate by adding a drop of saturated calcium nitrate solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, continue washing and testing until the washings are free from oxalate.
13. When the precipitate is free of oxalate, discard the washings and rinse and drain the conical flask.

NOTE! Show your demonstrator your precipitates. You must ask your demonstrator to sign your results sheet before proceeding to the next step.

14. Use a glass rod to break a small hole in the bottom of the filter paper and wash the precipitate through the hole into the conical flask with approximately 20 cm³ water. Take care to rinse the rod and the creases of the filter paper.
15. Use a Pasteur pipette to dissolve any traces of calcium oxalate that remain in the paper with 25 cm³ 3 M sulphuric acid, collecting the acid in the conical flask. Finally, rinse the paper with ~ 20 cm³ water.

Titration with permanganate

16. Make the volume up to about 100 cm³ with water, heat the solution to about 60 °C, then when all the calcium oxalate precipitate is dissolved, carefully titrate the hot solution with standard potassium permanganate solution.
CARE! It is not necessary to measure the temperature of the solution with a thermometer. 60 °C is uncomfortably hot to touch.
17. Discard the titrated solution into the residue bottle labelled "**Permanganate/Oxalate residues**".

Calculate the average concentration of calcium ion in the original calcium/magnesium solution that was provided.

Molar masses in g mol⁻¹: Ca 40.08, Mg 24.31, Mn 54.94, C 12.01, O 16.00.

SOLUTION

Model solution

Analysis of calcium/magnesium solution

Permanganate titration

Concentration of standard KMnO₄ solution: 0.02039 mol dm⁻³

Titration number	1	2	3
initial burette reading (cm ³)	0.90	0.80	3.00
final burette reading (cm ³)	28.55	28.45	30.80
volume of standard KMnO ₄ (cm ³)	27.65	27.65	27.80
Average titre (cm ³)	27.70		

In a 25 cm³ aliquot of dilute Ca/Mg solution:

$n(\text{KMnO}_4)$ required to titrate oxalate from dissolved calcium oxalate precipitate

$$n(\text{KMnO}_4) = 0.0198 \text{ mol dm}^{-3} \times 0.0277 \text{ dm}^3 = 5.485 \times 10^{-4} \text{ mol}$$

$n(\text{oxalate})$ from dissolved calcium oxalate precipitate:

$$n(\text{oxalate}) = 5/2 \times 5.485 \times 10^{-4} \text{ mol} = 1.371 \times 10^{-3} \text{ mol}$$

$n(\text{Ca}^{2+})$ from dissolved calcium oxalate precipitate = $n(\text{oxalate}) = 1.371 \times 10^{-3} \text{ mol}$

$$c(\text{Ca}) = 1.371 \times 10^{-3} \text{ mol} / 0.02500 \text{ dm}^3 = 0.0548 \text{ mol dm}^{-3}$$

In original Ca/Mg solution:

$$c(\text{Ca}) = 0.0548 \text{ mol dm}^{-3}$$

PROBLEM 2 (Practical)**Analysis of a Mixture of Cobalt(III) Complexes**

When the complex $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ is prepared in the laboratory, it often contains a considerable amount of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ by-product.

In this exercise, you must determine the amount of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ in a sample that also contains only $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ as a by-product, using a cation-exchange procedure. The cation exchange resin used in this exercise is a cross-linked polystyrene resin of the strong acid type. It contains $-\text{SO}_3\text{H}$ groups from which the H^+ can be exchanged. When a solution containing 1 mol of M^{n+} is allowed to react with the resin this liberates n mol of H^+ . In this exercise, the solution resulting from ion exchange of the mixture of the two different complex cations is used to titrate a standardised NaOH solution.

Preparation of the cation exchange resin

You are provided with about 10 g of wet resin in the H^+ form. Wash the resin using the following procedure to remove all traces of free acid:

1. Transfer your resin to a 250 cm³ beaker, washing it from the container with about 50 cm³ of water, then let the resin settle. This will take a few minutes.
2. Carefully pour off (decant) as much of the acidic solution as possible into a 'waste' beaker. Try to minimise loss of any of the resin in this process. Wash the resin with ~20 cm³ portions of distilled water and test a drop of washing solution using a glass rod and pH paper until the excess acid is completely removed ($\text{pH} \sim 5$). You should not need to use more than 200 cm³ of water to do this.
3. Drain off all but enough water to leave the resin just covered with water.
Be sure to put all your acidic wash solutions into a waste bottle labelled "acid waste" - not down the sink! Do not allow the resin to dry out.

Preparation and standardisation of approximately 0.0125 M NaOH

4. Prepare 250.0 cm³ of approximately 0.0125 M NaOH by accurately diluting your ~0.125 M NaOH with distilled water in a volumetric flask.
5. With the standard 0.01253 M HCl that is provided, titrate 25.00 cm³ aliquots of the diluted NaOH solution, using phenolphthalein indicator.

Analysis Procedure

You are provided with approximately 40 cm³ of a 0.00500 M solution of HCl that contains 0.2000 g of a mixture of the cobalt(III) complexes [Co(NH₃)₅NO₂]Cl₂ and [Co(NH₃)₆]Cl₃ in 40.00 cm³.

- Use a pipette to transfer a 25.00 cm³ aliquot of the cobalt complex solution into a 250 cm³ beaker (beaker No 1) and add ~25 cm³ water.
 - Use a plastic spoon to add about half (~5 g) of your wet resin to the cobalt(III) solution and allow to stand for at least 5 minutes for ion-exchange to take place, liberating H⁺. You should occasionally gently swirl the mixture to hasten the ion-exchange process.
 - Carefully wash the acidic solution into a second 250 cm³ beaker (beaker No 2) with about 20 cm³ of distilled water. Try to leave as much as possible of the resin behind. Notice that the solution is now much lighter in colour, indicating that most, but not all of the cobalt complex mixture is stuck to the resin. You must now remove the last traces of cobalt(III) from solution (liberating more acid in the process), with a second batch of resin.
 - Add most of the remainder of your resin (~4 g) to the solution in beaker No 2 and again allow to stand for at least 5 minutes to allow the cation exchange to take place, liberating more H⁺.
- At the end of this process, the solution should be colourless - if not, (perhaps you did not wait long enough for ion-exchange to take place) repeat the ion-exchange and washing steps with the last portion (~1 g) of your ion-exchange resin.
- Filter the two resin samples through a carefully washed filter paper, and collect the acidic filtrate in a 100 cm³ volumetric flask. Carefully wash the resin with small portions of water into the volumetric flask and make up to the mark with water.
 - With this acid solution titrate 25.00 cm³ aliquots of your standardized NaOH solution.

Calculate the number of moles of H⁺ liberated by the 25 cm³ aliquot of your mixture of cobalt(III) complexes and report the percentage of [Co(NH₃)₅NO₂]Cl₂ that is present in your sample.

Molar masses in g mol⁻¹: Co 58.93; N 14.01; H 1.01; Cl 35.45; O 16.00.

SOLUTION**Model solution****Standardization of 0.0125 M NaOH**Concentration of standard HCl in bottle: 0.01253... mol dm⁻³

Titration number	1	2	3
aliquot of NaOH	25.00	25.00	25.00
initial burette reading (cm ³)	13.60	17.40	10.35
final burette reading (cm ³)	37.75	41.50	34.45
volume of standard KMnO ₄ (cm ³)	24.15	24.10	24.10
Average titre (cm ³)	24.12		

$$c(\text{NaOH}) = 0.01250 \text{ mol dm}^{-3} \times 0.02412 \text{ dm}^3 = 0.01206 \text{ mol dm}^{-3}$$

Aliquot of cobalt complex solution used for ion-exchange: 25 cm³

Titration number	1	2	3
initial burette reading (cm ³)	26.25	16.10	3.80
final burette reading (cm ³)	48.50	38.40	26.20
volume of standard KMnO ₄ (cm ³)	22.25	22.30	22.40
Average titre (cm ³)	22.32		

Calculations $c(\text{H}^+)$ collected in 100 cm³ flask:

$$c(\text{H}^+) = 0.01206 \text{ mol dm}^{-3} \times (25.00 \text{ cm}^3) / (22.32 \text{ cm}^3) = 0.01351 \text{ mol dm}^{-3}$$

total $n(\text{H}^+)$ collected from column:

$$n(\text{H}^+) = 0.01351 \text{ mol dm}^{-3} \times 0.100 \text{ dm}^3 = 1.351 \times 10^{-3} \text{ mol}$$

 $n(\text{H}^+)$ from aliquot put onto column:

$$n(\text{H}^+) = 0.00500 \text{ mol dm}^{-3} \times 0.02500 \text{ dm}^3 = 1.250 \times 10^{-4} \text{ mol}$$

 $n(\text{H}^+)$ ion-exchanged from complexes in aliquot put onto column:

$$n(\text{H}^+) = 1.351 \times 10^{-3} \text{ mol} - 1.250 \times 10^{-4} \text{ mol} = 1.226 \times 10^{-3} \text{ mol}$$

let y = mass [Co(NH₃)₅NO₂]Cl₂ in 25.00 cm³ aliquot of mixture added to column mass of

$$\text{mixture added to column} = (25.00 \text{ cm}^3 / 40 \text{ cm}^3) \times 0.2000 \text{ g} = 0.1250 \text{ g}$$

then mass $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in aliquot = $(0.1250 - y)$ g

$n(\text{H}^+)$ ion-exchanged from $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$:

$$n(\text{H}^+) = 2 y / 261.00 \text{ g mol}^{-1} = 0.007663x \text{ mol}$$

$n(\text{H}^+)$ ion-exchanged from $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$:

$$n(\text{H}^+) = 3 (0.1250 - y) \text{ g} / 267.50 \text{ g mol}^{-1} = (0.001402 - 0.011214 y) \text{ mol}$$

Thus, $0.007663 y + (0.001402 - 0.011214 y) = 0.001226$ or $y = 0.04956$ g

$$\% [\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 = 100 (0.04956 \text{ g} / 0.1250 \text{ g}) = 39.6 \%$$

31st



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE THIRTY-FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 3–12 July 1999, BANGKOK, THAILAND

THEORETICAL PROBLEMS

PROBLEM 1

A compound **Q** (molar mass 122.0 g mol^{-1}) consists of carbon, hydrogen and oxygen.

PART A

The standard enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at $25.00 \text{ }^\circ\text{C}$ are -393.51 and $-285.83 \text{ kJ mol}^{-1}$, respectively. The gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

(Relative atomic masses : H = 1.0; C = 12.0; O = 16.0)

A sample of solid **Q** that weighs 0.6000 g , is combusted in an excess of oxygen in a bomb calorimeter, which initially contains 710.0 g of water at $25.000 \text{ }^\circ\text{C}$. After the reaction is completed, the temperature is observed to be $27.250 \text{ }^\circ\text{C}$, and 1.5144 g of $\text{CO}_2(\text{g})$ and 0.2656 g of $\text{H}_2\text{O}(\text{l})$ are produced.

1.1 Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of **Q**.

If the specific heat of water is $4.184 \text{ J g}^{-1} \text{ K}^{-1}$ and the internal energy change of the reaction (ΔU°) $-3079 \text{ kJ mol}^{-1}$.

1.2 Calculate the heat capacity of the calorimeter (excluding the water).

1.3 Calculate the standard enthalpy of formation (ΔH_f°) of **Q**.

PART B

The following data refer to the distribution of **Q** between benzene and water at $6 \text{ }^\circ\text{C}$, C_B and C_W being equilibrium concentrations of the species of **Q** in the benzene and water layers, respectively:

Assume that there is only one species of **Q** in benzene independent of concentration and temperature.

Concentration (mol dm ⁻³)	
C _B	C _W
0.0118	0.00281
0.0478	0.00566
0.0981	0.00812
0.156	0.0102

1.4 Show by calculation whether **Q** is monomer or dimer in benzene. Assume that **Q** is a monomer in water.

The freezing point depression, for an ideal dilute solution, is given by

$$T_f^0 - T_f = \frac{R(T_f^0)^2 X_s}{\Delta H_f}$$

where T_f is the freezing point of the solution, T_f^0 the freezing point of solvent, ΔH_f the heat of fusion of the solvent, and X_s the mole fraction of solute. The molar mass of benzene is 78.0 g mol⁻¹. At 1 atm pure benzene freezes at 5.40 °C. The heat of fusion of benzene is 9.89 kJ mol⁻¹.

1.5 Calculate the freezing point (T_f) of a solution containing 0.244 g of **Q** in 5.85 g of benzene at 1 atm.

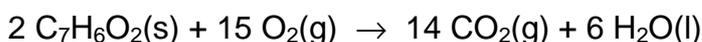
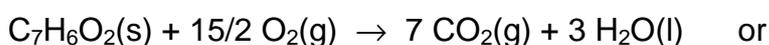
SOLUTION

PART A

$$1.1 \text{ Mole C : H : O} = \frac{1.5144 \times 12.0}{44.0} : \frac{0.2656 \times 2.0}{18.0} : \frac{0.1575}{16.0}$$

$$= 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2$$

The formula mass of C₇H₆O₂ = 122 which is the same as the molar mass given.



$$1.2 \quad n(Q) = \frac{0.6000}{122.0} = 4.919 \times 10^{-3} \text{ mol}$$

$$q_v = n \Delta U^0 = \frac{0.6000}{122.0} \times (-3079) = -15.14 \text{ kJ}$$

$$\text{Total heat capacity} = \frac{-q_v}{\Delta T} = \frac{15.14}{2.250} = 6.730 \text{ kJ K}^{-1}$$

$$\text{Heat capacity of water} = 710.0 \times 4.184 = 2971 \text{ J K}^{-1}$$

$$\text{Heat capacity of calorimeter} = 6730 - 2971 = 3759 \text{ J K}^{-1}$$

$$1.3 \quad \Delta n_g = 7 - 15/2 = -0.5 \text{ mol}$$

$$\Delta H^0 = \Delta U^0 + RT \Delta n_g = -3079 + (8.314 \times 10^{-3}) \times (298) \times (-0.5) = -3079 - 1 = -3080$$

$$\Delta H^0 = (7 \Delta_f H^0, \text{CO}_2(\text{g})) + 3 \Delta_f H^0, \text{H}_2\text{O}(\text{l}) - (\Delta_f H^0, \text{Q})$$

$$\Delta_f H^0 \text{ of Q} = 7 \times (-393.51) + 3 \times (-285.83) - (-3080) = \underline{\underline{-532 \text{ kJ mol}^{-1}}}$$

PART B

1.4 c_B (mol dm ⁻³)	0.0118	0.0478	0.0981	0.156
c_W (mol dm ⁻³)	0.00281	0.00566	0.00812	0.0102
either c_B/c_W	4.20	8.44	12.1	15.3
or c_B/c_W^2	1.49×10^3	1.49×10^3	1.49×10^3	1.50×10^3
(or $\sqrt{c_B}/c_W$	38.6	38.6	38.6	38.7)

From the results show that the ratio c_B/c_W varies considerably, whereas the ratio c_B/c_W^2 or $\sqrt{c_B}/c_W$ is almost constant, showing that in benzene, Q is associated into double molecule. Q in benzene is dimer.

1.5 If Q is completely dimerized in benzene, the apparent molecular mass should be 244.

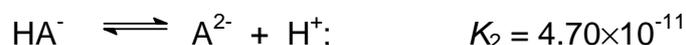
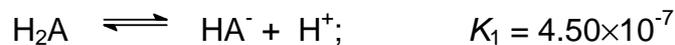
$$\text{Mole fraction of Q}_2 = \frac{\frac{0.244}{244}}{\frac{0.244}{244} + \frac{5.85}{78.0}} = 1.32 \times 10^{-2} \quad (0.01316)$$

$$\Delta T_f = \frac{8.314 \times 278.55^2}{9.89 \times 10^3} \times 1.32 \times 10^{-2} = 0.861$$

$$T_f = 5.40 - 0.861 = 4.54 \text{ }^\circ\text{C}$$

PROBLEM 2**PART A**

A diprotic acid, H_2A , undergoes the following dissociation reactions :



A 20.00 cm³ aliquot of a solution containing a mixture of Na_2A and $NaHA$ is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode *pH* meter. Two points on the titration curve are as follows :

<u>cm³ HCl added</u>	<u>pH</u>
1.00	10.33
10.00	8.34

- 2.1 On adding 1.00 cm³ of HCl, which species reacts first and what would be the product?
- 2.2 What is the amount (mmol) of the product formed in (2.1)?
- 2.3 Write down the main equilibrium of the product from (2.1) reacting with the solvent?
- 2.4 What are the amounts (mmol) of Na_2A and $NaHA$ initially present?
- 2.5 Calculate the total volume of HCl required to reach the second equivalence point.

PART B

Solutions I, II and III contain a *pH* indicator HIn ($K_{In} = 4.19 \times 10^{-4}$) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cell, are also given in the table. K_a of CH_3COOH is 1.75×10^{-5} .

Table:

	Solution I	Solution II	Solution III
Total concentration of indicator HIn	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400	0.000	0.300	?

- 2.6 Calculate the absorbance at 400 nm of solution III.
- 2.7 Apart from H₂O, H⁺ and OH⁻, what are all the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio?
- 2.8 What is the absorbance at 400 nm of the solution in (2.7)?
- 2.9 What is the transmittance at 400 nm of the solution in (2.7)?

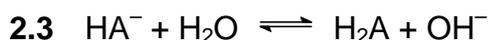
SOLUTION

PART A

- 2.1 Species which reacts first is A²⁻.

The product is HA⁻.

2.2 $n(\text{product}) = 1.00 \times 0.300 = 0.300 \text{ mmol}$



- 2.4 At pH 8.34 which is equal to $(pK_{a1} + pK_{a2}) / 2$ all A⁻ are protonated as HA⁻.

Therefore $n(\text{A}^{2-})$ initially present in the solution = $0.300 \times 10.00 = 3.00 \text{ mmol}$

At pH = 10.33, the system is a buffer in which the ratio of [A²⁻] and [HA⁻] is equal to 1.

Thus

$$[\text{HA}^-]_{\text{initial}} + [\text{HA}^-]_{\text{formed}} = [\text{A}^{2-}]_{\text{initial}} - [\text{HA}^-]_{\text{formed}}$$

$$n(\text{HA}^-)_{\text{initial}} = 3.00 - 0.300 - 0.300 \text{ mmol} = 2.40 \text{ mmol}$$

$$n(\text{Na}_2\text{A}) = \underline{3.00 \text{ mmol}}$$

$$n(\text{NaHA}) = \underline{2.40 \text{ mmol}}$$

2.5 Total volume of HCl required = $[(2 \times 3.00) + 2.40] / 0.300 = 28.00 \text{ cm}^3$

PART B

- 2.6 Solution III is the indicator solution at $1 \times 10^{-5} \text{ M}$ in a solution containing 1.0 M CH₃COOH.

To obtain the absorbance of the solution, it is necessary to calculate the concentration of the basic form of the indicator which is dependent on the $[H^+]$ of the solution.

$$[H^+] \text{ of solution III} = \sqrt{K_a c} = \sqrt{1.75 \times 10^{-5} \times 1.0} = 4.18 \times 10^{-3}$$

$$K_{in} = \frac{[H^+][In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_{in}}{[H^+]} = \frac{1 \times 10^{-3.38}}{1 \times 10^{-2.38}} = 0.100$$

$$\text{Since } [HIn] + [In^-] = 1 \times 10^{-5}$$

$$10 [In^-] + [In^-] = 1 \times 10^{-5}$$

$$[In^-] = 0.091 \times 10^{-5}$$

$$\text{Absorbance of solution III} = \frac{0.091 \times 10^{-5}}{1.00 \times 10^{-5}} \times 0.300 = 0.027$$

2.7 All the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio (apart from H^+ , OH^- and H_2O) are the following: CH_3COOH , CH_3COO^- , Na^+ , HIn , In^- .

2.8 When solutions II and III are mixed at 1 : 1 volume ratio, a buffer solution of 0.05 M CH_3COO^- / 0.45 M CH_3COOH is obtained.

$$[H^+] \text{ of the mixture solution} = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.75 \times 10^{-5} \times \frac{0.45}{0.05} = 15.75 \times 10^{-5}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_{in}}{[H^+]} = \frac{1 \times 10^{-3.38}}{15.75 \times 10^{-5}} = 2.65$$

$$\text{Since } [HIn] + [In^-] = 1 \times 10^{-5}$$

$$\frac{[In^-]}{2.65} + [In^-] = 1 \times 10^{-5}$$

$$[In^-] = 0.726 \times 10^{-5}$$

$$\text{Absorbance of solution} = \frac{0.726 \times 10^{-5}}{1.00 \times 10^{-5}} \times 0.300 = 0.218$$

2-9 Transmittance of solution = $10^{-0.218} = 0.605 \Rightarrow 60.5\%$

PROBLEM 3

One of naturally occurring radioactive decay series begins with ${}^{232}_{90}\text{Th}$ and ends with a stable ${}^{208}_{82}\text{Pb}$.

- 3.1 How many beta (β^-) decays are there in this series? Show by calculation.
- 3.2 How much energy in MeV is released in the complete chain?
- 3.3 Calculate the rate of production of energy (power) in watts ($1 \text{ W} = \text{J s}^{-1}$) produced by 1.00 kilogram of ${}^{232}\text{Th}$ ($t_{1/2} = 1.40 \times 10^{10}$ years).
- 3.4 ${}^{228}\text{Th}$ is a member of the thorium series. What volume in cm^3 of helium at 0°C and 1 atm collected when 1.00 gram of ${}^{228}\text{Th}$ ($t_{1/2} = 1.91$ years) is stored in a container for 20.0 years. The half-lives of all intermediate nuclides are short compared to the half-life of ${}^{228}\text{Th}$.
- 3.5 One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic masses are :

$${}^4_2\text{He} = 4.00260 \text{ u}, \quad {}^{208}_{82}\text{Pb} = 207.97664 \text{ u}, \quad {}^{232}_{90}\text{Th} = 232.03805 \text{ u}; \text{ and } 1 \text{ u} = 931.5 \text{ MeV}$$

$$1 \text{ MeV} = 1.602 \times 10^{-13} \text{ J}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

The molar volume of an ideal gas at 0°C and 1 atm is $22.4 \text{ dm}^3 \text{ mol}^{-1}$.

SOLUTION

- 3.1 $A = 232 - 208 = 24$; $24/4 = 6$ alpha particles

The nuclear charge is therefore reduced by $2 \times 6 = 12$ units, however, the difference in nuclear charges is only $90 - 82 = 8$ units. Therefore there must be

$$12 - 8 = 4 \beta^- \text{ emitted.}$$

$$\text{Number of beta decays} = 4$$

- 3.2 ${}^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Pb} + 6 {}^4_2\text{He} + 4 \beta^-$

Energy released is Q value

$$Q = [m(^{232}\text{Th}) - m(^{208}\text{Pb}) - 6 m(^4\text{He})] c^2$$

(the mass of $4e^-$ are included in daughters)

$$= [232.03805 u - 207.97664 u - 6 \times 4.00260 u] \times 931.5 \text{ MeV } u^{-1} =$$

$$= (0.04581 u) \times (931.5 \text{ MeV}) = 42.67 \text{ MeV}$$

3.3 The rate of production of energy (power) in watts ($1 \text{ W} = \text{J s}^{-1}$) produced by 1.00 kilogram of ^{232}Th ($t_{1/2} = 1.40 \times 10^{10}$ years).

$$1.00 \text{ kg contains} = \frac{1000 \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{232 \text{ g mol}^{-1}} = 2.60 \times 10^{24} \text{ atoms}$$

Decay constant for ^{232}Th :

$$\lambda = \frac{0.693}{1.40 \times 10^{10} \text{ y} \times 3.154 \times 10^7 \text{ sy}^{-1}} = 1.57 \times 10^{-18} \text{ s}^{-1}$$

For activity: $A = N \lambda = 2.60 \times 10^{24} \times 1.57 \times 10^{-18} = 4.08 \times 10^6 \text{ dis s}^{-1}$
(disintegrations s^{-1})

Each decay liberates 42.67 MeV

Rate of production of energy (power):

$$4.08 \times 10^6 \text{ dis s}^{-1} \times 42.67 \text{ MeV dis}^{-1} \times 1.602 \times 10^{-13} \text{ J MeV}^{-1} =$$

$$= 2.79 \times 10^{-5} \text{ J s}^{-1} = 2.79 \times 10^{-5} \text{ W}$$

3.4 The volume in cm^3 of helium at 0°C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2} = 1.91$ years) is stored in a container for 20.0 years.



The half-lives of various intermediates are relatively short compared with that of ^{228}Th .

$$A = \lambda N = \frac{0.693}{1.91 \text{ y}} \times \frac{1.000 \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{228 \text{ g mol}^{-1}} = 9.58 \times 10^{20} \text{ y}^{-1}$$

Number of He collected:

$$N_{\text{He}} = 9.58 \times 10^{20} \text{ y}^{-1} \times 20.0 \text{ y} \times 5 \text{ particles} = 9.58 \times 10^{22} \text{ particles of He}$$

$$V_{\text{He}} = \frac{9.58 \times 10^{22} \times 22.4 \text{ dm}^3 \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.56 \text{ dm}^3 = 3.56 \times 10^3 \text{ cm}^3$$

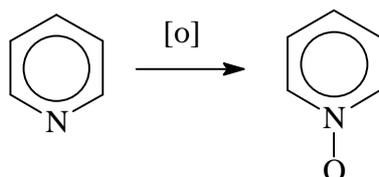
3.5 The half-life:

$$A = \lambda N$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693 N}{A} = \frac{0.693 \times 510 \times 10^{10} \text{ atoms}}{3440 \text{ atoms min}^{-1}} = 3.02 \times 10^6 \text{ min} = 5.75 \text{ years}$$

PROBLEM 4

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70 – 80 °C for 3 hrs. The final product **L** crystallizes out as fine needles and its molecular mass is 188. An analogous reaction with pyridine is ;



Complexes of **L** with Fe and Cr have the formulae of $\text{FeL}_m(\text{ClO}_4)_n \cdot 3 \text{H}_2\text{O}$ (**A**) and $\text{CrL}_x\text{Cl}_y(\text{ClO}_4)_z \cdot \text{H}_2\text{O}$ (**B**), respectively. Their elemental analyses and physical properties are given in Tables 4a and 4b. The relationship of colour and wavelength is given in Table 4c.

Table 4a: Elemental analyses.

Complex	Elemental analyses , (wt. %)
A	Fe 5.740, C 37.030, H 3.090 , Cl 10.940, N 8.640
B	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080

Use the following data:

Atomic number: Cr = 24, Fe = 26

Relative atomic mass: H = 1, C = 12, N = 14, O = 16, Cl = 35.45, Cr = 52, Fe = 55.8

Table 4b: Physical properties

Complex	Magnetic moment , $\mu \text{ B.M.}$	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

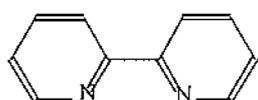
Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

- 4.1 Write down the molecular formula of **L**.
- 4.2 If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L**.
- 4.3 Does the ligand **L** have any charge, i. e. net charge?
- 4.4 Draw the structure when one molecule of **L** binds to metal ion (M).
- 4.5 From the data in Table 4a, determine the empirical formula of **A**. What are the values of *m* and *n* in $\text{FeL}_m(\text{ClO}_4)_n \cdot 3 \text{H}_2\text{O}$? Write the complete formula of **A** in the usual IUPAC notation. What is the ratio of cation to anion when **A** dissolves in water?
- 4.6 What is the oxidation number of Fe in **A**? How many d-electrons are present in Fe ion in the complex? Write the high spin and the low spin configurations that may exist for this complex. Which configuration, high or low spin, is the correct one? What is the best evidence to support your answer?
- 4.7 From Table 4c, estimate λ_{max} (nm) of **A**.
- 4.8 Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the 'spin-only' magnetic moment of this compound.
- 4.9 Compound **B** is a 1 : 1 type electrolyte. Determine the empirical formula of **B** and the values of *x*, *y*, *z* in $\text{CrL}_x\text{Cl}_y(\text{ClO}_4)_z \cdot \text{H}_2\text{O}$.

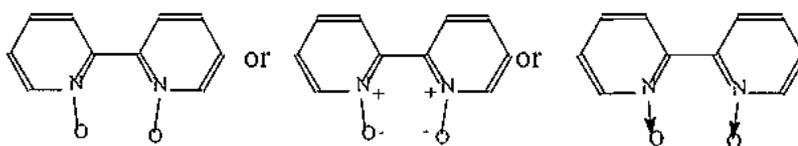
SOLUTION

4.1 Knowing that L was synthesized from bipyridine and during the reaction bipyridine was simply oxidized to bipyridine oxide. The molecular mass of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of L is 188. The difference of 32 is due to 2 atoms of oxygen. Therefore, the molecular formula of L is $C_{10}H_8N_2O_2$.

4.2 The structures of bipyridine and L:



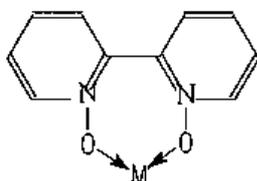
Structure of bipyridine



structure of L

4.3 The ligand L has no charge.

4.4 The structure when one molecule of L binds to metal ion (M):



4.5 The empirical formula of A. Calculation:

	Fe	C	H	Cl	N	O
%	5.740	37.030	3.090	10.940	8.640	34.560*
mol	0.103	3.085	3.090	0.309	0.617	2.160
mol ratio	1.000	29.959	30.00	2.996	5.992	20.971
atom ratio	1	30	30	3	6	21

*) Percentage of O is obtained by difference.)

The empirical formula of A is $FeC_{30}H_{30}Cl_3N_6C_{21}$

The values of m and n in $FeL_m(C_{104})_n \cdot 3H_2O$:

Since the molecular formula contains one atom of Fe, so in this case the empirical formula is equivalent to the molecular formula. The molecular formula of L has been

obtained previously in (4a) and (4b), therefore we can work to find $m = 3$. Having obtained the value of m , one can work out for n and find that $n = 3$.

The complete formula of **A** is $[\text{FeL}_3](\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$

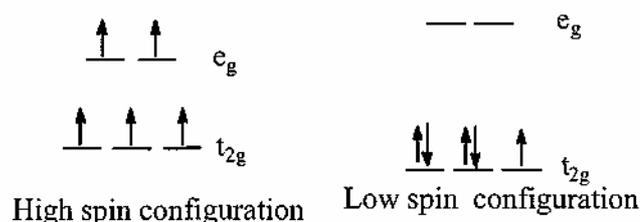
The ratio of cation to anion is equal to 1 : 3.

The three ClO_4^- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as $[\text{FeL}_3]^{3+}$ and 3 ClO_4^- in solution.

4.6 The oxidation number of Fe in complex **A** is +3 or III.

The number of d -electrons in Fe^{3+} ion in the complex = 5.

The high spin and the low spin configuration that may exist for this complex:



The correct answer is high spin configuration.

The best evidence to support your answer for this high/low spin selection is magnetic moment.

There exist a simple relation between number of unpaired electrons and the magnetic moment as follows:

$$\mu = \sqrt{n(n+2)}$$

where μ is the so-called 'spin-only' magnetic moment and n is the number of unpaired electrons. Thus, for high spin configuration in the given case,

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M.}$$

For low spin case:

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ B.M.}$$

The measured magnetic moment, for **A** is 6.13 B.M. (Table 4b) which is in the range for high spin configuration. Therefore, we can conclude that **A** can exist as a high spin complex.

4.7 From Table 4c, the color absorbed is complementary to the color seen. Thus, λ_{max} for complex A is 450 nm.

4.8 The 'spin-only' magnetic moment of complex B.

For Cr^{3+} : $n = 3$

Therefore, $\mu = \sqrt{3(3 + 2)} = \sqrt{15} = 3.87 \text{ B.M.}$

4.9 The empirical formula of B is $\text{Cr}_{20}\text{H}_{18}\text{N}_4\text{Cl}_3\text{O}_9$, i.e. $x = 2, y = 2, z = 1$.

PROBLEM 5

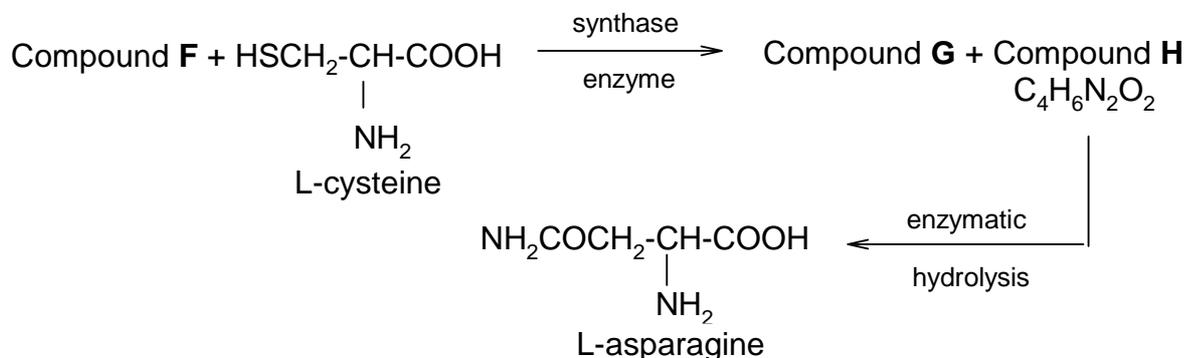
Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedict's or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$ and (-) **E**, $C_8H_8O_3$.

C has a β -glycosidic linkage and gives positive test with Benedict's or Fehling's solution. Methylation of **C** with MeI/Ag_2O gives $C_{20}H_{38}O_{11}$, which upon acidic hydrolysis gives 2,3,4-tri-*O*-methyl-D-glucopyranose and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose.

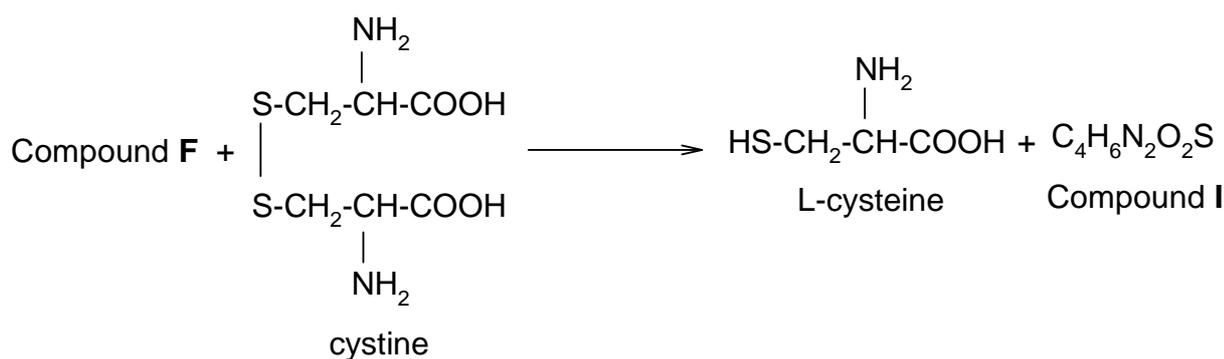
(\pm)**B** can be prepared from benzaldehyde and $NaHSO_3$ followed by $NaCN$. Acidic hydrolysis of (\pm)**B** gives (\pm)**E**, $C_8H_8O_3$.

5.1 Write structures of **A** – **D** with appropriate stereochemistry in Haworth projection, except for **B**.

Glycoside **A** is found to be toxic and believed to be due to extremely toxic compound **F**, liberated under the hydrolytic conditions. Detoxification of compound **F** in plant may be accompanied by the reactions (stereochemistry not shown).



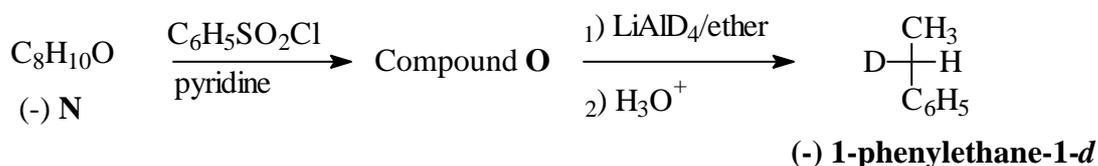
A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).



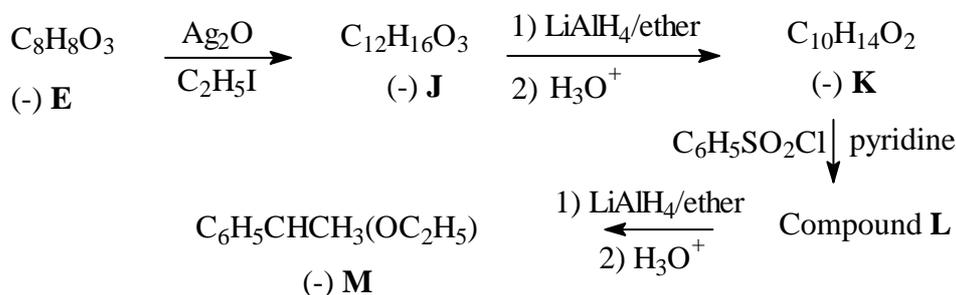
Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

5.2 Write molecular formula for compounds **F** and **G**, and structural formula for compounds **H** and **I** and indicate stereochemistry of **H**. (Table 5.1 may be useful for structure identification.)

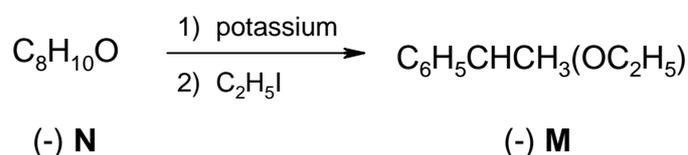
(-)-1-Phenylethane-1-*d*, $\text{C}_6\text{H}_5\text{CHDCH}_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_{\text{D}}$ is equal to -0.6.



The absolute configuration of (-)-1-phenylethane-1-*d* is related to (-) **E** according to the following reactions.



Compound (-) **M** can also be obtained from compound **N** as follows.



5.3 Deduce the absolute configuration of (-) **E** and the structure with configuration of each intermediate (**J** – **O**) in the sequence with the proper *R,S*-assignment as indicated in the answer sheet.

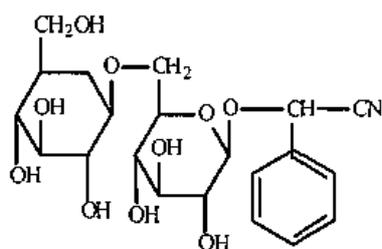
5.4 Choose the mechanism involved in the conversion of compound **O** to 1-phenylethane-1-*d*.

Table 5.1 Characteristic Infrared Absorption

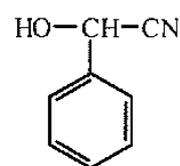
Stretching Vibration	Region (cm ⁻¹)	Stretching Vibration	Region (cm ⁻¹)
C-H (alkane)	2850-2960	O-H (free alcohol)	3400-3600
C-H (alkene)	3020-3100	O-H (H-bonded alcohol)	3300-3500
C=C	1650-1670	O-H (acid)	2500-3100
C-H (alkyne)	3300	C-O	1030-1150
C≡C	2100-2260	NH, NH ₂	3310-3550
C-H (aromatics)	3030	C-N	1030, 1230
C=C (aromatics)	1500-1600	C=N	1600-1700
C-H (aldehyde)	2700-2775, 2820-2900	C≡N	2210-2260
C=O	1670-1780		

SOLUTION

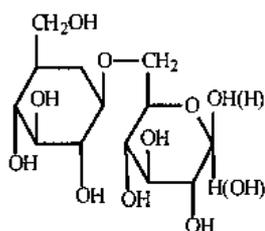
5.1



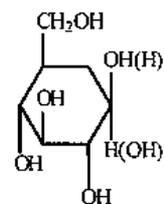
A



B



C

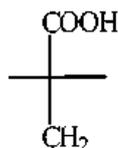


D

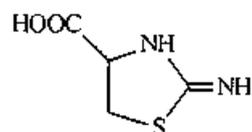
5.2

Molecular formula of compound **F** = HCN

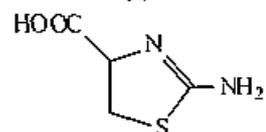
Molecular formula of compound **G** = H₂S



Compound **H**

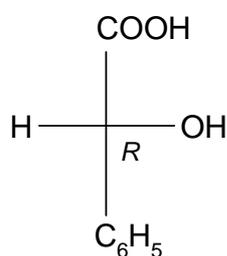


or

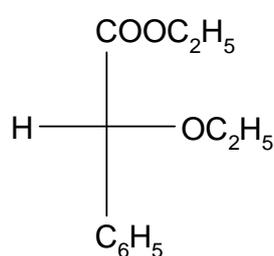


Compound **I**

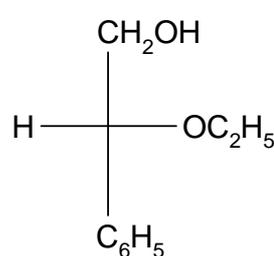
5.3



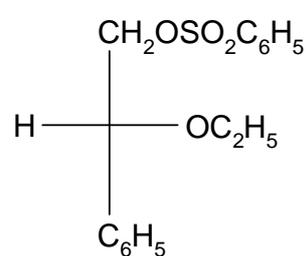
(-) **E**



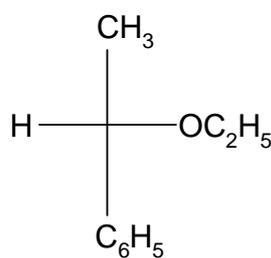
(-) **J**



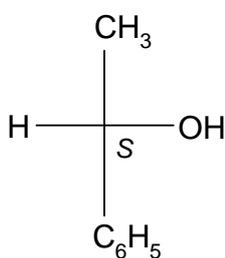
(-) **K**



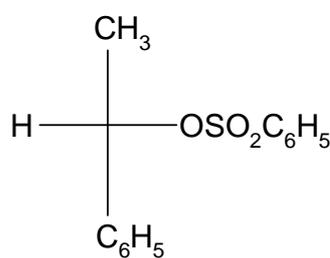
Compound **L**



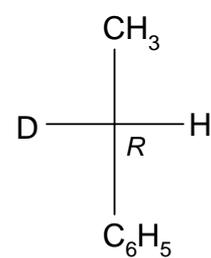
(-) **M**



(-) **N**



Compound **O**



(-) **1-phenylethane-1-d**

5.4 The mechanism involved in the conversion of compound **O** to (-) 1-phenylethane-1-d is S_N2.

PROBLEM 6

Peptide **A** has a molecular weight of 1007. Complete acid hydrolysis gives the following amino acids in equimolar amounts: Asp, Cystine, Glu, Gly, Ile, Leu, Pro, and Tyr (see Table 1). Oxidation of **A** with HCO_2OH gives only **B** which carries two residues of cysteic acid (**Cya** which is a cysteine derivative with its thiol group oxidized to sulfonic acid).

6.1 How many sulphonic acid groups are formed from oxidation of a disulfide bond ?

Partial hydrolysis of **B** gives a number of di and tri-peptides (B1-B6). The sequence of each hydrolysis product is determined in the following ways.

The N-terminal amino acid is identified by treating the peptide with 2,4-dinitrofluorobenzene (DNFB) to give DNP-peptide. After complete acid hydrolysis of the DNP-peptide, a DNP-amino acid is obtained which can be identified readily by comparison with standard DNP-amino acids.

6.2 B1, on treatment with DNFB followed by acid hydrolysis gives a product, DNP-Asp.

This suggests that B1 has aspartic acid at the N-terminus. Write down the complete structure of DNP-Asp at its isoelectric point (no stereochemistry required).

Next, the C-terminal amino acid is identified by heating the peptide at 100 °C with hydrazine, which cleave all the peptide bonds and convert all except C-terminal amino acids into amino acid hydrazides, leaving the C-terminal carboxyl group intact.

In this way N- and C-terminal amino acids are identified and the complete sequences of B1-B6 are as shown :

B1	Asp-Cya	B4	Ile-Glu
B2	Cya-Tyr	B5	Cya-Pro-Leu
B3	Leu-Gly	B6	Tyr-Ile-Glu

Hydrolysis of **B** with an enzyme from *Bacillus subtilis* gives B7-B9 with the following compositions:

B7	Gly-NH ₂ (Glycinamide)
B8	Cya, Glu, Ile, Tyr
B9	Asp, Cya, Leu, Pro

6.3 Write down the sequence of B8, if DNP-Cya is obtained on treatment of B8 with DNFB followed by complete acid hydrolysis.

- 6.4 If the N- and C-terminal amino acids of B9 are identified as Asp and Leu respectively, write down the sequence of B9.
- 6.5 Write down the complete structure of **A** using abbreviation in Table 1, indicating the position of the disulfide bond.

However, the calculated molecular weight of **A** based on the above sequence is 2 mass units higher than the experimental value. On careful observation of the mixture from complete acid hydrolysis of **A**, 3 molar equivalents of ammonia are also produced in addition to the amino acids detected initially.

- 6.6 Suggest the revised structure of **A** and circle the site(s) of the structure to indicate all the possible source of ammonia.
- 6.7 Using the information in Table 2, calculate the isoelectric point of **A**.

Table 1: Formulae and symbols of common amino acids at isoelectric point

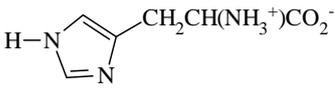
Name	Formula	Three-letter symbol
Alanine	$\text{CH}_3\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Ala
Arginine	$\text{H}_2\text{NC}(=\text{NH})\text{NH}(\text{CH}_2)_3\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Arg
Asparagine	$\text{H}_2\text{NCOCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Asn
Aspartic Acid	$\text{HO}_2\text{CCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Asp
Cysteine	$\text{HSCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Cys
Cystine	$[\text{SCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-]_2$	-
Glutamic Acid	$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Glu
Glutamine	$\text{H}_2\text{NCOCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Gln
Glycine	$^+\text{H}_3\text{NCH}_2\text{CO}_2^-$	Gly
Histidine		His
Isoleucine	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Ile
Leucine	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Leu
Lysine	$\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Lys

Table 1 (continued)

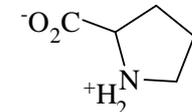
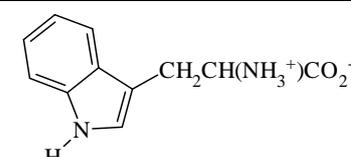
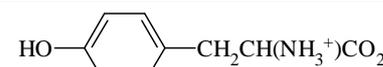
Methionine	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Met
Phenylalanine	$\text{PhCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Phe
Proline		Pro
Serine	$\text{HOCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Ser
Threonine	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Thr
Tryptophan		Trp
Tyrosine		Tyr
Valine	$(\text{CH}_3)_2\text{CHCH}(\text{NH}_3^+)\text{CO}_2^-$	Val

 Table 2: pK_a of some important groups in amino acids

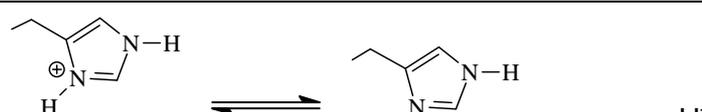
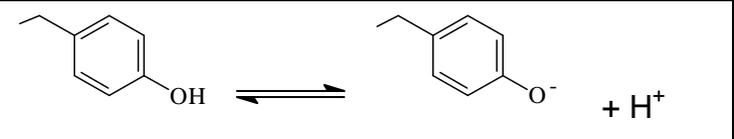
Groups	Equilibrium	pK_a
Terminal carboxyl	$-\text{CO}_2\text{H} \rightleftharpoons -\text{CO}_2^- + \text{H}^+$	3.1
Asp /or Glu side- chain carboxyl	$-\text{CO}_2\text{H} \rightleftharpoons -\text{CO}_2^- + \text{H}^+$	4.4
His side-chain		6.5
Terminal amino	$-\text{NH}_3^+ \rightleftharpoons -\text{NH}_2 + \text{H}^+$	8.0
Cys side-chain	$-\text{SH} \rightleftharpoons -\text{S}^- + \text{H}^+$	8.5

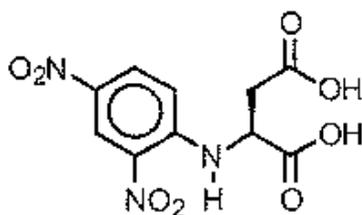
Table 2 (continued)

Tyr side-chain		10.0
Lys side-chain amino	$-\text{NH}_3^+ \rightleftharpoons -\text{NH}_2 + \text{H}^+$	10.0
Arg side-chain	$-\text{NH}(\text{NH}_2)\text{C}=\text{NH}_2^+ \rightleftharpoons -\text{NH}(\text{NH}_2)\text{C}=\text{NH} + \text{H}^+$	12.0

SOLUTION

6.1 Two sulphonic acid groups are formed from oxidation of a disulfide bond.

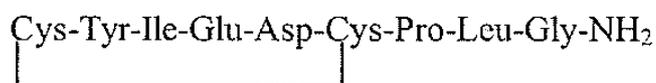
6.2 Complete structure of DNP-Asp at its isoelectric point is



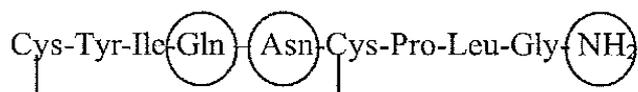
6.3 The sequence of B8 is: Cys-Tyr-Ile-Glu

6.4 The sequence of B9 is: Asp-Cys-Pro-Leu

6.5 The *complete* structure of A is



6.6 Write the revised structure of A below and circle the site(s) to indicate all the possible source of ammonia



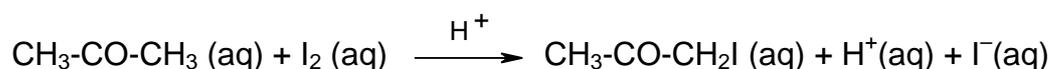
6.7 The isoelectric point of A is 9.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

The reaction between acetone and iodine in aqueous solution is catalyzed by H^+ .



In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of $I_2(aq)$ has been shown to have the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k[CH_3COCH_3]^x [I_2]^y [H^+]^z$$

where H^+ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x , y and z , the initial rate of reaction is measured.

$$\text{Initial rate} = k[CH_3COCH_3]_0^x [I_2]_0^y [H^+]_0^z$$

where $[]_0$ are the initial concentrations of acetone, I_2 and H^+ , respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the $I_2(aq)$ concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H^+ to produce acetic acid and so reducing the concentration of H^+ . The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution should be titrated immediately after the addition of the sodium acetate solution.

The remaining iodine $I_2 (aq)$ is determined by titration with sodium thiosulphate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour disappears.

Chemicals

1. Aqueous iodine solution in 0.4 M KI 80 cm³
2. 0.100 M aq. HCl 50 cm³
3. 0.50 M aq. CH₃COONa 80 cm³
4. Standard 0.02 M Na₂S₂O₃(aq) solution 200 cm³
(the exact concentration will be announced at the beginning of practical part)
5. Aqueous acetone (50% by volume) 50 cm³
(Density of pure acetone; 0.787 g cm⁻³, MW. = 58.08)
6. Starch indicator 7 cm³

Procedure**A. Standardization of Iodine Solution**

1. Pipet 5.00 cm³ of aqueous iodine into a clean 125 cm³ Erlenmeyer flask.
2. Add 10 cm³ of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02 M sodium thiosulphate solution until the colour of the solution is pale yellow.
4. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulphate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5).
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution

1. Label the stoppered flasks as follows: Flask I, II, III and IV.
2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50 % acetone:

Flask No.	Volume (cm ³)		
	water	0.100 M HCl	50 % acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

Stopper each flask immediately after addition of the solutions.

- Measure out 10 cm³ of 0.50 M aq. CH₃COONa into the graduated cylinder.
- Set the stop-watch to 0.0000 display.
- Pipet 5.00 cm³ of iodine solution into the stoppered Flask No. I.
Start the stop-watch as soon as the first drop of iodine solution is added.
- Stopper the flask and swirl continuously.
- Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm³ of sodium acetate solution (from step 3) into the reaction flask. Shake well.
- Titrate the remaining iodine with standard thiosulphate solution.
- Record the volume of the thiosulphate solution.
- Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I₂(aq) solution to each flask as indicated:

Flask II: 10.00 cm³ I₂ solution

Flask III: 5.00 cm³ I₂ solution

Flask IV: 5.00 cm³ I₂ solution

Calculations

- Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.
- Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.
- Calculate the initial reaction rate for Flasks I to IV in M s⁻¹.
- The rate of reaction has the form

$$\text{Rate} = -\frac{d[\text{I}_2]}{dt} = k [\text{CH}_3\text{COCH}_3]^x [\text{I}_2]^y [\text{H}^+]^z$$

Calculate the reaction orders x , y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x , y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k , for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

SOLUTION

The competitors were required to perform the following tasks:

In part A: Using the concentration of standard $\text{Na}_2\text{S}_2\text{O}_3$ solution (in bottle) and titration results it was required to calculate the concentration of iodine in the solution. Results were expected to be shown in a table in the answer sheet.

In part B: The following calculations B1 – B5 were required to be shown in the answer sheet:

B-1. *Calculation for initial concentrations (M) in the solution mixtures.*

B-2. *Calculation of the concentration (M) of iodine remaining in flasks I to IV at 7 minutes.*

B-3. *Calculation of initial rate of disappearance of I_2 at 7 minutes in flasks I to IV.*

$$\text{Rate of disappearance of iodine (M s}^{-1}\text{)} = -\frac{d[\text{I}_2]}{dt} = \frac{c(\text{I}_2)_{\text{initial}} - c(\text{I}_2)_{7 \text{ min}}}{7 \times 60 \text{ s}}$$

B-4. *Calculation of x , y , and z in the rate equation:*

$$\text{rate} = -\frac{d[\text{I}_2]}{dt} = k[\text{CH}_3\text{COCH}_3]^x [\text{I}_2]^y [\text{H}^+]^z$$

In comparing the rates in solutions II : I, III : I, and IV : I one can calculate the following values:

$$x = 1; \quad y = 0; \quad z = 1$$

The rate equation has the form: $\text{rate} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$

B-5. *Calculation of the rate constants for solution mixtures I to IV and the mean value of the rate constant.*

PROBLEM 2 (Practical)

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)

Unknown **Y** (in a vial)

Anhydrous Na₂SO₄ (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH₃, 5 % aq. AgNO₃, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. NaHCO₃, 1 % FeCl₃ in EtOH, 0.2 % aq. KMnO₄, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm³ round bottomed flask for distillation and a 10 cm³ round bottomed flask to collect the distillate. Heat the sand bath to approximately 150 °C before proceeding the next step.

Simplified Steam Distillation: Mix 1 g of ground sample with 15 cm³ of water in the 25 cm³ round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170 °C) to provide a steady rate of distillation. At least 5 cm³ of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. Be sure that the condenser is dry before using in the next step

Extraction of the Essential Oil: Transfer the distillate to a 15 cm³ capped centrifuge tube and add 1 cm³ of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 cm³ test tube. Repeat this extraction with fresh 1 cm³ dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na₂SO₄ and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm³ conical vial. Use approximately 1 cm³ of clean dichloromethane to wash Na₂SO₄ using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na₂SO₄ into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm³. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 cm³) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. AgNO₃ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH₃ to the tube until all the precipitate dissolved. The solution is ready for the test.

2. Structure elucidation of the main essential oil (S)

Reaction of the main essential oil (**S**) with CH₃I in the presence of K₂CO₃ gives compound **X** (C₁₁H₁₄O₂). Oxidation of **X** gives unknown **Y** (C₁₀H₁₂O₄) as the main product and CO₂.

3. Structure elucidation of the unknown Y:

Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.

Hand in your copy of answer sheet PART I (Demonstrator copy) of functional group analysis and ask for ^1H NMR spectra. ^1H NMR spectra will be given only when the functional group analysis is completed.

- Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^1H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.
- Draw the structures of compound X and unknown Y. Assign each proton of unknown Y from the provided ^1H NMR spectra in the same manner as in (4).

SOLUTION

- It was expected to obtain at least 5 cm^3 of distillate.
- Functional group analysis of the distilled essential oil:

Reagents	Positive test	Negative test
0.2 % KMnO_4	✓	
1 % FeCl_3	✓	
2,4-DNP		✓
Ceric ammonium nitrate	✓	
Tollen's Reagent		✓

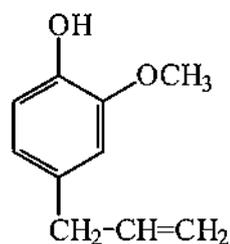
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

- Functional group analysis of the unknown compound Y:

Reagents	Positive test	Negative test
5 % HCl		✓
5 % NaOH	✓	
5 % NaHCO_3	✓	
0.2 % KMnO_4		✓
1 % FeCl_3		✓
2,4-DNP		✓
Ceric ammonium nitrate		✓
Tollen's Reagent		✓

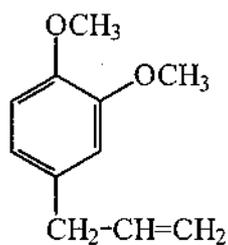
Functional groups in Unknown Y	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

4. The structure which represents the main essential oil (S):

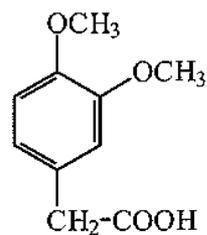


5. The structure of compound **X** and unknown **Y**:

Compound **X**



Compound **Y**

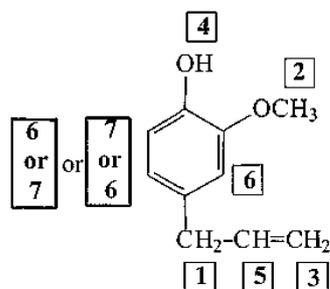


NMR spectrum of the main essential oil (S):

(See peak number in the given ¹H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.31	2H	d
2	3.84	3H	s
3 4	5.0 – 5.1	2H	m
5	5.6	1H	s
	5.9 – 6.0	1H	m
6	6.7	2H	s
			d or m
7	6.87	1H	d

NMR assignment of the main essential oil (S):

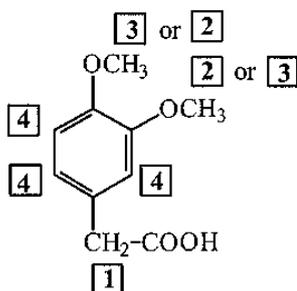


NMR spectrum of the unknown Y:

(See peak number in the given ¹H NMR spectrum. Labile proton does not appear in the spectrum.)

Peak No.	Chemical shift (δ , ppm)	No. of proton(s)	Multiplicity
1	3.59	2H	s
2	3.86	3H	s
3	3.88	3H	s
4	6.81	3H	s

NMR assignment of the main essential oil (S):



32nd



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE THIRTY-SECOND INTERNATIONAL CHEMISTRY OLYMPIAD 2-11 JULY 2000, COPENHAGEN, DENMARK

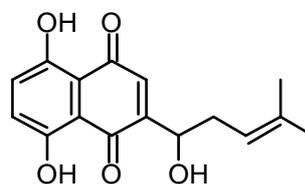
THEORETICAL PROBLEMS

PROBLEM 1

Synthesis of Compounds with Wound Healing Properties



Shikonin is a red compound found in the roots of the plant *Lithospermum erythrorhizon* which grows in Asia. Extracts of the root have been used for centuries in folk medicine and are used today in ointments for healing of wounds.

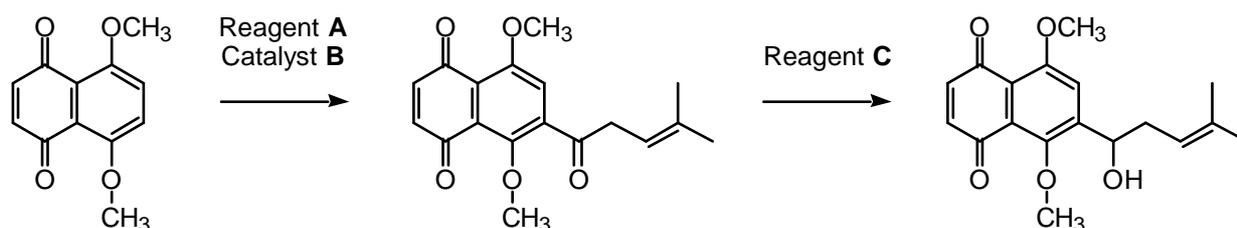


Shikonin

- 1.1 How many stereoisomers of Shikonin are possible ?
- 1.2 Do all stereoisomers of Shikonin have the same melting point? Mark with an X.

yes	no

The following sequence is part of a synthetic route to Shikonin:



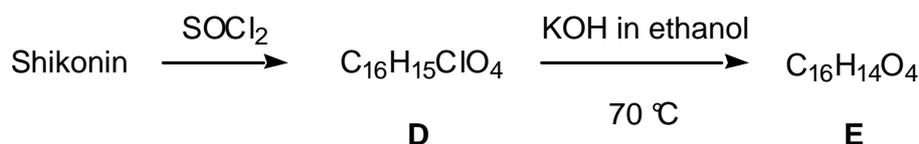
1.3 Draw the structural formula of reagent **A**.

1.4 Indicate (by means of an X in the appropriate check-box) the correct IUPAC name for reagent **A**.

- 2-Methyl-2-pentenoyl chloride
- 1-Chloro-4-methyl-3-pentene
- 4-Methyl-3-pentenoyl chloride
- 4-Methyl-3-pentene-1-ol
- 4,4-Dimethyl-3-butenoyl chloride

1.5 Write the molecular formula of reagent **C**.

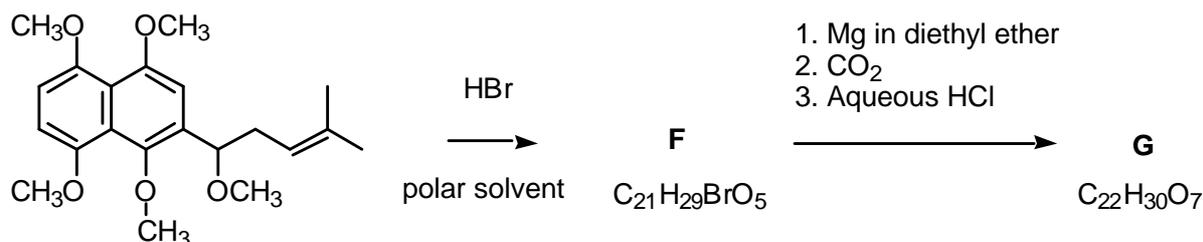
Numerous Shikonin analogues have been synthesized with a view to obtaining more potent compounds. One reaction sequence is shown below:



1.6 Draw the structural formula of compound **E**.

1.7 How many stereoisomers of compound **E**, if any, are possible

Another route to useful Shikonin analogues is the following:



1.8 Draw the structural formula of compound **F**.

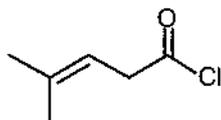
1.9 Draw the structural formula of compound **G**.

SOLUTION

1.1 2 stereoisomers.

1.2 Stereoisomers of Shikonin have the same melting point.

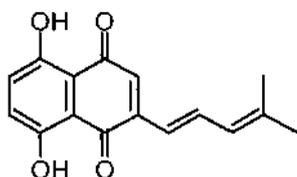
1.3 The structural formula of reagent **A**:



1.4 The correct IUPAC name for reagent **A** is 4-Methyl-3-pentenoyl chloride.

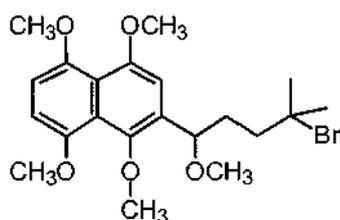
1.5 NaBH_4 (LiAlH_4 will be accepted)

1.6 The structural formula of compound **E**:

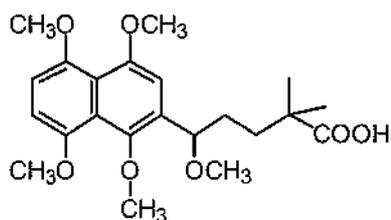


1.7 2 stereoisomers

1.8 The structural formula of compound **F**:



1.9 The structural formula of compound **G**:



PROBLEM 2

Bridge between Denmark and Sweden



On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. Consider the following reaction:



The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar:

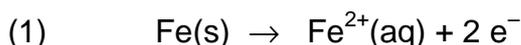
Compound	$\Delta_f H$ (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)
CaSO ₄ · 2 H ₂ O(s)	-2021.0	194.0
CaSO ₄ · ½ H ₂ O(s)	-1575.0	130.5
H ₂ O(g)	-241.8	188.6

Gas constant: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$

0 °C = 273.15 K.

- 2.1** Calculate ΔH (in kJ) for transformation of 1.00 kg of CaSO₄ · 2 H₂O(s) to hemihydrate CaSO₄ · ½ H₂O(s). Is this reaction endothermic or is it exothermic?
- 2.2** Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing CaSO₄ · 2 H₂O(s), CaSO₄ · ½ H₂O(s) and H₂O(g) at 25 °C.
- 2.3** Calculate the temperature at which the equilibrium water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH and ΔS are temperature independent.

Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:



An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 °C. The cell is represented by the following cell diagram:



Standard electrode potentials (at 25 °C):



Nernst factor: $RT \ln 10 / F = 0.05916 \text{ volt (at 25 °C)}$

Faraday constant: $F = 96485 \text{ C mol}^{-1}$

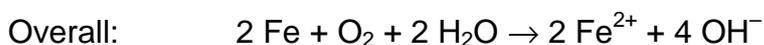
- 2.4** Calculate the standard electromotive force (the standard cell voltage), E , at 25 °C.

- 2.5 Write down the overall reaction which takes place during discharge of the cell under standard conditions.
- 2.6 Calculate the equilibrium constant at 25 °C for the overall cell reaction.
- 2.7 The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe²⁺ after 24 hours. Oxygen and water may be assumed to be present in excess.
- 2.8 Calculate E for the cell at 25 °C for the following conditions :
 $[\text{Fe}^{2+}] = 0.015 \text{ M}$, $pH_{\text{right-hand half-cell}} = 9.00$, $p(\text{O}_2) = 0.700 \text{ bar}$.

SOLUTION

- 2.1 $\Delta H^0 = -1575.0 \text{ kJ mol}^{-1} + 1.5 \times (-241.8) \text{ kJ mol}^{-1} - (-2021.0 \text{ kJ mol}^{-1}) = 83.3 \text{ kJ mol}^{-1}$
 $n = m / M = 1000 \text{ g} / 172.18 \text{ g mol}^{-1} = 5.808 \text{ mol}$
 $\Delta H^0 = 484 \text{ kJ}$
 The reaction is endothermic.
- 2.2 $\Delta S^0 = 130.5 \text{ J K}^{-1} \text{ mol}^{-1} + 3/2 \times 188.6 \text{ J K}^{-1} \text{ mol}^{-1} - 194.0 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta G^0 = \Delta H^0 - T\Delta S^0 = 17886 \text{ J mol}^{-1}$
 $\Delta G^0 = -RT \ln K$
 $K = (p(\text{H}_2\text{O}))^{3/2} = 7.35 \times 10^{-4}$ (pressure in bar)
 $p(\text{H}_2\text{O}) = 8.15 \times 10^{-3} \text{ bar}$
- 2.3 $p(\text{H}_2\text{O}) = 1.00 \text{ bar}$ implies $K = 1.00$ and $\Delta G^0 = -RT \ln K = 0$
 $\Delta G = \Delta H - T\Delta S$
 $0 = 83300 \text{ J K}^{-1} - T 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$
 $T = 380 \text{ K}$ or $107 \text{ }^\circ\text{C}$
- 2.4 $E^0(\text{cell}) = E^0(\text{right}) - E^0(\text{left}) = 0.40 \text{ V} - (-0.44 \text{ V}) = 0.84 \text{ V}$

2.5 Oxidation takes place at the negative, left half-cell.



2.6 $K = [\text{Fe}^{2+}]^2 [\text{OH}^-]^4 / p(\text{O}_2)$ (conc. in M and pressure in bar)

$$\Delta G = -nFE(\text{cell}) = -RT \ln K$$

$$K = 6.2 \times 10^{56}$$

2.7 $Q = It = 0.12 \text{ A} \times 24 \times 60 \times 60 \text{ s} = 10\,368 \text{ C}$

$$n(\text{e}^-) = Q / F = 10\,368 \text{ C} / 96485 \text{ C mol}^{-1} = 0.1075 \text{ mol}$$

$$m(\text{Fe}) = n(\text{Fe}) M(\text{Fe}) = 1/2 \times 0.1075 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 3.0 \text{ g}$$

2.8 $E(\text{cell}) = E^0(\text{cell}) - \frac{0.05916 \text{ V}}{n} \log \frac{[\text{Fe}^{2+}]^2 [\text{OH}^-]^4}{p(\text{O}_2)}$

$$pH = 9.00 \text{ implies } [\text{H}^+] = 1 \times 10^{-9} \text{ and } [\text{OH}^-] = 1 \times 10^{-5}$$

$$E(\text{cell}) = 0.84 \text{ V} - \frac{0.05916 \text{ V}}{4} \log \frac{0.015^2 [1 \times 10^{-5}]^4}{0.700} = 1.19 \text{ V}$$

PROBLEM 3**Bioinorganic Chemistry**

The square planar complex *cis*-diammine dichloroplatinum(II) is an important drug for the treatment of certain cancers.

3.1 Draw the structures of *cis*- and *trans*-diammine dichloroplatinum(II) and label each structure as *cis* or *trans*.

A number of ionic compounds also have the empirical formula Pt(NH₃)₂Cl₂.

3.2 Write molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has

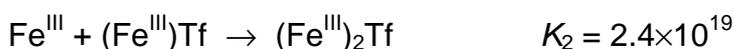
- 1) empirical formula Pt(NH₃)₂Cl₂,
- 2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex,
- 3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound

3.3 How many *5d* electrons are there in the platinum(II) ion?

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3.4 Which of the five *5d* orbitals attain the highest energy (*i. e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 at biological conditions except that the temperature is 25 °C corresponding to the reactions:



In the diferric protein, $(\text{Fe}^{\text{III}})_2\text{Tf}$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(\text{Fe}^{\text{III}})\text{Tf}$, can be denoted $\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}$ and $\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}$. Their relative abundance at equilibrium is given by the constant

$$K = \frac{[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}][\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}^{-1}]}{[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}][\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}^{-1}]} = 5.9.$$

3.5 Calculate the values of the two constants $K_1' = \frac{[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}][\text{Fe}^{\text{III}}]^{-1}[\text{Tf}]^{-1}}{[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}][\text{Fe}^{\text{III}}]^{-1}[\text{Tf}]^{-1}}$ and $K_1'' = \frac{[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}][\text{Fe}^{\text{III}}]^{-1}[\text{Tf}]^{-1}}{[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}][\text{Fe}^{\text{III}}]^{-1}[\text{Tf}]^{-1}}$, respectively, corresponding to the formation of each monoferric form of transferrin.

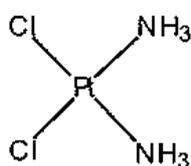
3.6 Calculate the values of the two constants $K_2' = \frac{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}^{-1}]}{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}^{-1}]}$ and $K_2'' = \frac{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}^{-1}]}{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}^{-1}]}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms.

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

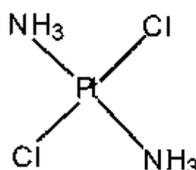
3.7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

SOLUTION

3.1 The structures of *cis*- and *trans*-diammine dichloroplatinum(II)



cis



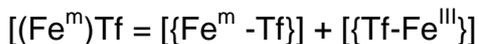
trans

3.2 $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$
 $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$
 $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$
 $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$

3.3 Eight *d*-electrons.

3.4 Orbital $5d_{x^2-y^2}$. In a square planar complex the four ligand atoms fall on the *x* and *y* axes along which this orbital, if filled, would also have electron density concentrated.

3.5 The concentration of monoferric forms of transferrin is



$$K_1' + K_1'' = K_1 \quad K_1' K_1'' = K_1$$

$$K_1' = \frac{K_1}{1 + K_1''} = \frac{4.7 \times 10^{20}}{1 + 5.9} = 6.8 \times 10^{19}$$

$$K_1'' = K_1 - K_1' = (4.7 - 0.68) \times 10^{20} = 4.0 \times 10^{20}$$

3.6 $K_1' K_2' = K_1'' K_2'' = K_1 K_2$

$$K_1' = \frac{K_1 K_2}{K_1''} = \frac{4.7 \times 10^{20} \times 2.19 \times 10^{19}}{6.8 \times 10^{19}} = 1.7 \times 10^{20}$$

$$K_1'' K_2'' = K_1 K_2$$

$$K_2'' = \frac{K_1 K_2}{K_1''} = \frac{4.7 \times 10^{20} \times 2.4 \times 10^{19}}{4.0 \times 10^{20}} = 2.8 \times 10^{19}$$

3.7 (= 2 (CO₃²⁻) + 1 (Asp(O⁻)) + 2 (2 × Tyr(O⁻)))

PROBLEM 4**A Naturally Occurring Compound**

A naturally occurring compound **A** containing only C, H and O has the following elemental composition, percentage mass,

C: 63.2 %, H: 5.3%, O: 31.5%.

4.1 Derive the empirical formula of compound **A**.

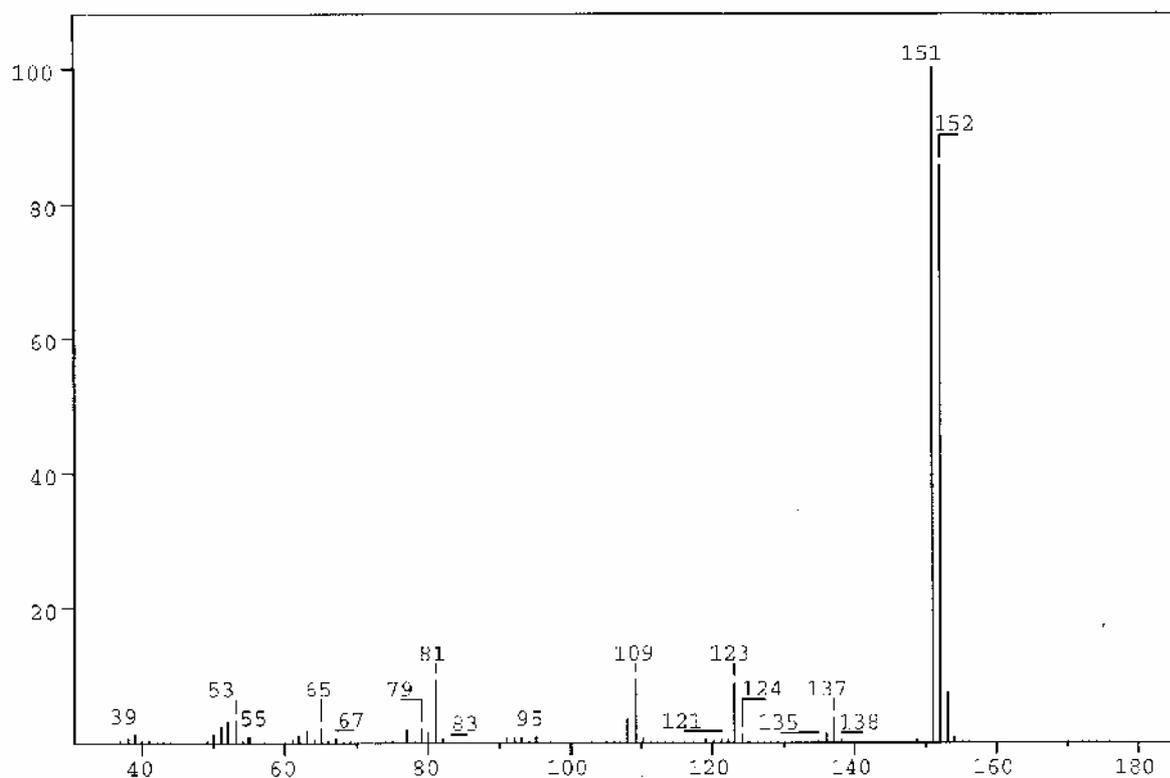


Figure 1

The mass spectrum of compound **A** is shown in Figure 1.

4.2 What is the molecular formula for compound **A**?

A solution of **A** in ether is shaken with an aqueous solution of NaOH. After this, no **A** remains in the ether phase. Another solution of **A** in ether is shaken with an aqueous solution of NaHCO₃. **A** remains in the ether phase.

4.3 Which of the following classes of compounds does **A** belong to according to these experiments? Mark with an X.

- alcohol phenol aldehyde ketone
 acid ester ether

Compound **A** gave rise to formation of a silver mirror with Tollens' reagent ($\text{Ag}(\text{NH}_3)_2^+$).

4-1 Which of the following functional groups does this indicate the presence of in **A**? Mark with an X.

- hydroxy group of an alcohol hydroxy group of a phenol
 carbonyl group of an aldehyde carbonyl group of a ketone
 carboxylic group ester group
 alkoxy group of an ether

Table of Integrals

FROM	TO	VALUE
10.00 PPM	9.69 PPM	0.94
7.56 PPM	7.32 PPM	1.91
7.15 PPM	6.92 PPM	0.93
6.41 PPM	6.20 PPM	0.94
4.02 PPM	3.89 PPM	3.10

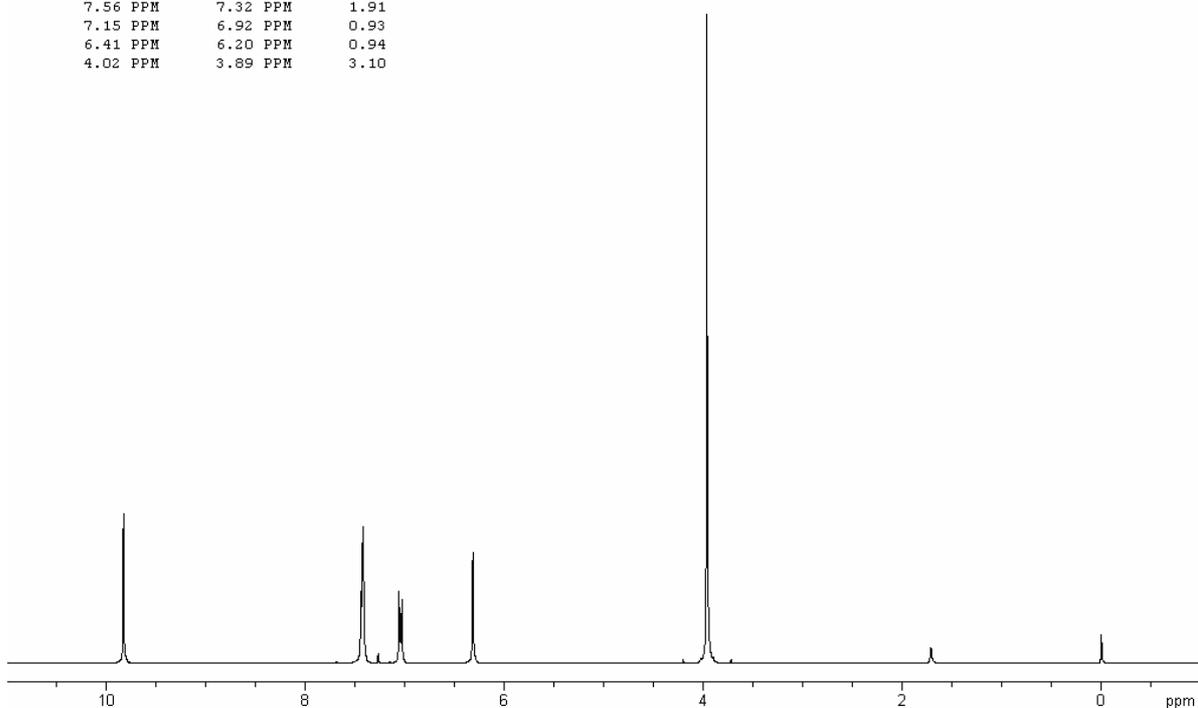


Figure 2a

The ^1H NMR spectrum of compound **A** recorded at 300 MHz is shown in Figure 2a (solvent CDCl_3 (7.27 ppm), reference tetramethylsilane). The signals at 3.9, 6.3 and 9.8 ppm are singlets. Figure 2b is an expansion of the region 6.9 – 7.6 ppm.

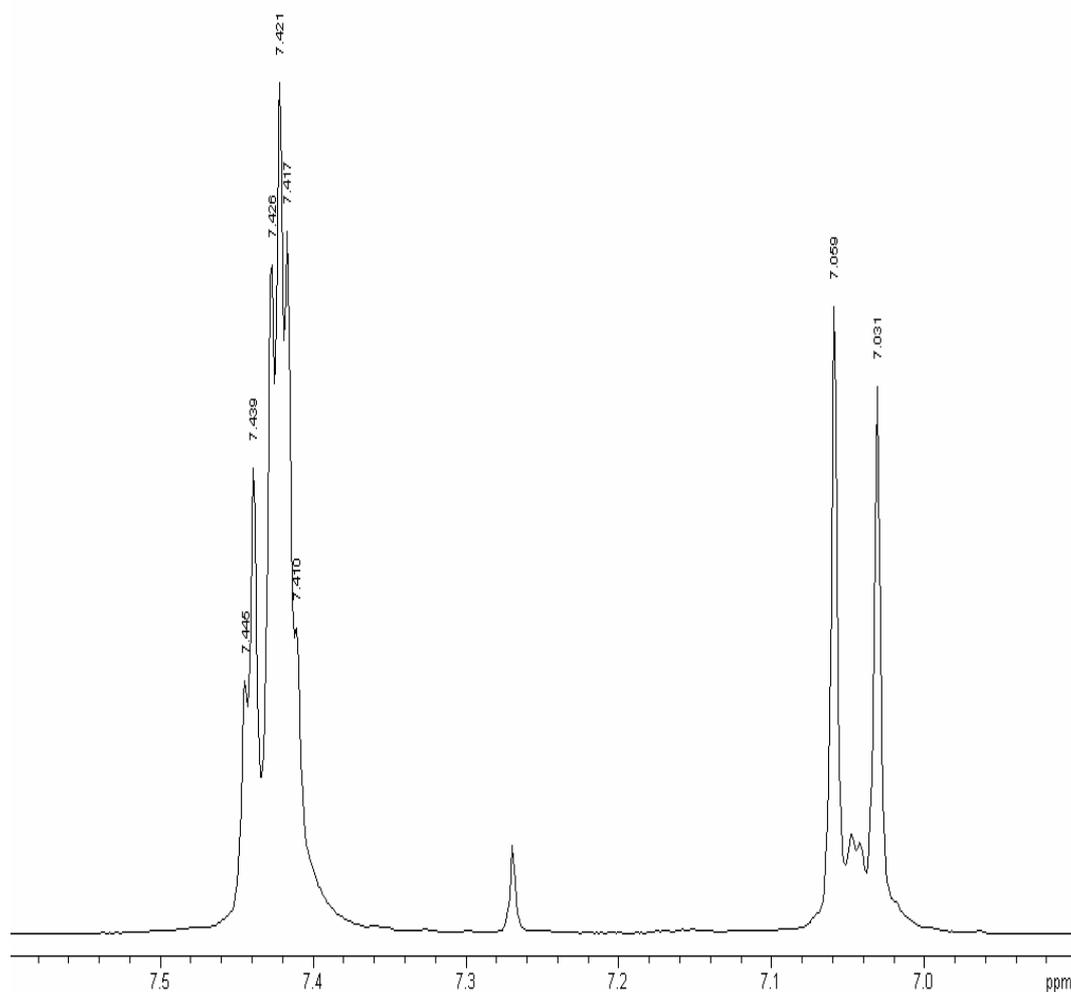


Figure 2b

Selected chemical shift and coupling constant values are given in Table 1.

The signal at 6.3 ppm disappears when a drop of D_2O is added.

4.5 Which of the following does this indicate? Mark with an X.

- Exchange of carbon-bonded hydrogen
- Exchange of oxygen-bonded hydrogen
- Dilution effect
- Hydrolysis

The same signal moves to a lower ppm value upon dilution with CDCl_3 .

4.6 Which of the following does this indicate?

Indicate the true statements (more than one).

- Increased hydrogen bonding
- Decrease in hydrogen bonding
- Intermolecular hydrogen bonding
- Intramolecular hydrogen bonding
- No hydrogen bonding

4.7 Draw the four possible structural formulas for compound **A** based on the information given above

4.8 Give structural formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum.

4.9 Two of the isomers have a lower pK_a value than the others. Write the formulas for those.

Table 1. ^1H Chemical Shift δ

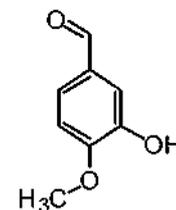
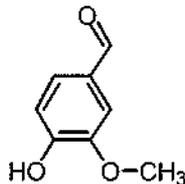
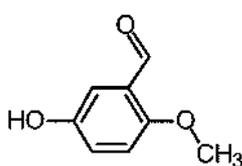
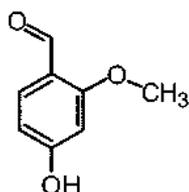
Hydrogens attached to carbon		
<i>Methyl</i>	$\text{CH}_3\text{-C-}$ $\text{CH}_3\text{-C=O-}$ $\text{CH}_3\text{-O-R}$ $\text{CH}_3\text{-OCOR}$	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
<i>Methylene</i>	$\text{CH}_2\text{-C-}$ $\text{CH}_2\text{-C=O-}$ $\text{CH}_2\text{-OR}$ $\text{CH}_2\text{-OCOR}$	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
<i>Methine</i>	CH-	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
<i>Alkene</i>		4.0 – 7.3 ppm depending on the substituent
<i>Aldehyde</i>	R-CHO	9.0 – 10.0 ppm

Table 1 (continued) ¹H Chemical Shift δ

Hydrogens attached to oxygen		
<i>Alcohols</i>	ROH	0.5 – 5.0 ppm
<i>Phenols</i>	ArOH	4.0 – 7.0 ppm
<i>Carboxylic acids</i>	RCOOH	10.0 – 13.0 ppm
Selected spin-spin coupling constants		
<i>Alkanes</i> (free notation)	H-C-C-H vicinal	6 – 8 Hz
<i>Alkenes</i>	trans	11 – 18 Hz
	cis	6 – 12 Hz
	geminal	0 – 3 Hz
<i>Aromates</i>	ortho	6 – 10 Hz
	meta	1 – 4 Hz
	para	0 – 2 Hz

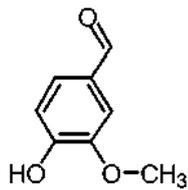
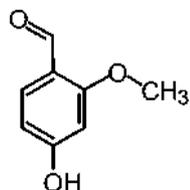
SOLUTION

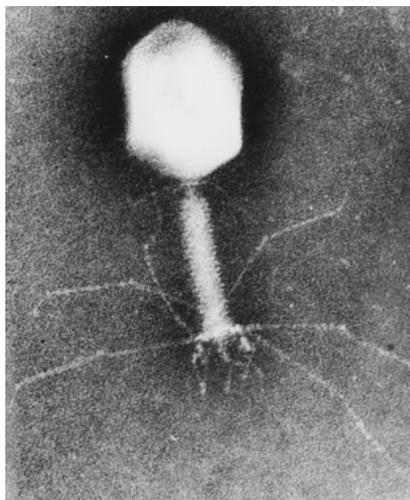
- 4.1 The empirical formula of **A** is C₈H₈O₃.
- 4.2 The molecular formula of compound **A**: C₈H₈O₃.
- 4.3 The compound **A** is a phenol.
- 4.4 Compound **A** forms a mirror with Tollen's reagent. This indicates the presence of carbonyl group of an aldehyde.
- 4.5 It indicates exchange of oxygen-bonded hydrogen.
- 4.6 It indicates:
decrease in hydrogen bonding,
intermolecular hydrogen bonding.
- 4.7 Four possible structural formulas for compound **A**:



4.8 Formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum: CH_3 , HC=O .

4.9 Two isomers having a lower pK_a value than the others:



PROBLEM 5**Protein and DNA**

DNA is composed of 2'-deoxy-nucleotides carrying the bases adenine (A), guanine (G), cytosine (C) and thymine (T). The molar mass of the 2'-deoxy-nucleotide-5'-triphosphates is given in table 2:

Table 2

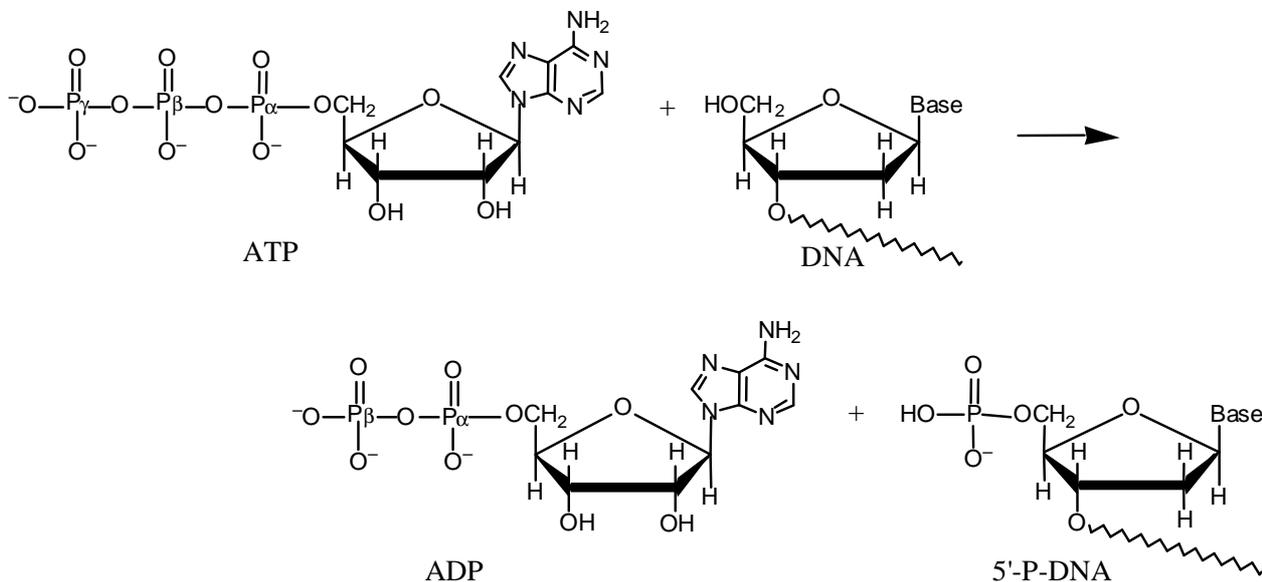
dNTP	Molar mass /g mol ⁻¹
dATP	487
dGTP	503
dCTP	464
dTTP	478

5.1 Calculate the molar mass of a double stranded DNA fragment consisting of 1000 base pairs with a uniform distribution of the four bases.

This DNA fragment can be isolated and cloned by using the PCR method (polymerase chain reaction), in which a heat stable DNA polymerase enzyme multiplies the number of molecules of a specific piece of DNA in a cyclic process. Under optimal conditions the number of double-stranded DNA copies doubles in each cycle. Using the PCR method you perform 30 cycles starting from a single double stranded DNA molecule.

5.2 Calculate the approximate mass of the DNA you obtain from this experiment.

The bacteria-virus T4 enzyme - polynucleotide kinase (PNK) catalyzes the transfer of the terminal phosphate of ATP (γ -orthophosphate) to the 5'-hydroxyl termini of ribo- and deoxyribonucleotides:



PNK is commonly used to label DNA at the 5'-end with the radioactive phosphorus isotope ^{32}P using ATP in which the γ -P (the outermost of the phosphorus atoms) is replaced with ^{32}P . The amount of ^{32}P and thus the amount of labelled DNA can be measured.

A 10 μL solution containing double stranded DNA is labelled 100 % with $[\gamma\text{-}^{32}\text{P}]\text{ATP}$ by PNK. 37 days ago, the specific activity of $[\gamma\text{-}^{32}\text{P}]\text{ATP}$ was 10 Ci/mmol or $370 \cdot 10^9$ Bq/mmol. ^{32}P has a half-life of 14.2 days, and during the decay a β -particle is emitted. Now the labelled DNA emits 40000 β -particles/s.

5-3 Calculate the concentration of the DNA solution.

In an experiment in which PNK is incubated with $[\gamma\text{-}^{32}\text{P}]\text{ATP}$ and single stranded DNA, the reaction can be monitored by isolating labeled DNA and measuring the β -particle emission. Using this kind of measurements in a 1 cm^3 experimental mixture, a labeling of 9 nmol DNA/min was calculated. PNK has a catalytic rate constant (turnover number) of 0.05 s^{-1} and molar mass of 34620 g mol^{-1} .

5.4 Calculate the concentration (in mg/cm^3) of PNK in the experimental mixture.

Aromatic amino acids, tryptophan, tyrosine and phenylalanine absorb UV light of a wavelength between 240 nm and 300 nm. In a protein containing several aromatic amino acids, the sum of the molar absorptivity per amino acid $\Sigma \epsilon_{\text{amino acid}}$, is approximately equal to the molar absorptivity, $\epsilon_{\text{protein}}$, for the protein. The molar absorptivity, $\epsilon_{\text{amino acid}}$, at 280 nm for tyrosine, tryptophan and phenylalanine is $1400 \text{ M}^{-1} \text{ cm}^{-1}$, $5600 \text{ M}^{-1} \text{ cm}^{-1}$ and $5 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The absorbance of a $10 \mu\text{M}$ solution of PNK is 0.644 at 280 nm and with 1.00 cm light path. The amino acid sequence of PNK contains 14 tyrosines and 9 phenylalanines.

($M = \text{mol dm}^{-3}$)

5.5 Calculate the number of tryptophan residues in a PNK molecule.

SOLUTION

5.1 Calculation of the molar mass of a double stranded DNA fragment under given conditions:

dNTP average mass = 483 g mol^{-1} ; $M(\text{HP}_2\text{O}_7^{2-}) = 175 \text{ g mol}^{-1}$;

1000 bp double stranded DNA $M(\text{DNA}) = ((483 - 175) \times 2 \times 1000 + 2 \times 17) \text{ g mol}^{-1} = 616034 \text{ g mol}^{-1}$.

5.2 Calculation of the approximate mass of the DNA you obtaining from the described experiment.

2^{30} copies = 1073741824 copies

Total mass of DNA: $m(\text{DNA}) = 1073741824 / N_A \times 616350 \text{ g mol}^{-1} = 1.1 \text{ ng}$

5.3 Calculation of the concentration of the DNA solution.

$$A = A_0 e^{-kt} \text{ and } k = \frac{\ln 2}{t_{1/2}} \Rightarrow A_0 = \frac{40000}{e^{-0.0488 \times 37}} \text{ dps} = 243464 \text{ dps}$$

It corresponds to $\frac{243464}{370} \text{ pmol } 5' -^{32} \text{ P-DNA} = 658 \text{ pmol } 5' -^{32} \text{ P-DNA}$.

Since volume of the labelled DNA is $10 \mu\text{L}$, the concentration of the DNA is thus approx. $66 \mu\text{M}$.

5.4 Since 9 nmol DNA is labelled per min and the turnover number is 0.05 s^{-1} the amount of PNK that catalyses the labelling is:

$$\frac{9 \text{ nmol min}^{-1}}{0.05 \times 60 \text{ s}} = 3 \text{ nmol}$$

which corresponds to $3 \text{ nmol} \times 34620 \text{ g mol}^{-1} = 0.1 \text{ mg}$.

The concentration of the PNK in mg cm^{-3} is thus 0.1 mg cm^{-3} .

5-5 $\epsilon_{\text{Tryptophan}} = 5600 \text{ M}^{-1} \text{ cm}^{-1}$;

$$\epsilon_{\text{Tyrosine}} = 1400 \text{ M}^{-1} \text{ cm}^{-1}$$
;

$$\epsilon_{\text{Phenylalanine}} = 5 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\epsilon = \frac{A}{c l} \Rightarrow \epsilon_{\text{PNK}} = \frac{0.644}{10 \mu\text{M} \times 1.00 \text{ cm}} = 64400 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\Sigma(\epsilon_{\text{Tyrosine}} + \epsilon_{\text{Phenylalanine}}) = (14 \times 1400) + (9 \times 5) \text{ M}^{-1} \text{ cm}^{-1} = 19645 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\Sigma \epsilon_{\text{Tryptophan}} = \epsilon_{\text{PNK}} - \Sigma(\epsilon_{\text{Tyrosine}} + \epsilon_{\text{Phenylalanine}}) \Rightarrow$$

$$\Sigma \epsilon_{\text{Tryptophan}} = (64400 - 19645) \text{ M}^{-1} \text{ cm}^{-1} = 44755 \text{ M}^{-1} \text{ cm}^{-1}$$

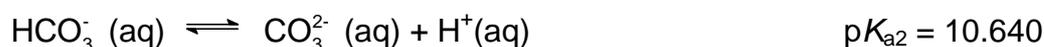
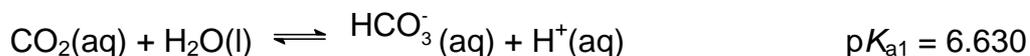
The number of tryptophan residues in a PNK molecule is thus:

$$\frac{44755 \text{ M}^{-1} \text{ cm}^{-1}}{5600 \text{ M}^{-1} \text{ cm}^{-1}} = 8 \text{ residues}$$

PROBLEM 6**Hard Water**

In Denmark the subsoil consists mainly of limestone. In contact with ground water containing carbon dioxide some of the calcium carbonate dissolves as calcium hydrogen carbonate. As a result, such ground water is hard, and when used as tap water the high content of calcium hydrogen carbonate causes problems due to precipitation of calcium carbonate in, for example, kitchen and bathroom environments.

Carbon dioxide, CO₂, is a diprotic acid in aqueous solution. The pK_a-values at 0 °C are:



The liquid volume change associated with dissolution of CO₂ may be neglected for all of the following problems. The temperature is to be taken as being 0 °C.

6.1 The total concentration of carbon dioxide in water which is saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar is 0.0752 mol dm⁻³. Calculate the volume of carbon dioxide gas which can be dissolved in one litre of water under these conditions.

The gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$

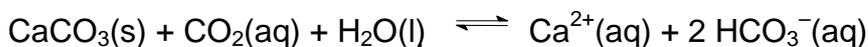
6.2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO₂ in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.3 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium hydrogen carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.4 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effects.

6.5 The solubility of calcium carbonate in water at 0 °C is 0.0012 g per 100 cm³ of water. Calculate the concentration of calcium ions in a saturated solution of calcium carbonate in water.

The hard groundwater in Denmark is formed via contact of water with limestone in the subsoil which reacts with carbon dioxide dissolved in the groundwater according to the equilibrium equation:



The equilibrium constant, K , for this reaction is $10^{-4.25}$ at 0 °C.

- 6.6** Calculate the concentration of calcium ions in water in equilibrium with calcium carbonate in an atmosphere with a partial pressure of carbon dioxide of 1.00 bar.
- 6.7** A 0.0150 M solution of calcium hydroxide is saturated with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the solution by considering the equilibrium equation given above in connection with problem 6.6.
- 6.8** The calcium hydroxide solution referred to in problem 6.7 is diluted to twice the volume with water before saturation with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the resulting solution saturated with CO_2 .
- 6.9** Calculate the solubility product constant for calcium carbonate from the data given above.

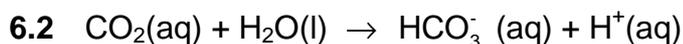
SOLUTION

6.1 $c(\text{CO}_2) = 0.0752 \text{ M}$ $n(\text{CO}_2) = 0.0752 \text{ mol}$

The ideal gas equation: $p V = n R T$

$$1.00 \text{ bar} \times V = 0.0752 \text{ mol} \times 0.08314 \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}$$

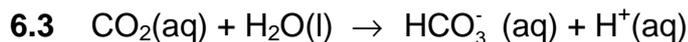
$$V = 1.71 \text{ dm}^3$$



$$[\text{H}^{+}] = [\text{HCO}_3^{-}] = x \quad \text{and} \quad [\text{CO}_2] + [\text{HCO}_3^{-}] = 0.0752$$

$$K_a = 10^{-6.63} = \frac{[\text{H}^{+}][\text{HCO}_3^{-}]}{[\text{CO}_2]} = \frac{x^2}{0.0752 - x}$$

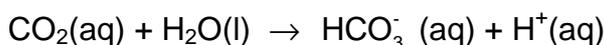
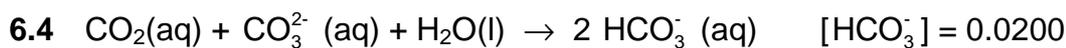
$$[\text{H}^{+}] = 0.000133 \quad \text{and} \quad [\text{CO}_2] = 0.0751$$



$$[\text{CO}_2] = 0.0751 \quad \text{and} \quad [\text{HCO}_3^-] = 0.0100$$

$$K_a = 10^{-6.63} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x \cdot 0.0100}{0.0751}$$

$$x = [\text{H}^+] = 1.76 \times 10^{-6}$$



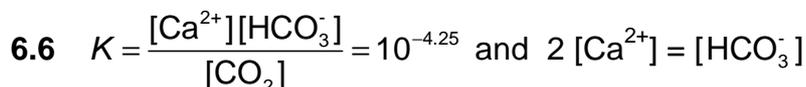
$$K_a = 10^{-6.63} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x \cdot 0.0200}{0.0751}$$

$$x = [\text{H}^+] = 8.8 \times 10^{-7}$$

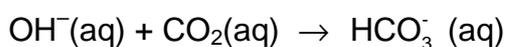
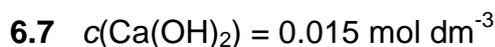


$$0.0012 \text{ g} / 100 \times 0.872 \text{ g mol}^{-1} = 0.000012 \text{ mol CaCO}_3 \text{ in } 100 \text{ cm}^3 \text{ of water}$$

$$[\text{Ca}^{2+}] = 1.2 \times 10^{-4} \quad c(\text{Ca}^{2+}) = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$$



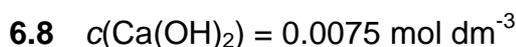
$$\frac{4 [\text{Ca}^{2+}]}{0.0751} = 10^{-4.25} \quad [\text{Ca}^{2+}] = 1.02 \times 10^{-2} \quad c(\text{Ca}^{2+}) = 1.02 \times 10^{-2} \text{ mol dm}^{-3}$$



All hydroxide has been consumed ($K = 10^{7.37}$).

From problem 6.6 we found that the maximum possible calcium ion concentration is smaller, *i.e.* precipitation of CaCO_3

$$[\text{Ca}^{2+}] = 1.02 \times 10^{-2} \quad c(\text{Ca}^{2+}) = 1.02 \times 10^{-2} \text{ mol dm}^{-3}$$



From problem 6.6 we found that the maximum possible calcium ion concentration we can have, is $1.02 \times 10^{-2} \text{ mol dm}^{-3}$, *i.e.* no precipitation of CaCO_3 occurs.

$$[\text{Ca}^{2+}] = 0.75 \times 10^{-2} \quad c(\text{Ca}^{2+}) = 0.75 \times 10^{-2} \text{ mol dm}^{-3}$$

6.9

$$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{CO}_2]} \times \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{CO}_3^{2-}][\text{H}^+]} = \frac{K_{sp} K_{a1}}{K_{a2}}$$

$$K_{sp} = 10^{-8.26}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

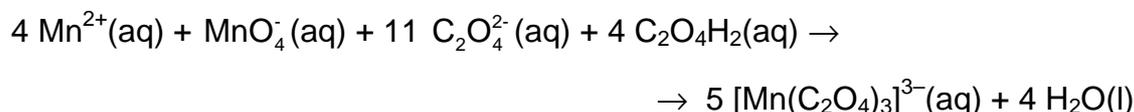
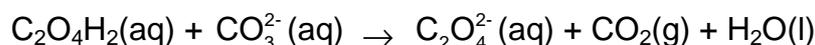
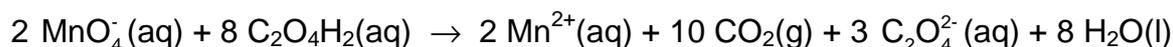
This experiment includes one preparation of a metal complex salt and two analyses of a provided sample of the same compound. The compound is a “classic” within inorganic photo chemistry.

Preparation of Potassium tris(oxalato)manganate(III) Hydrate, $K_3[Mn(C_2O_4)_3] \cdot xH_2O$

Note 1: The $[Mn(C_2O_4)_3]^{3-}$ ion is photosensitive and should therefore be protected from light as far as possible. Also, the thermal stability of the title compound is low.

Note 2: Before starting the synthesis, write down the thermometer reading in ice-water.

The synthesis comprises a reduction of manganese(VII) to manganese(II) with oxalic acid at 70 – 75 °C. After the addition of the sufficient amount of potassium ions in form of potassium carbonate, manganese(III) is formed by the addition of manganese(VII) at a temperature below 2 °C.



Dissolve 5.00 g of $C_2O_4H_2 \cdot 2 H_2O$ in 35 cm³ of water in a 150 cm³ beaker by heating to 70 °C. Slowly add 1.00 g of $KMnO_4$ with magnetic stirring. The temperature must not exceed 70 - 75 °C. When the mixture is colourless, add 1.10 g of K_2CO_3 in small portions and cool the mixture in ice. When the temperature of the mixture has fallen to 25 - 30 °C, add 25 g of crushed ice. Meanwhile, cool the hotplate with a beaker containing ice.

Maintain the temperature of the reaction mixture not more than 2 °C above your reported temperature of ice-water while adding 0.24 g of KMnO_4 in small portions with vigorous stirring. Stir for another 10 min and filter off the white precipitate and unmelted ice, if any, using the 60 cm^3 filter syringe (see procedure A). Collect the filtrate in a 250 cm^3 beaker cooled in ice. Add 35 cm^3 of ice-cold ethanol to the cherry-red filtrate (just swirl the beaker; stirring will lead to the formation of tiny crystals), wrap the beaker in aluminium foil and cool it in ice for 2 h (swirl the beaker three or four times during this period).

Clean the filter - first with 4 M HCl, then with water. Collect the cherry-red crystals by filtration using a 60 cm^3 filter syringe, then wash them two times 5 cm^3 of ethanol and then two times with 5 cm^3 of acetone, and dry the product in air and protect it from light for at least one hour. A brown vial with lid should be taken to be tared by the lab assistant. When dry, the product is placed in the vial. Write name and student code on the vial. Then close the vial and take it and your answer sheet to the lab. assistant who will weigh your sample. The theoretical yield is 7.6 mmol.

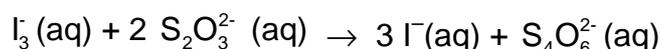
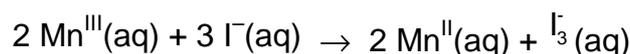
1.1 Record the yield in grams.

1.2 Suggest a molecular formula of the white precipitate which is removed in the first filtration.

Analysis of the Provided Sample of $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot x \text{H}_2\text{O}$ for Oxidizing Ability

Note 3: The burette contains a cleanser and should therefore be rinsed 3 - 4 times with water before use.

Manganese(III) is reduced to manganese(II) by iodide ions and the triiodide ions formed are then titrated with thiosulfate.



In a 250 cm^3 conical flask dissolve 1.0 g of KI in 25 cm^3 of demineralized water and add 10 cm^3 of 4 M HCl. Immediately after an accurately preweighed sample (approx. 200 mg) of the provided complex is transferred (as much as possible is poured directly into the

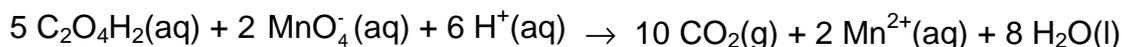
liquid in small portions before the residue is washed down) quantitatively with demineralized water to the flask. Titrate the I_3^- formed with the standardized, approx. 0.025 M $Na_2S_2O_3$ solution. When the brown colour has faded to light yellow, add 2 cm³ of starch indicator solution and continue the titration until the colour changes from blue to colourless.

1.3 Calculate the molar mass of the analyzed compound from the titration data.

Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x H_2O$ for Reducing Ability

Note 4: The burette should be rinsed 2 - 3 times with water before this titration.

Manganese(III) is reduced to manganese(II) by the oxalate ligands, and excess oxalate is titrated with permanganate.



Transfer an accurately preweighed sample (approx. 200 mg) of the provided complex quantitatively with demineralized water to a 250 cm³ conical flask. Add 25 cm³ of 2 M sulphuric acid and heat the solution to 75 – 80 °C. Without further heating, titrate with the standardized, approx. 0.025 M $KMnO_4$ solution. Near the end of the titration add the titrant slowly, until one drop gives the solution a rose colour which does not fade on standing for 0.5 min.

1.4 Calculate the molar mass of the analyzed compound from the titration data.

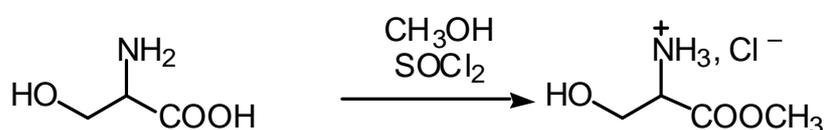
The results of the two types of analysis may differ by up to 10 %. Use only the result from the titration with $KMnO_4$ for the following calculation.

1.5 Calculate the value of x in the formula $K_3[Mn(C_2O_4)_3] \cdot x H_2O$ and the yield of your preparation in percent of the theoretical yield.

PROBLEM 2 (Practical)**Synthesis of Amino Acid Methyl Ester Hydrochloride**

In the synthesis of peptides, one amino acid is reacted with another to form an amide bond between them. In order to ensure that the individual amino acids do not form amide bonds with themselves and that only one product is formed, the amino group in the first amino acid and the carboxyl group in the second amino acid are masked before the peptide synthesis.

The procedure described below can be used for masking the carboxylic acid groups in amino acids before peptide formation.



The experiment should be performed in a ventilated hood since thionyl chloride is an irritant and since irritating gases are evolved during the reaction.

Thionyl chloride is a corrosive acid chloride. Avoid contact with skin and eyes. Splashes in eyes or on skin should be flushed immediately with water. Thionyl chloride in larger amounts reacts violently with water.

Procedure

Absolute methanol (2.0 cm³) is transferred quickly to a dry test tube which is then closed with a piece of aluminium foil. The foil is used as a lid throughout the subsequent manipulations with the tube. This protects the content from moisture from the air. The methanol is cooled in an ice-bath for 1 – 2 min. Thionyl chloride, handle with care, see above (0.52 cm³) is drawn up into a 1 cm³ graduated syringe with polyethylene tube tip, as described in separate procedure B, and is cautiously added to the methanol over a period of approximately 5 min.

The mixture is kept at 0 °C for approx. 2 min. (S)-Serine (0.210 g, weighed sample provided) is added and the mixture is kept at room temperature for approx. 2 min before gently heating to boiling (using a sand bath) for 10 min. All material should then have dissolved.

The mixture is cooled in an ice-bath for approx. 2 min. Dry *tert.*-butyl methyl ether (10 cm³) is then added. The inside wall of the test tube is scratched at the surface region of the solution with a glass spatula for about 1 min. and the test tube is then left in the ice-bath for a further 5 –15 min for crystallization. The separated crystals are then isolated by filtration as described in separate procedure A. The filtrate is collected in a 100 cm³ beaker.

The crystals are washed two times on the filter, each time with 1 cm³ of *tert.*-butyl methyl ether. The filter cake is finally pressed with the piston, and the crystals are pre-dried by pumping air through the filter cake with the piston.

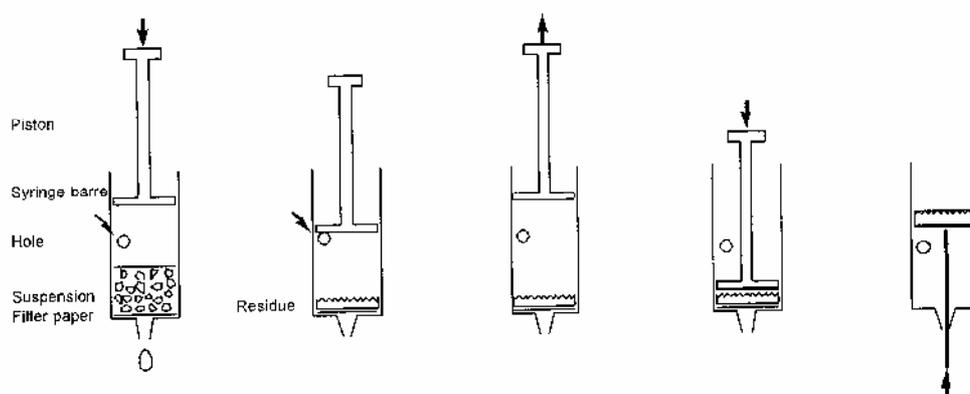
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

PROCEDURE A

Filtration procedures

Modified syringes are used for filtration in the laboratory tasks. A 60 cm³ syringe with a disc of porous polypropylene is used in task 1, while a 10 cm³ syringe with a disc of filtration paper is used in task 2. The procedure is sketched on Fig. 1.

Fig. 1: Micro-scale filtration in plastic syringe



Procedure:

1. Fill the syringe from above with suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Close hole and press piston for filtration.
3. Stop before passing the hole.
4. Open hole and draw piston back.
5. Repeat steps 2-4 a couple of times.
6. Remove piston and place filter paper on top of the filter cake.
7. Press piston against filter cake.
8. Push filter cake out with straightened- out paper clip.

Filtration procedure for practical problem 1

The provided filter syringe to be used in this experiment is made from a 60 cm³ standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 35 cm³ mark. With a plastic spatula a disc of porous polypropylene, which fits tightly inside the syringe, is pressed down to be positioned at the base of the syringe. The mixture to be filtered is applied without the piston inserted. Drops of solution may be moved downwards by tapping the syringe against a solid surface,

The piston is now placed in the syringe and gently pressed down while keeping the hole closed with a finger so to promote the passage of solvent through the filter. When the piston reaches just above the hole, the finger is removed from the hole, and the piston is drawn back again to the top position. This cycle can then be repeated a couple of times, until the filter cake looks dry. Remember to close the drilled hole, then the piston is moved downwards and to open the hole, when the piston is moved upwards. The filter cake can be washed and the washing solution pressed out using similar cycles.

Solvent remaining in the outlet can be sucked up with a small piece of tissue paper. The solid is then removed from the syringe and collected on a piece of weighing paper for drying.

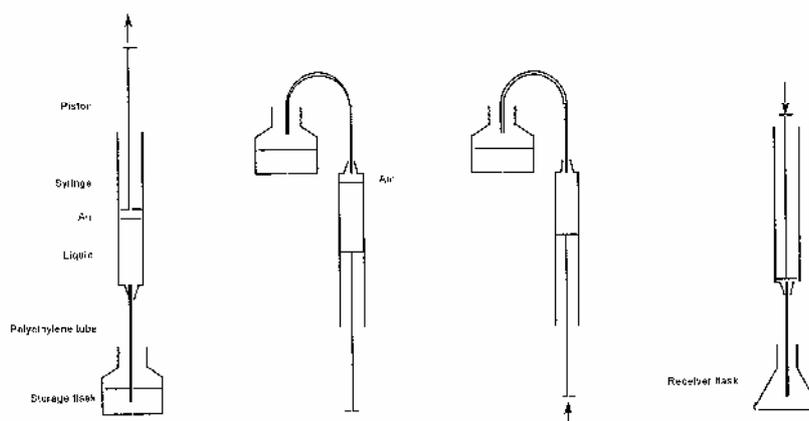
Filtration procedure for practical problem 2

The provided filter syringe to be used in this experiment is made from a 10 cm³ standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 5.5 cm³ mark. A piece of filter paper which fits snugly in the syringe is pressed down to the bottom with the piston. Filtration and washing are then performed as described for task 1. Before removing the filter cake the piston is withdrawn. A piece of filter paper fitting the syringe is then pressed all the way down to the filter cake using the piston. The filter cake is pressed by means of the piston. Then the piston is then drawn back and out the syringe (slowly, until the hole is reached). This leaves the filter cake between two pieces of filter paper. Solvent remaining in the outlet can be sucked up with a small piece of tissue paper.

The filter cake is cautiously pushed out of the syringe using an straightened-out metal paper clip introduced through the outlet of the syringe. The solid material is then removed from the syringe, if possible as a coherent plug. The residue is collected on a piece of filter paper for drying by using a small metal spatula. Filter paper from the filtration can be fixed with the paper clip tip while adhering solid is removed using the spatula.

PROCEDURE B

Fig. 2. Measuring volumes of liquids using a syringe



Procedure:

1. Suck up a slight excess of liquid in syringe.

2. Turn syringe upside down; the tip of the tube is kept in the storage nottle. Air in the syringe is accumulated at its top.
 3. Air in the syringe is removed by pressing the piston. Press further until desired volume of liquid is left in the syringe. The tip of the tube is kept in the storage bottle.
 4. Turn the syringe, place tip of the tube in the receiver flask and press piston until desired volume of liquid has left the syringe.
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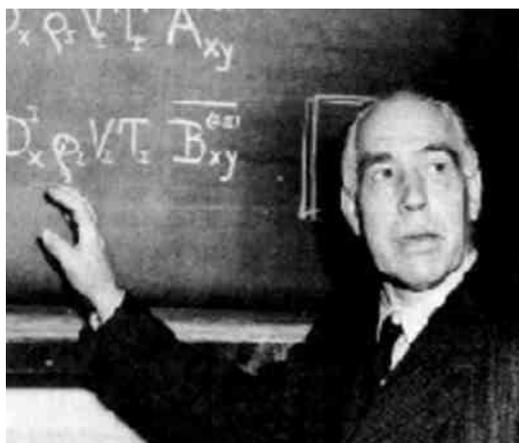
**7 theoretical problems
3 practical problems**

THE THIRTY-THIRD INTERNATIONAL CHEMISTRY OLYMPIAD 6–15 JULY 2001, MUMBAI, INDIA

THEORETICAL PROBLEMS

PROBLEM 1

Hydrogen Atom and Hydrogen Molecule



Niels Bohr (1885-1962)

The observed wavelengths in the line spectrum of hydrogen atom were first expressed in terms of a series by Johann Jakob Balmer, a Swiss teacher. Balmer's empirical formula is

$$\frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{2^2} - \frac{1}{n^2} \right); \quad n = 3, 4, 5, \dots$$

Here, $R_{\text{H}} = \frac{m_e e^4}{8 \epsilon_0^2 h^3 c} = 109\,678 \text{ cm}^{-1}$

is the Rydberg konstant, m_e is the mass of an electron. Niels Bohr derived this expression theoretically in 1913. The formula is easily generalized to any one electron atom/ion.

1.1 Calculate the longest wavelength in Å ($1 \text{ Å} = 10^{-10} \text{ m}$) in the 'Balmer series' of singly ionized helium (He^+). Ignore nuclear motion in your calculation.

1.2 A formula analogous to Balmer's formula applies to the series of spectral lines which arise from transitions from higher energy levels to the lowest energy level of hydrogen atom. Write this formula and use it to determine the ground state energy of a hydrogen atom in eV.

A 'muonic hydrogen atom' is like a hydrogen atom in which the electron is replaced by a heavier particle, the muon. The mass of a muon is about 207 times the mass of an electron, while its charge is the same as that of an electron. A muon has a very short lifetime, but we ignore its unstable nature here.

1.3 Determine the lowest energy and the radius of the first Bohr orbit of the muonic hydrogen atom. Ignore the motion of the nucleus in your calculation. The radius of the first Bohr orbit of a hydrogen atom

(called the Bohr radius, $a_0 = \frac{\epsilon_0 h^2}{m_e e^2 \pi}$) is 0.53 Å.

The classical picture of an "orbit" in Bohr's theory has now been replaced by the quantum mechanical notion of an 'orbital'. The orbital $\psi_{1s}(r)$ for the ground state of a hydrogen atom is given by

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi} a_0^3} e^{-\frac{r}{a_0}}$$

where r is the distance of the electron from the nucleus and a_0 is the Bohr radius.

1.4 Consider a spherical shell of radius a_0 and thickness $0.001a_0$. Estimate the probability of finding the electron in this shell. Volume of a spherical shell of inner radius r and small thickness Δr equals $4\pi r^2 \Delta r$.

The H₂ molecule can dissociate through two different channels:

- (i) H₂ → H + H (two separate hydrogen atoms)
- (ii) H₂ → H⁺ + H⁻ (a proton and a hydride ion)

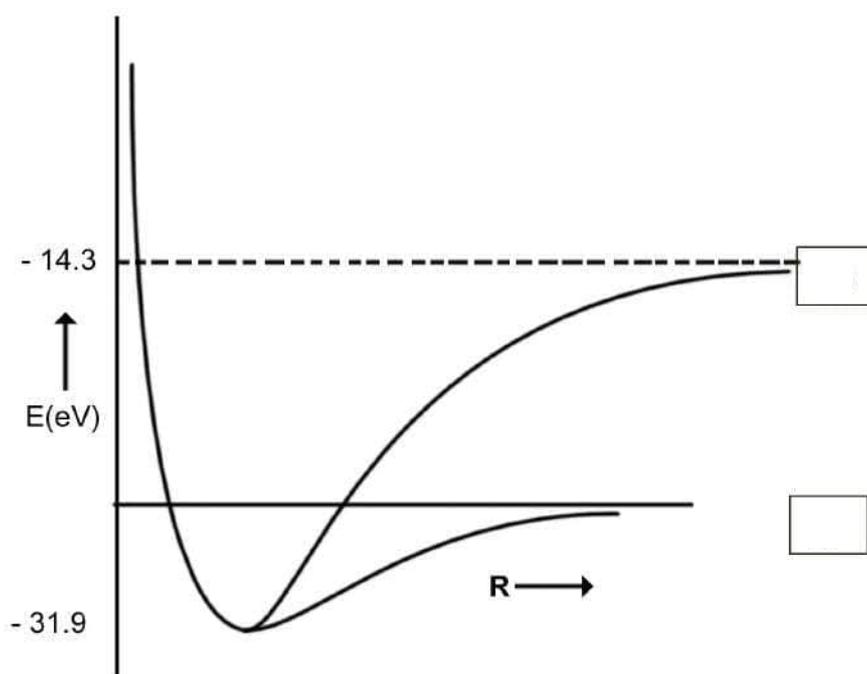
The graph of energy (E) vs internuclear distance (R) for H₂ is shown schematically in the figure. The atomic and molecular energies are given in the same scale.

1.5 Put appropriate channel labels (i) or (ii) in the boxes below.

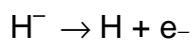
1.6 Determine the values of the dissociation energies (D_e in eV) of the H_2 molecule corresponding to

channel (i)

channel (ii)



1.7 From the given data, calculate the energy change for the process



1.8 H^- is a two-electron atomic system. Assuming that the Bohr energy formula is valid for each electron with nuclear charge Z replaced by Z_{eff} , calculate Z_{eff} for H^- .

SOLUTION

1.1 Longest wavelength λ_L corresponds to $n = 3$

For He^+

$$\frac{1}{\lambda} = 4R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

$$\lambda_L = 1641.1 \text{ \AA}$$

$$1.2 \quad \frac{1}{\lambda} = 4R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$$

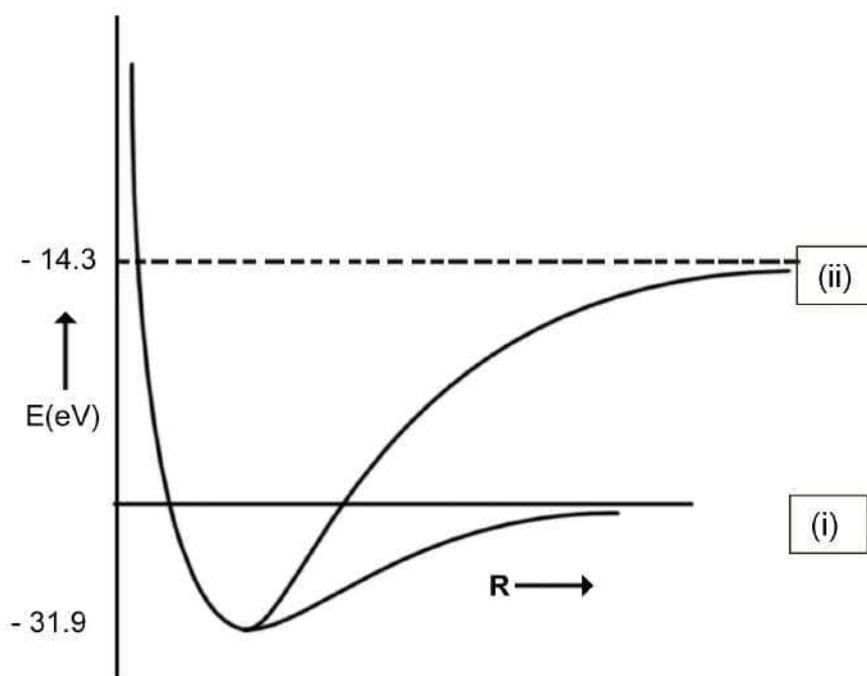
$$E = -hcR_H = -13.6 \text{ eV}$$

$$1.3 \quad \text{Lowest energy} = -207 \times 13.6 = -2.82 \text{ keV}$$

$$\text{Radius of the first Bohr orbit} = 0.53 / 207 = 2.6 \times 10^{-3} \text{ \AA}$$

$$1.4 \quad \text{Probability} = |\psi(a_0)|^2 4\pi a_0^2 \times 0.001 a_0 = 0.004 e^{-2} = 5.41 \times 10^{-4}$$

1.5



$$1.6 \quad \text{Channel (i): } 4.7 \text{ eV}$$

$$\text{Channel (ii): } 17.6 \text{ eV}$$

$$1.7 \quad \text{Electron affinity} = -13.6 - (-14.3) = 0.7 \text{ eV}$$

$$1.8 \quad Z_{\text{eff}} = -13.6 + 27.2 Z_{\text{eff}}^2 = 0.7$$

PROBLEM 2

Phosphoric Acid

Phosphoric acid is of a great importance in fertilizer industry. Besides, phosphoric acid and its various salts have a number of applications in metal treatment, food, detergent and toothpaste industries.

2.1 The pK values of the three successive dissociations of phosphoric acid at 25 °C are:

$$pK_{1a} = 2.12$$

$$pK_{2a} = 7.21$$

$$pK_{3a} = 12.32$$

Write down the conjugate base of dihydrogen phosphate ion and determine its pK_b value.

Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and root beers. A cola having a density of 1.00 g cm⁻³ contains 0.05 % by weight of phosphoric acid.

2.2 Determine the pH of the cola (ignoring the second and the third dissociation steps for phosphoric acid). Assume that the acidity of the cola arises only from phosphoric acid.

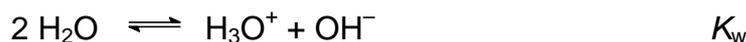
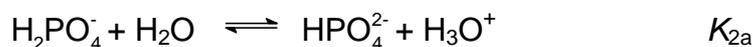
2.3 Phosphoric acid is used as a fertiliser for agriculture. 1.00×10^{-3} M phosphoric acid is added to an aqueous soil suspension and the pH is found to be 7.00.

Determine the fractional concentrations of all the different phosphate species present in the solution. Assume that no component of the soil interacts with any phosphate species.

2.4 Zinc is an essential micronutrient for plant growth. Plant can absorb zinc in water soluble form only. In a given soil water with $pH = 7.0$, zinc phosphate was found to be the only source of zinc and phosphate. Calculate the concentration of $[Zn^{2+}]$ and $[PO_4^{3-}]$ ions in the solution. K_{sp} for zinc phosphate is 9.1×10^{-33} .

SOLUTION

2.1 The conjugate base of dihydrogen phosphate (H_2PO_4^-) is monohydrogen phosphate (HPO_4^{2-}):



$$pK_{2a} + pK_{2b} = pK_w = 14$$

$$pK_{2b} = 6.79$$

2.2 Concentration of $\text{H}_3\text{PO}_4 = \frac{0.5}{98} = 0.0051 \text{ M}$



$$0.0051 - x \quad \quad \quad x \quad + \quad x$$

$$pK_{1a} = 2.12 \quad \text{gives} \quad K_{1a} = 7.59 \times 10^{-3}$$

$$7.59 \times 10^{-3} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{0.0051 - x}$$

$$x = [\text{H}_3\text{O}^+] = 3.49 \times 10^{-3}$$

$$pH = 2.46$$

2.3 Let $f_0 = \frac{[\text{H}_3\text{X}]}{C}$, $f_1 = \frac{[\text{H}_2\text{X}^-]}{C}$,

$$f_2 = \frac{[\text{HX}^{2-}]}{C} \quad \text{and} \quad f_3 = \frac{[\text{X}^{3-}]}{C}$$

denote the fractional concentrations of different phosphate species. C is the total initial concentration of H_3X . ($\text{X} = \text{PO}_4$)

$$f_0 + f_1 + f_2 + f_3 = 1$$

$$K_{1a} = \frac{[\text{H}_2\text{X}^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{X}]} = \frac{f_1}{f_0} [\text{H}_3\text{O}^+]$$

$$K_{2a} = \frac{[\text{HX}^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{X}^-]} = \frac{f_2}{f_1} [\text{H}_3\text{O}^+]$$

$$K_{3a} = \frac{[X^{3-}][H_3O^+]}{[HX^{2-}]} = \frac{f_3}{f_2} [H_3O^+]$$

These equations lead to

$$f_0 = \frac{[H_3O^+]^3}{D}, \quad f_1 = \frac{K_{1a}[H_3O^+]^2}{D}, \quad f_2 = \frac{K_{1a}K_{2a}[H_3O^+]}{D}, \quad f_3 = \frac{K_{1a}K_{2a}K_{3a}}{D}$$

$$\text{where } D = K_{1a}K_{2a}K_{3a} + K_{1a}K_{2a}[H_3O^+] + K_{1a}[H_3O^+]^2 + [H_3O^+]^3$$

From the values of pK_{1a} , pK_{2a} , pK_{3a} and pH one gets

$$K_{1a} = 7.59 \times 10^{-3}; \quad K_{2a} = 6.17 \times 10^{-8}; \quad K_{3a} = 4.79 \times 10^{-13}; \quad [H_3O^+] = 1 \times 10^{-7}$$

The fractional concentrations of different phosphate species are:

$$H_3PO_4 \quad (f_0) = 8.10 \times 10^{-6}$$

$$H_2PO_4^- \quad (f_1) = 0.618$$

$$HPO_4^{2-} \quad (f_2) = 0.382$$

$$PO_4^{3-} \quad (f_3) = 1.83 \times 10^{-6}$$

2.4 Let S (mol dm^{-3}) be the solubility of $Zn_3(PO_4)_2$ in soil water.

$$[Zn^{2+}] = 3S$$

Total concentration of different phosphate species = $2S$

$$[PO_4^{3-}] = f_3 \times 2S$$

f_3 can be determined from the relation derived in **2.3**

$$\text{For } pH = 7, \quad f_3 = 1.83 \times 10^{-6}$$

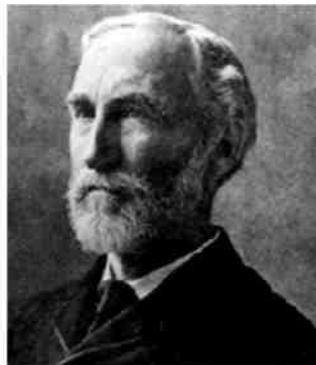
$$K_{sp} = [Zn^{2+}]^3 [PO_4^{3-}]^2$$

$$9.1 \times 10^{-33} = (3S)^3 (f_3 \times 2S)^2$$

$$[Zn^{2+}] = 9 \times 10^{-5}$$

$$[PO_4^{3-}] = 1.1 \times 10^{-10}$$

$$\text{Solubility of } Zn_3(PO_4)_2 = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$$

PROBLEM 3**Second Law of Thermodynamics**

J.W. Gibbs (1839–1903)

The second law of thermodynamics is a fundamental law of science. In this problem we consider the thermodynamics of an ideal gas, phase transitions and chemical equilibrium.

3.00 mol of CO₂ gas expands isothermally (in thermal contact with the surroundings; temperature = 15 °C) against a fixed external pressure of 1.00 bar. The initial and final volumes of the gas are 10.0 dm³ and 30.0 dm³, respectively.

3.1 Choose the correct option for change in the entropy of the system (ΔS_{sys}) and of the surroundings (ΔS_{sur}):

- | | | | |
|-----|-----------------------------|-----------------------------|--------------------------|
| (a) | $\Delta S_{\text{sys}} > 0$ | $\Delta S_{\text{sur}} = 0$ | <input type="checkbox"/> |
| (b) | $\Delta S_{\text{sys}} < 0$ | $\Delta S_{\text{sur}} > 0$ | <input type="checkbox"/> |
| (c) | $\Delta S_{\text{sys}} > 0$ | $\Delta S_{\text{sur}} < 0$ | <input type="checkbox"/> |
| (d) | $\Delta S_{\text{sys}} = 0$ | $\Delta S_{\text{sur}} = 0$ | <input type="checkbox"/> |

(Mark X in the correct box.)

3.2 Calculate ΔS_{sys} assuming CO₂ to be an ideal gas.

3.3 Calculate ΔS_{sur} .

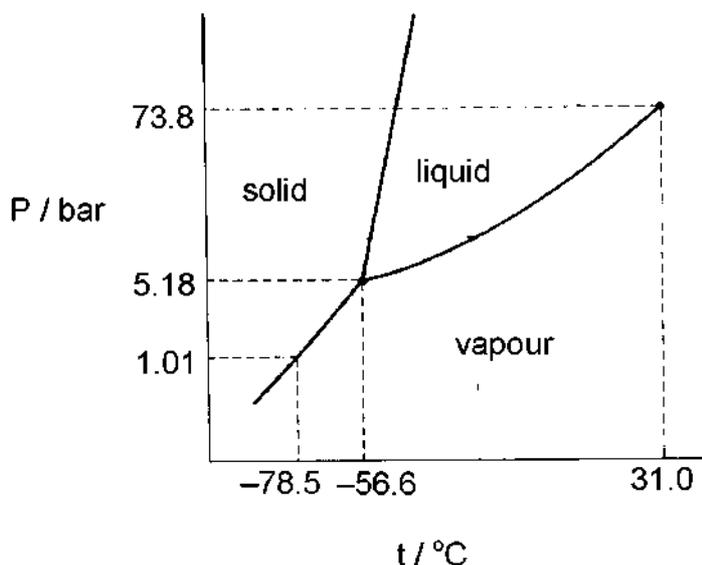
3.4 Calculate the change in entropy of the universe.

Does your answer agree with the Second Law of Thermodynamics?

(Mark X in the correct box.)

Yes No

The pressure – temperature phase diagram of CO₂ is given below schematically. The diagram is not to scale.



Phase diagram of CO₂

3.5 CO₂ gas, initially at a pressure of 4.0 bar and temperature of 10.0 °C is cooled at constant pressure. In this process,

(a) it goes first to the liquid phase and then to the solid phase.

(b) it goes to the solid phase without going through the liquid phase.

3.6 Starting with the same pressure and temperature as above (in 3.5), CO₂ is compressed isothermatically. In this process,

(a) it goes first to the liquid phase and then to the solid phase.

(b) it goes to the solid phase without going through the liquid phase.

3.7 From the data given in the phase diagram, calculate the molar enthalpy change of sublimation of CO₂. Write down the formula used.

3.8 CO gas, used extensively in organic synthesis, can be obtained by reacting CO₂ gas with graphite. Use the data given below to show that the equilibrium constant at 298.15 K is less than unity.

At 298.15 K

CO₂(g): $\Delta H_f^0 = -393.51 \text{ kJ mol}^{-1}$; $S^0 = 213.79 \text{ J K}^{-1} \text{ mol}^{-1}$

CO(g): $\Delta H_f^0 = -110.53 \text{ kJ mol}^{-1}$; $S^0 = 197.66 \text{ J K}^{-1} \text{ mol}^{-1}$

C(graphite) $S^0 = 5.74 \text{ J K}^{-1} \text{ mol}^{-1}$

- 3.9** Estimate the temperature at which the reaction would have an equilibrium constant equal to 1. Ignore slight variations in the thermodynamic data with temperature.
- 3.10** The reaction above (in 3.8) is carried out between CO₂ and excess hot graphite in a reactor maintained at about 800 °C and a total pressure of 5.0 bar. The equilibrium constant K_p under these conditions is 10.0. Calculate the partial pressure of CO at equilibrium.

SOLUTION

3.1 Correct solution: (c) $\Delta S_{\text{sys}} > 0$ $\Delta S_{\text{sur}} < 0$

3.2 Since ΔS_{sys} is independent of path, it is the same as for isothermal reversible expansion of an ideal gas.

$$\Delta S_{\text{sys}} = nR \ln \frac{V_f}{V_i} = 27.4 \text{ JK}^{-1}$$

3.3 $q = p_{\text{ext}} \Delta V$

$$\Delta S_{\text{sur}} = -\frac{q}{T} = -6.94 \text{ JK}^{-1}$$

3.4 $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 20.5 \text{ JK}^{-1}$

The answer agrees with the second law of thermodynamics (correct is YES)

3.5 Correct answer:

(b) it goes to the solid phase without going through the liquid phase.

3.6 Correct answer:

(a) it goes first to the liquid phase and then to the solid phase.

$$\mathbf{3.7} \quad \ln \frac{p_2}{p_1} = -\frac{\Delta H_{\text{sub}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta H_{\text{sub}} = 26.1 \text{ kJ mol}^{-1}$$

$$3.8 \quad \Delta H^0 = 172.45 \text{ kJ mol}^{-1}$$

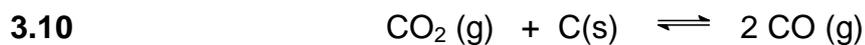
$$\Delta S^0 = 176 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 120 \text{ kJ mol}^{-1}$$

$$\Delta G^0 > 0 \text{ implies } K < 1$$

$$3.9 \quad \Delta G^0 = 0 \text{ when } \Delta H^0 = T\Delta S^0$$

$$T = 980 \text{ K}$$



$$1 - \alpha \qquad \qquad \qquad 2\alpha$$

$$\text{Partial pressure: } \frac{1-\alpha}{1-\alpha} \times 5 \qquad \qquad \qquad \frac{2\alpha}{1-\alpha} \times 5$$

$$K_p = \frac{p^2(\text{CO})}{p(\text{CO}_2)}$$

$$p(\text{CO}) = 3.7 \text{ bar}$$

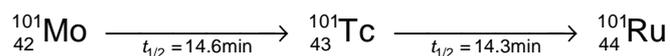
PROBLEM 4**Beach Sand Mineral in Kerala**

Beach sand mineral, monazite, is a rich source of thorium, available in large quantities in the state of Kerala in India. A typical monazite sample contains about 9 % ThO₂ and 0.35 % U₃O₈. ²⁰⁸Pb and ²⁰⁶Pb are the stable end-products in the radioactive decay series of ²³²Th and ²³⁸U, respectively. All the lead (Pb) found in monazite is of radiogenic origin.

The isotopic atom ratio ²⁰⁸Pb/²³²Th, measured mass spectrometrically, in a monazite sample was found to be 0.104. The half-lives of ²³²Th and ²³⁸U are 1.41×10¹⁰ years and 4.47×10⁹ years, respectively. Assume that ²⁰⁸Pb, ²⁰⁶Pb, ²³²Th and ²³⁸U remained entirely in the monazite sample since the formation of monazite mineral.

- 4.1 Calculate the age (time elapsed since its formation) of the monazite sample.
- 4.2 Estimate the isotopic atom ratio ²⁰⁶Pb/²³⁸U in the monazite sample.
- 4.3 Thorium-232 is a fertile material for nuclear energy. In thermal neutron irradiation, it absorbs a neutron and the resulting isotope forms ²³³U by successive β⁻ decays. Write the nuclear reactions for the formation of ²³³U from ²³²Th.

In nuclear fission of ²³⁵U a complex mixture of radioactive fission products is formed. The fission product ¹⁰¹Mo initially undergoes radioactive decay as shown below:



- 4.4 A freshly prepared radiochemically pure sample of ¹⁰¹Mo contains 5000 atoms of ¹⁰¹Mo initially. How many atoms of
 - i) ¹⁰¹Mo
 - ii) ¹⁰¹Tc
 - iii) ¹⁰¹Ru
 will be present in the sample after 14.6 min?

SOLUTION

$$4.1 \quad N = N_0 e^{-\frac{0.6931 t}{t_{1/2}}}$$

$$\frac{N_0 - N}{N} = e^{\frac{+0.6931 t}{t_{1/2}}} - 1$$

$(N_0 - N)$ = Total number of ^{232}Th atoms decayed. = Total number of ^{208}Pb atoms formed.

$$\frac{N_0 - N}{N} = 0.104$$

$$e^{\frac{0.6931 t}{1.41 \times 10^{10}}} = 1.104$$

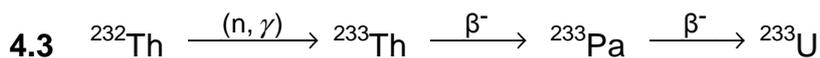
$$t = 2.01 \times 10^9 \text{ years.}$$

4.2 Let x be the required ratio.

$$x = e^{\frac{+0.6931 t}{t_{1/2}}} - 1$$

where $t = 2.01 \times 10^9$ years, and $t_{1/2} = 4.47 \times 10^9$ years.

$$x = 0.366$$



4.4 (i) The number of atoms of ^{101}Mo (N_1) in the sample after one half-life is :

$$N_1 = 2500$$

(ii) The number of atoms of ^{101}Tc (N_2) is given by

$$N_2 = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where $N_0 (= 5000)$ is the initial number of atoms of ^{101}Mo .

$$\lambda_1 = \frac{0.693}{14.6} \text{ min}^{-1}$$

$$\lambda_2 = \frac{0.693}{14.3} \text{ min}^{-1}$$

At $t = 14.6$ min

$$N_2 = 1710$$

(iii) Number of atoms of ^{101}Ru (N_3) at $t = 14.6$ min is :

$$N_3 = N_0 - N_1 - N_2 = 790 \text{ atoms}$$

PROBLEM 5

Halogen Chemistry

Halogens in their reactions among themselves and with a variety of other elements give rise to a large number of compounds with diverse structure, bonding and chemical behaviour. Metal halides, halogen derivatives and interhalogens represent major types of halogen compounds.

(A) Photography

A "black and white" photographic film contains a coating of silver bromide on a support such as cellulose acetate.

- 5.1 Write the photochemical reaction that occurs when light falls on AgBr(s) coated on a film.
- 5.2 During the developing process, unexposed AgBr is washed away by complexation of Ag(I) by sodium thiosulphate solution. Write down this chemical reaction.
- 5.3 These washings are often disposed of as waste. However, metallic silver can be recovered from them by adding cyanide, followed by zinc. Write down the reactions involved.

(B) Shapes, spectra and reactivity

The most reactive halogen, fluorine, reacts with other halogens Cl₂, Br₂ and I₂ under controlled conditions giving a tetra-atomic, hexa-atomic and an octa-atomic molecule, respectively.

- 5.4 Write the formulae and 3-dimensional structures of these interhalogen molecules on the basis of VSEPR theory. Show the disposition of the lone pairs on the central atom, where appropriate.

A mixture of iodine vapour and chlorine gas when fed into a mass spectrometer gave two sets (A and B) of mass spectral peaks corresponding to molecular ions of two chemical species at m/z :

A: 162, 164

B: 464, 466, 468, 470, 472, 474, 476

5.5 Identify the molecular species corresponding to $m/z = 162$, 164 , 466 and 476 . Draw the structure of the heaviest species ($m/z = 476$) indicating clearly the lone pairs on atom(s) of I (iodine). Show the isotopic composition of each species.

In aqueous medium chlorine gas oxidises sodium thiosulphate to an ion containing the highest oxidation state of sulphur.

5.6 Write down the chemical equation for this reaction.

5.7 Write down the Lewis dot structure of the thiosulphate ion. Circle the sulphur atom that has the lower oxidation state.

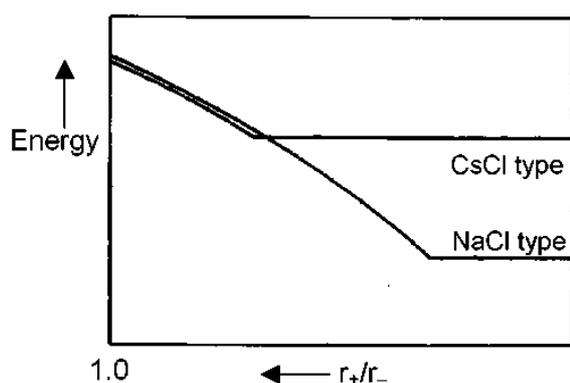
5.8 Chlorine dioxide reacts with sodium hydroxide as shown below. Identify the products X and Y (both containing chlorine) and balance the equation.

5.9 Reaction of chlorine an alkali is used by manufacturing bleach. Write the chemical reaction for its formation.

5.10 Write the oxidation state(s) of chlorine in bleach.

(C) Alkali metal halides and X-ray crystallography

X-ray crystallography reveals many aspects of the structure of metal halides. The radius ratio (r_+/r_-) is a useful parameter to rationalise their structure and stability. A table of radius ratio (r_+/r_-) for some alkali halides with radius ratio (r_- kept constant) is shown schematically for NaCl-type and CsCl-type crystal structures.



	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Cl ⁻	0.33	0.52	0.74	0.82	0.93
Br ⁻	0.31	0.49	0.68	0.76	0.87
I ⁻	0.28	0.44	0.62	0.69	0.78

5.11 For a given anion, the graph for NaCl-type structure levels off at low r_+/r_- values because of

- (a) cation-cation contact along the face diagonal.
- (b) anion-anion contact along the face diagonal.
- (c) cation-anion contact along the cell edge.

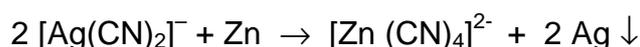
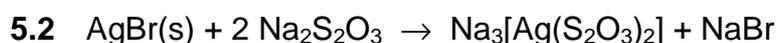
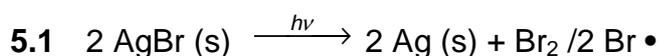
(Mark X in the correct box.)

- 5.12 Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl-type to CsCl-type structure with change of temperature and / or pressure?
- 5.13 Show by calculation the radius ratio (r_+/r_-) at which the energy of CsCl-type structure levels off.
- 5.14 Using $\text{CuK}\alpha$ X-rays ($\lambda = 154 \text{ nm}$), diffraction by a KCl crystal (fcc structure) is observed at an angle (θ) of 14.2° . Given that (i) diffraction takes place from the planes with $h^2 + k^2 + l^2 = 4$, (ii) in a cubic crystal $d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$, where "d" is the distance between adjacent hkl planes and "a" is a lattice parameter, and (iii) reflections in an fcc structure can occur only from planes with "all odd" or "all even" hkl (Miller) indices, calculate the lattice parameter "a" for KCl.
- 5.15 Indicate in the table given below the required information for the 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

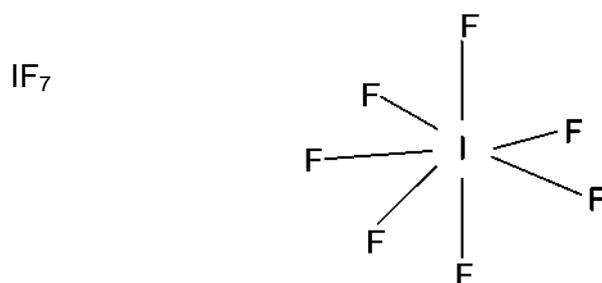
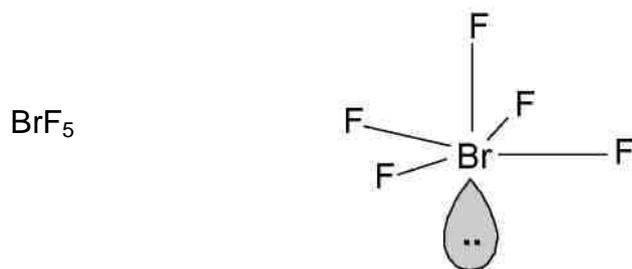
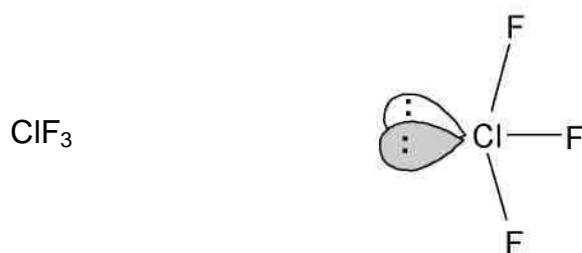
2 nd nearest neighbours			3 rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

- 5.16 Determine the lowest value of diffraction angle θ possible for the KCl structure.

SOLUTION

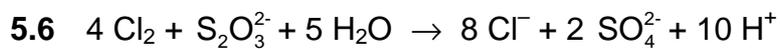


5.4

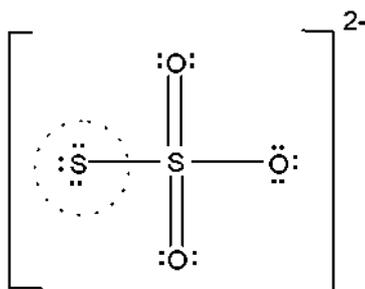


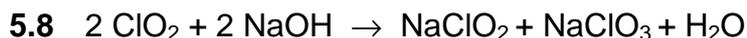
5.5.

Mass:	162	164	466	476
Species:	I^{35}Cl	I^{37}Cl	$\text{I}_2^{35}\text{Cl}_5^{37}\text{Cl}$	$\text{I}_2^{37}\text{Cl}_6$

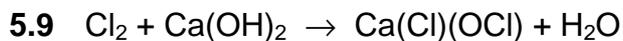


5.7

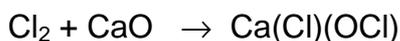




X Y



or



or



5.10 The oxidation state(s) of chlorine in bleach is (are): -I and I

5.11 Correct answer: (b) anion–anion contact along the face diagonal.

5.12 RbBr

5.13 In CsCl-type structure,

Cell edge, $a = 2r$

Body diagonal: $\sqrt{3}a = 2(r_+ + r_-)$

$$\frac{r_+}{r_-} = \sqrt{3} - 1 = 0.732$$

5.14 $\lambda = 2d \sin \theta$

$$d_{200} = \frac{\lambda}{2 \sin \theta} = 314 \text{ pm}$$

$$d_{200} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} = \frac{a}{(2^2 + 0^2 + 0^2)^{1/2}} = \frac{a}{2}$$

$$a = 628 \text{ pm}$$

5.15 The 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2 nd nearest neighbours			3 rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)
12	+	444	8	-	544

5.16 Lowest θ value is for the plane with $hkl = (111)$

$$d = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{628}{\sqrt{3}} = 363 \text{ pm}$$

$$\sin \theta_{111} = \frac{\lambda}{2 d_{111}} = \frac{154 \text{ pm}}{2 \times 363 \text{ pm}} = 0.212$$

$$\theta_{111} = 12.2^\circ$$

PROBLEM 6**Organic Chemistry of Indian Spices**

The rhizomes of ginger (*Zingiber officinale*) are well known for their medicinal and flavouring properties. In Ayurveda (the traditional system of medicine in India) different formulations of ginger are used for the treatment of gastrointestinal problems, common cold and other ailments. Several compounds are responsible for the pungency of ginger. Many are simple substituted aromatic compounds with different side chains. Three of them, Zingerone, (+)[6] Gingerol (to be referred hereafter as Gingerol only), and Shogaol are particularly important.

Zingerone: $C_{11}H_{14}O_3$

Gingerol: $C_{17}H_{24}O_4$

Shogaol: $C_{17}H_{24}O_3$

6.1 Zingerone gives positive $FeCl_3$ and 2,4-DNP (2,4-dinitrophenylhydrazine) tests. It does not react with Tollen's reagent. Therefore, Zingerone contains the following functional groups: (Mark X in the correct boxes.)

- | | | | |
|------------------------|--------------------------|------------------|--------------------------|
| (a) alcoholic hydroxyl | <input type="checkbox"/> | (e) ester | <input type="checkbox"/> |
| (b) aldehydic carbonyl | <input type="checkbox"/> | (f) alkoxy | <input type="checkbox"/> |
| (c) ketonic carbonyl | <input type="checkbox"/> | (g) unsaturation | <input type="checkbox"/> |
| (d) phenolic hydroxyl | <input type="checkbox"/> | | |

The data obtained from the 1H NMR spectrum of Zingerone are shown in Table 1. Some other relevant information is given in Table 2.

Table 1: ¹H NMR spectral data on Zingerone

Chemical shifts (δ)	Multiplicity	Relative intensity
2.04	singlet	3
2.69, 2.71	two (closely spaced) triplets of equal intensity	4
3.81	singlet	3
5.90	broad singlet (D ₂ O exchangeable)	1
6.4 – 6.8	two doublets with similar chemical shifts and one singlet	3

*) For clarity, some of the data have been altered slightly.)

Table 2: Approximate ¹H chemical shifts (δ) and spin-spin coupling constants (J) of some protons

¹ H Chemical shifts			
alkyl - H	0.9 - 1.5	$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ -\text{C}-\text{CH}-\text{C}- \\ \end{array}$	3.4 - 3.6
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{CH} \\ \diagup \quad \diagdown \end{array}$	2.0 - 2.7	$\begin{array}{c} \quad \quad \quad \text{H} \\ \quad \quad \quad / \\ \diagdown \text{C}=\text{C} \diagup \\ \diagup \quad \diagdown \end{array}$	4.0 - 7.0
Ph - CH	2.3 - 2.9	Ph - H	6.0 - 8.0
- O - CH	3.3 - 3.9	Ar - OH	4.0 - 11.0

Spin-spin coupling constants (J)

Alkenes	<i>cis</i>	5 – 14 Hz (commonly around 6 – 8 Hz)
	<i>trans</i>	11 – 19 Hz (commonly around 14 – 16 Hz)

Zingerone on bromination with bromine water gives only one nuclear mono brominated product. The IR spectrum of Zingerone indicates the presence of a weak *intramolecular* hydrogen bond. The same is present even after Clemmensen reduction (Zn – Hg/HCl) of Zingerone.

6.2 From the information above deduce the following:

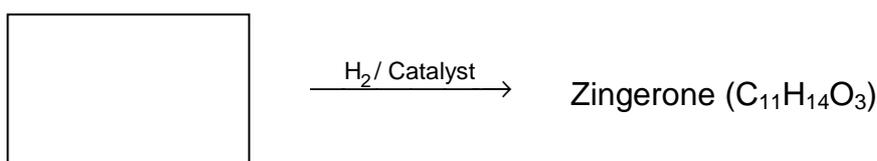
- i) side chain in Zingerone
- ii) substituent on the aromatic ring
- iii) relative positions of the substituents on the ring

6.3 Draw a possible structure of Zingerone based on the above inferences.

6.4 Complete the following reaction sequence for the synthesis of Zingerone.

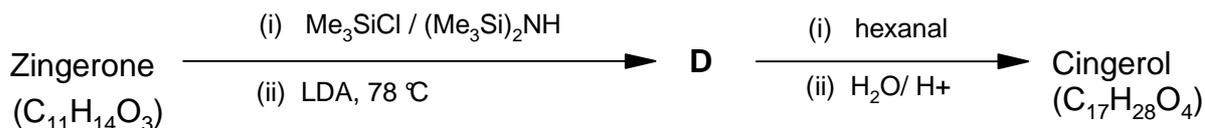


A + **B** (C₃H₆O)



C

6.5 Zingerone can be easily converted into Gingerol by the following reaction sequence:



Notes: (1) Me₃SiCl / (Me₃Si)₂NH is used to convert OH into –OSiMe₃; the group –SiMe₃ can be removed by acid hydrolysis.

(2) LDA is lithium diisopropylamine, a strong, very hindered, non-nucleophilic base.

- i) Draw the structure of **D**.
- ii) Draw the structure of Gingerol.
- iii) Complete the Fischer projection of the *R*-enantiomer of Gingerol.
- iv) In the above reaction sequence (6.5), about 2 – 3 % another constitutional isomer (**E**) of Gingerol is obtained. Draw the likely structure of **E**.
- v) Will the compound **E** be formed as
- | | |
|--|--------------------------|
| (a) a pair of enantiomers? | <input type="checkbox"/> |
| (b) a mixture of diastereomers? | <input type="checkbox"/> |
| (c) a mixture of an enantiomeric pair and a meso isomer? | <input type="checkbox"/> |
- (Mark X in the correct box.)
- vi) Gingerol (C₁₇H₂₆O₄) when heated with a mild acid (such as KHSO₄) gives Shogaol (C₁₇H₂₄O₃). Draw the structure of Shogaol.

6.6 Turmeric (*Curcuma longa*) is a commonly used spice in Indian food. It is also used in Ayurvedic medicinal formulations. Curcumin (C₂₁H₂₀O₆), an active ingredient of turmeric, is structurally related to Gingerol. It exhibits keto-enol tautomerism. Curcumin is responsible for the yellow colour of turmeric and probably also for the pungent taste.

The ¹H NMR spectrum of the keto form of Curcumin shows aromatic signal similar to that of Gingerol. It also shows a singlet around δ 3.5 (2H) and two doublets (2H each) in the region δ 6 – 7 with *J* = 16 Hz. It can be synthesized by condensing TWO moles of **A** (refer to **6.4**) with one mole of pentan-2,4-dione.

- i) Draw the stereochemical structure of Curcumin.
- ii) Draw the structure of the enol form of Curcumin.
- iii) Curcumin is yellow in colour because it has
- | | |
|-----------------------------|--------------------------|
| (a) a phenyl ring | <input type="checkbox"/> |
| (b) a carbonyl group | <input type="checkbox"/> |
| (c) an extended conjugation | <input type="checkbox"/> |
| (d) a hydroxyl group | <input type="checkbox"/> |
- (Mark X in the correct box.)

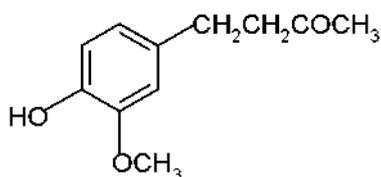
SOLUTION

6.1 Zingerone contains the following functional groups:

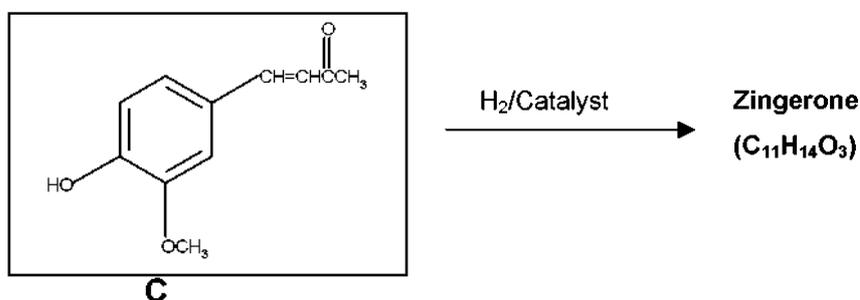
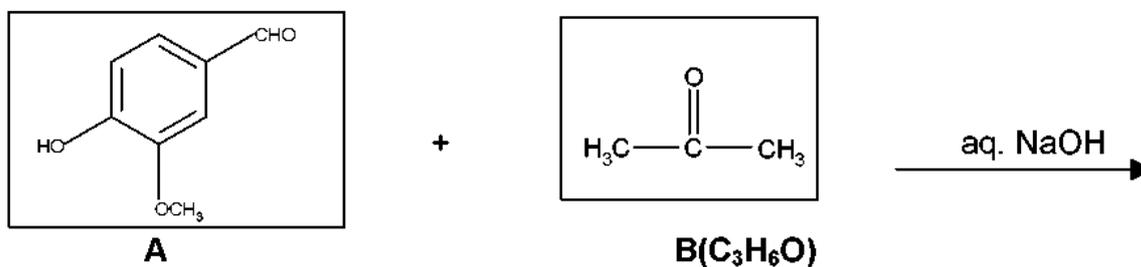
- (c) ketonic carbonyl
- (d) phenolic hydroxyl

- 6.2 i) side chain in Zingerone: $\text{CH}_2\text{CH}_2\text{COCH}_3$
 ii) substituents on the aromatic ring: OH , OCH_3
 iii) relative positions of the substituents on the ring: 1, 2, 4

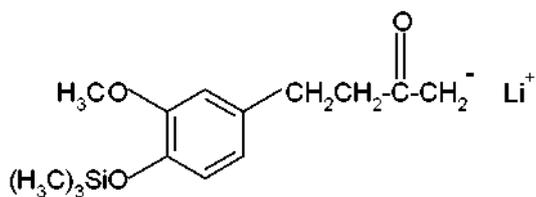
6.3



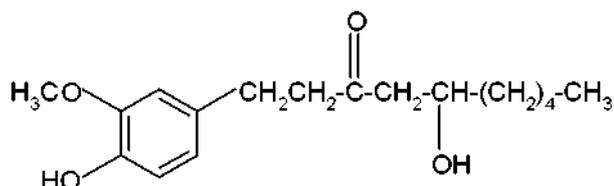
6.4



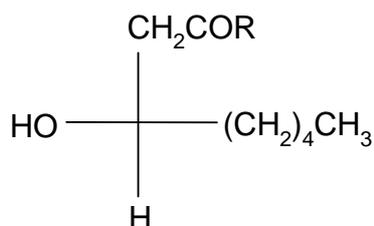
6.5 i)



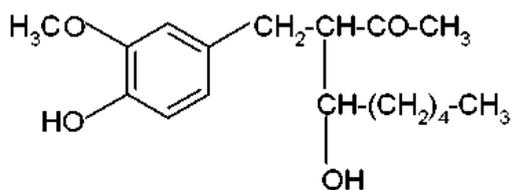
ii)



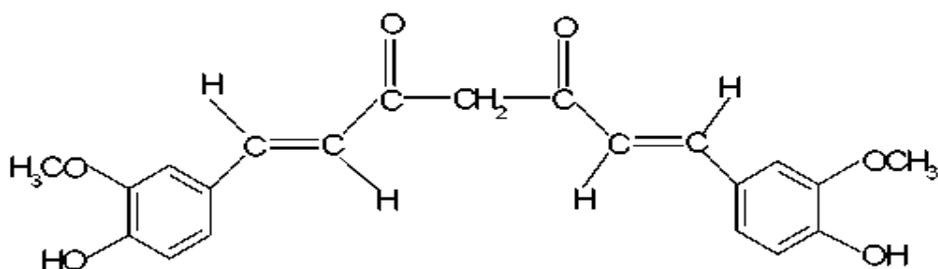
iii)



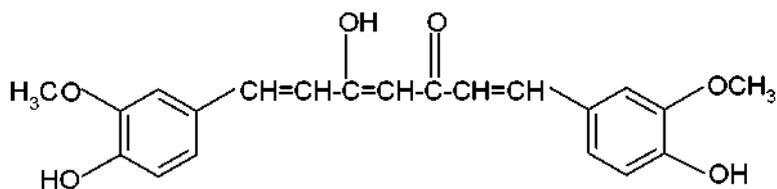
iv)


 v) Compound **E** will be formed as: (b) a mixture of diastereomers

6.6 i)



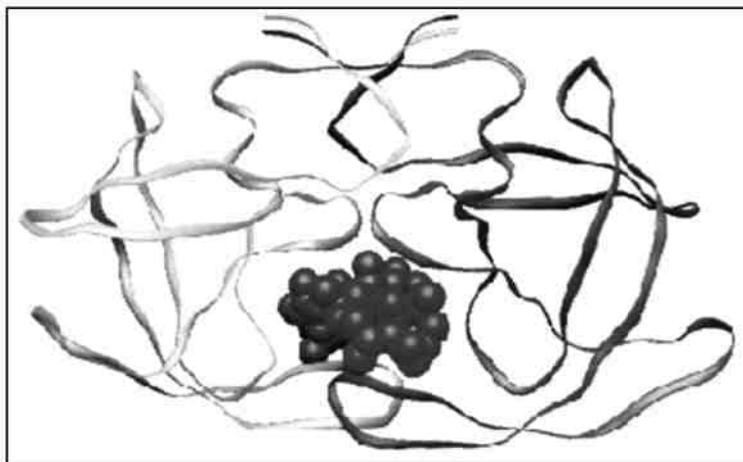
ii)



iii) Curcumin is yellow in colour because it has:
(c) an extended conjugation.

PROBLEM 7

Peptides and Proteins

*Protein folding*

Proteins (polypeptides) are known to assume a variety of backbone conformations. In one conformation, the backbone is almost fully extended arrangement (as in a parallel or anti-parallel β -sheet), and in another conformation it is in a fully folded arrangement (as in an α -helix).

7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately:

- (a) 10 Å
- (b) 15 Å
- (c) 20 Å
- (d) 25 Å

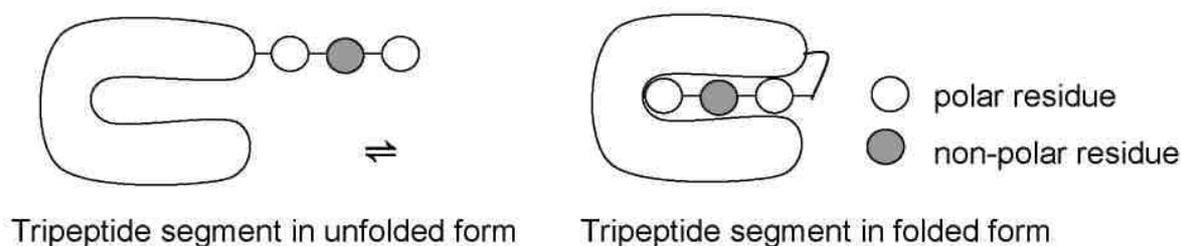
(Mark X in the correct box.)

7.2 Assuming that the following hexapeptide is a α -helix conformation, draw a connecting arrow between an oxygen atom and an amide NH with which it is hydrogen bonded.

7.3 The following hexapeptides (**A** and **B**) display contrasting conformations in water at *pH* 7.0, especially when their serine hydroxyls are phosphorylated. **A** is moderately helical and it becomes a stronger helix on serine phosphorylation. **B** is weakly helical and it is completely disordered on serine phosphorylation. Draw connecting arrows to indicate the interactions between the residues that are responsible for this differing behaviour.

Consider the following process of folding/unfolding of a tripeptide segment in a large protein. The free energy change (ΔG) will depend on the interaction of the unfolded tripeptide with the solvent (water) and with the rest of the protein in the folded state (see below). Assume that the tripeptide is made up of one non-polar (hydrophobic; shaded) and two polar (hydrophilic; unshaded) residues. Assume the following approximate changes in the interaction free energies :

- (a) a non-polar residue and the solvent (water): $\Delta G = +8 \text{ kJ mol}^{-1}$
 (b) a non-polar residue and the rest of the protein: $\Delta G = -4 \text{ kJ mol}^{-1}$
 (c) a polar residue and the solvent (water): $\Delta G = -16 \text{ kJ mol}^{-1}$
 (d) a polar residue and the rest of the protein: $\Delta G = -14 \text{ kJ mol}^{-1}$

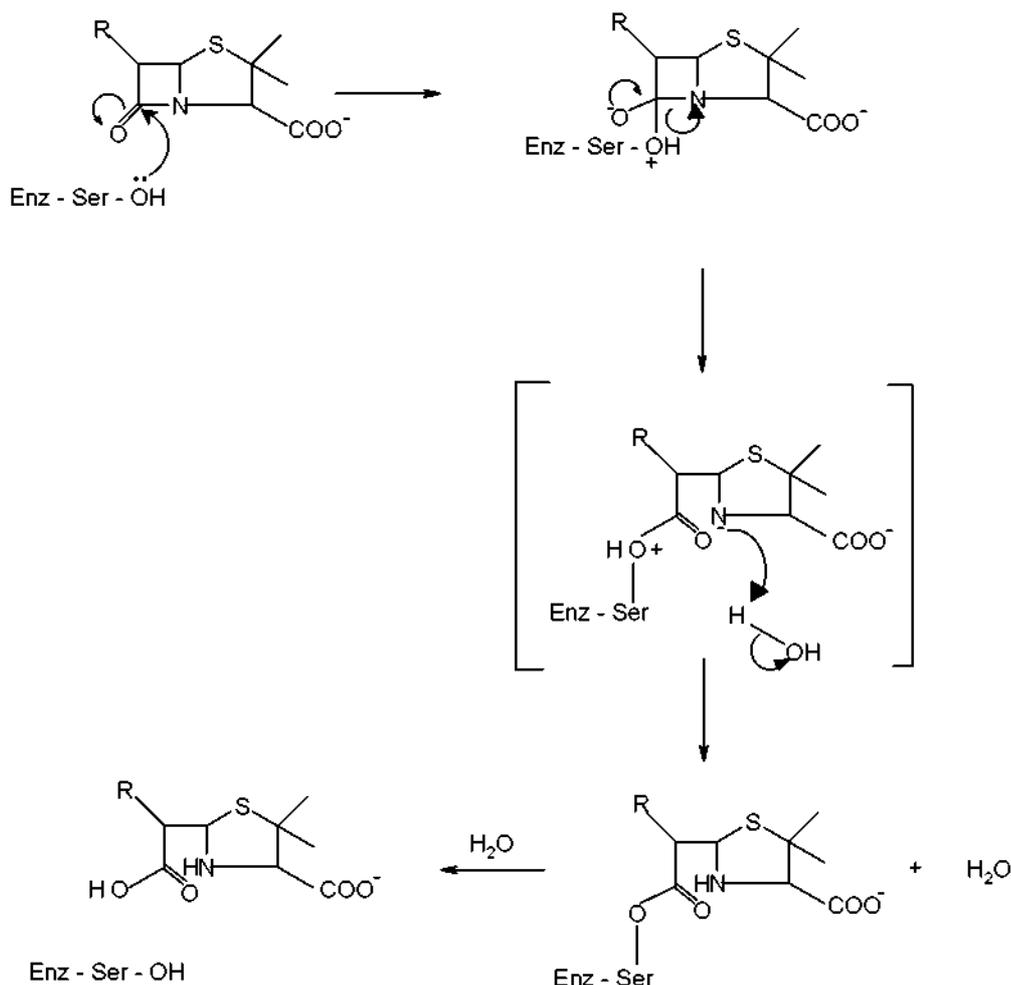


7.4 Calculate ΔG for the folding of the tripeptide segment.

7.5 Calculate ΔG for the folding of the tripeptide segment if all the three residues are polar.

β - lactamase and drug resistance

Penicillins are effective drugs in combating bacterial infections. An alarming development over the years has, however, been the emergence of drug resistant bacteria. Penicillin resistance arises due to the secretion of an enzyme called β -lactamase (also known as penicillinase), which inactivates penicillin by opening its β -lactam ring. The mechanism for this β -lactam ring opening involves the nucleophilic attack by serine-OH at the active site of the enzyme as shown below.



An attempt was made to characterize the β -lactamase from *Staphylococcus aureus*. When the pure enzyme was treated with a radiolabelled [^{32}P] phosphorylating agent, only the active site serine got labelled. On analysis, this serine {molecular mass = 105 mass units (Da)} constituted 0.35% by weight of the β -lactamase.

7.6 Estimate the minimal molecular mass of this β -lactamase.

7.7 The approximate number of amino acid residues present in a protein of this size is :

- (a) 100
- (b) 150
- (c) 275
- (d) 375

[Mark X in the correct box.]

To map its active site, the β -lactamase was hydrolysed using trypsin, a specific enzyme. This resulted in a hexapeptide P1 containing the active site serine. Amino acid analysis revealed the following in equimolar proportion : Glu, Leu, Lys, Met, Phe and Ser. Treatment of P1 with Edman's reagent (phenyl isothiocyanate) yielded phenyl thiohydantoin (PTH) derivative of phenylalanine and a peptide P2.

Treatment of P1 with cyanogen bromide (CNBr) gave an acidic tetrapeptide P3 and a dipeptide P4.

Treatment of P2 with 1-fluoro-2,4-dinitrobenzene, followed by complete hydrolysis, yielded N-2,4-dinitrophenyl-Glu. P1, P2, and P3 contain the active site serine.

7.8 From the above information, deduce the amino acid sequence of P1, P2, P3 and P4.

7.9 Calculate the molecular mass of P3 in mass units (Da) from the information given in the attached Table.

The β -lactamase active site provides a unique microenvironment that makes the catalytic serine-OH an unusually reactive nucleophile. The first order rate constant for β -lactamase catalysed reaction is 350 s^{-1} . For penicillin hydrolysis by free serine-OH (at 1 M) in solution, the pseudo first order rate constant is 0.5 s^{-1} .

7.10 From the information above, calculate the effective concentration of this nucleophile at the enzyme active site?

A molecule competing with penicillin for binding to the β -lactamase active site can inhibit the enzyme. Dissociation constants (K_D) for the inhibitor-lactamase complex for three different inhibitors are given below :

	Inhibitor Dissociation constant (K_D)
A	2.0×10^{-3}
B	1.0×10^{-6}
C	5.0×10^{-9}

7.11 Indicate which of these inhibitors is most effective in protecting penicillin against β -lactamase. [Mark X in the correct box]

- A
- B
- C

A β -lactamase inhibitor was designed rationally. On binding to the enzyme active site, a nucleophilic attack by the OH group of serine resulted in the opening of the β -lactam moiety of the inhibitor and elimination of Br^- . A reactive electrophile is generated as a result and it captures an active site residue X, inactivating the enzyme.

7.12 Based on the above information, identify the electrophile (A) generated and the final product (B) formed in the enzyme inactivation by the inhibitor shown.

Table

Amino Acid	Structure	Molecular mass (Da)
Glu – Glutamic acid	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{COOH} \\ \\ \text{H} \end{array}$	147
Hms – Homoserine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ \\ \text{H} \end{array}$	119
Leu – Leucine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	131
Met – Methionine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{S} - \text{CH}_3 \\ \\ \text{H} \end{array}$	149
Lys – Lysine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \\ \\ \text{H} \end{array}$	146
Phe – Phenylalanine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{C}_6\text{H}_5 \\ \\ \text{H} \end{array}$	165

Table (continued)

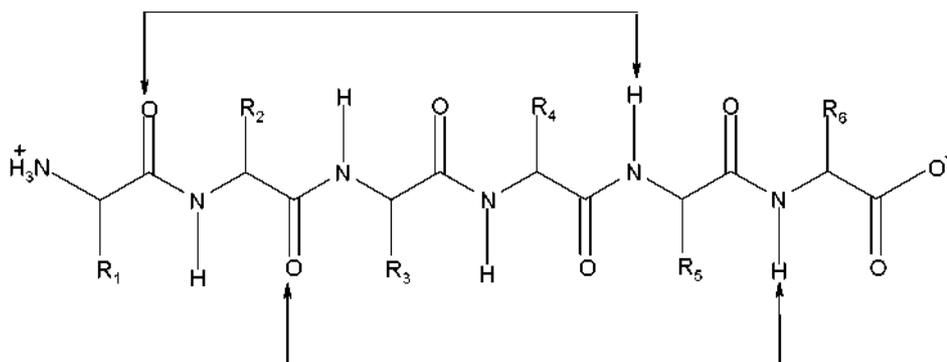
Arg – Arginine	$ \begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{C} \begin{array}{l} / \text{NH}_2 \\ \backslash \text{NH} \end{array} \\ \\ \text{H} \end{array} $	174
Ser – Serine	$ \begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{OH} \\ \\ \text{H} \end{array} $	105

SOLUTION

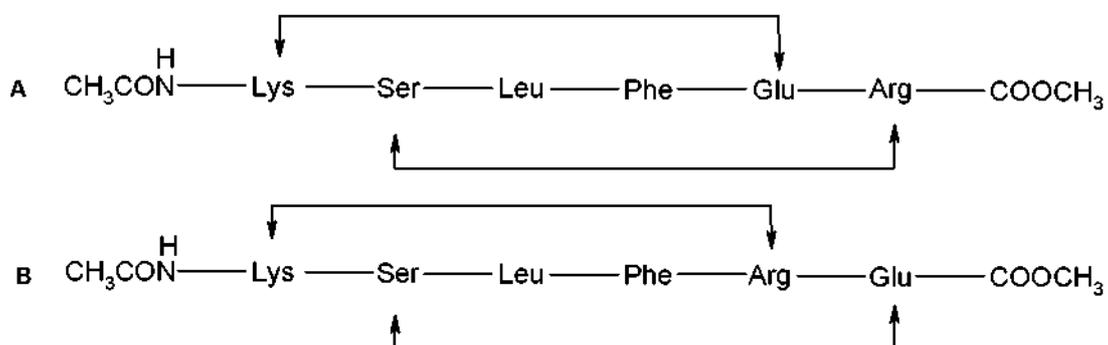
7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately :

(c) 20 Å

7.2



7.3



7.4 $\Delta G = -8 - (-16 \times 2) + (-4 \times 1) + (-14 \times 2) = -8 \text{ kJ mol}^{-1}$

7.5 $\Delta G = -(14 \times 3) - (-16 \times 3) = +6 \text{ kJ mol}^{-1}$

7.6 $\frac{105 \times 100}{0.35} = 30000 \text{ Da}$

7.7 The approximate number of amino acid residues present in a protein of this size is:

(c) 275

7.8 P1: Phe – Glu – Ser – Met – Leu – Lys

P2: Glu – Ser – Met – Leu – Lys

P3: Phe – Glu – Ser – Hms/Met

P4: Leu – Lys

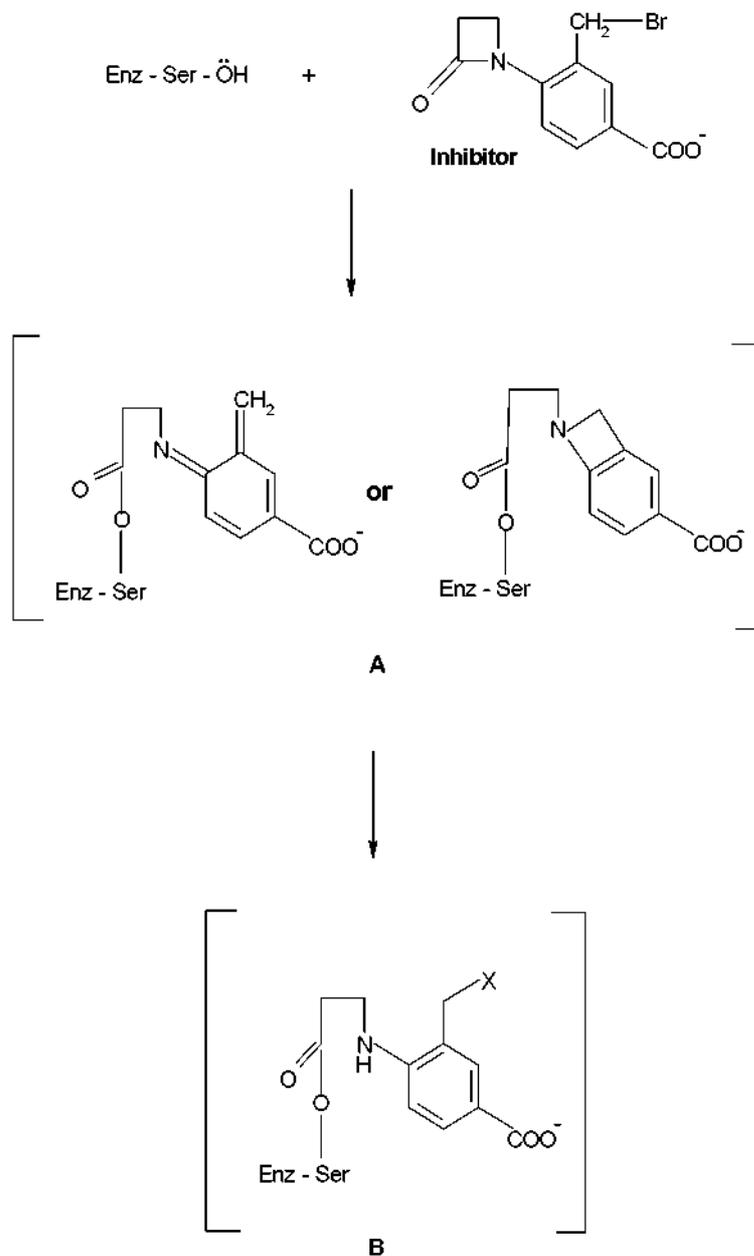
7.9 Phe - Glu - Ser - Hms

$$(165 + 147 + 105 + 119) - 3 \text{ H}_2\text{O} = 536 - 54 = 482 \text{ Da}$$

7.10 700 M

7.11 The most effective inhibitor is C.

7.12



PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Preparation of 2-Iodobenzoic Acid

This laboratory task involves preparation of 2-iodobenzoic acid from 2-aminobenzoic acid. The procedure consists of diazotization of 2-aminobenzoic acid followed by reaction with KI (in H₂SO₄).

Procedure

- 1) Quantitatively transfer the given sample of solid 2-aminobenzoic acid into a 100 cm³ beaker placed in the ice-bath. Add 7.2 cm³ of H₂SO₄ (2.6 M) (labelled H₂SO₄) and mix the contents thoroughly for 1 minute with the help of a glass rod. Cool the solution for 5 minutes.
- 2) Using a measuring cylinder, measure out 4.4 cm³ of supplied cooled NaNO₂ solution from the vial placed in the ice-bath.
- 3) With the help of a dropper, slowly add the cooled NaNO₂ solution to the acid solution with constant gentle stirring using a glass rod to obtain an almost clear solution (3 – 5 minutes).
- 4) Remove the beaker from the ice bath and then slowly add 9.4 cm³ of KI solution from the stoppered tube, with stirring.
- 5) Get hot water from the laboratory expert. Keep the beaker in hot water for 5 minutes.
- 6) Filter the crude product and wash it thoroughly with distilled water (10 cm³). Collect the washings along with the main filtrate.
- 7) Neutralize the combined filtrate by gradually adding the given solid Na₂CO₃ until effervescence ceases. Dispose of the filtrate in the appropriate plastic bucket.

Purification of the crude product

Place the funnel containing the precipitate on a 100 cm³ conical flask. Pour about 15 to 20 cm³ of the supplied NaHCO₃ solution (using test tube) over the filter paper so as to dissolve the precipitate completely.

- 8) Add the supplied charcoal powder to the filtrate and mix it thoroughly. Filter the solution to remove charcoal.

- 9) Add dilute H_2SO_4 gradually to the filtrate till effervescence ceases. Filter the purified product. Use 10 -15 cm^3 distilled water to wash the precipitate. Keep the filter paper with the product on a watch glass.
- 10) Cover the product with the same funnel and hand over the product to the laboratory expert for drying (for a minimum of one hour).

Towards the end of the practical session have the product weighed by the laboratory expert and record the same.

SOLUTION

The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield (based on 2 aminobenzoic acid) in g.
- The yield obtained as a percentage of the theoretical yield.
- Colour of the product obtained.

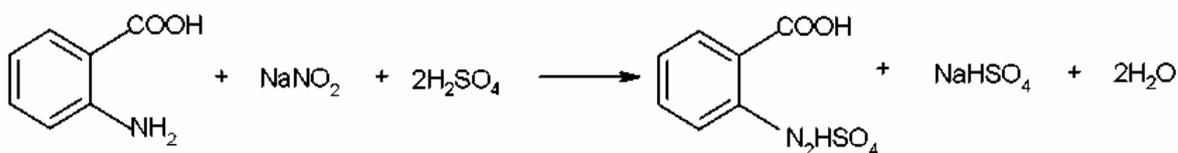
Tasks:

Write down the balanced chemical equations for:

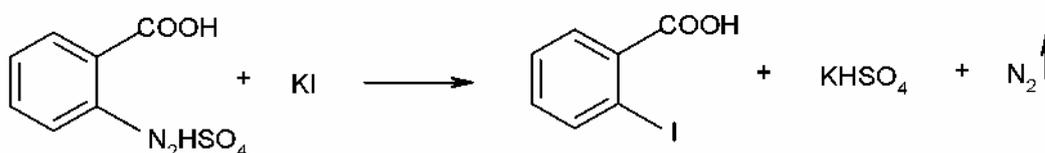
- (a) diazotization of 2-aminobenzoic acid using NaNO_2 and H_2SO_4 .
- (b) the reaction of KI with the diazotized product.

Solutions of the tasks:

a)



b)



PROBLEM 2 (Practical)

Estimation of Mn(II) and Mg(II) Present in the Given Sample

In this experiment, estimation of the amounts of Mn (II) and Mg (II) present in the given sample is carried out by complexometric titration using standard Na₂EDTA solution. Total metal ion content is obtained from the first titration. At this stage, by using adequate solid NaF, selective and quantitative release of EDTA present in Mg-EDTA complex is achieved. The EDTA thus released is bound again by the addition of a known excess of standard Mn (II) solution. The unused Mn (II) is estimated by a back titration using the same standard Na₂EDTA solution. From these two different titre values, individual amounts of metal ions present can be obtained. Both the titrations are performed using a buffer ($pH = 10$) and Erichrome black T indicator.

The sample in duplicate is given in two 250 cm³ conical flasks (labelled as Trial I and Trial II). Perform the titrations for both and record your readings on the answer sheet.

Procedure

Two burettes (25 cm³) are supplied to you. Fill one with the given standard Na₂EDTA solution and the other with the given standard Mn (II) solution.

Titration 1

To the sample solution (supplied in the 250 cm³ conical flask), add all of the solid hydroxylamine hydrochloride given in one vial followed by 50 cm³ of distilled water. With the help of a measuring cylinder, add 10 cm³ buffer solution ($pH = 10$) and one metal spatula full of the solid indicator. Shake the contents of the flask thoroughly and titrate the solution against the standard Na₂EDTA solution until the colour changes from wine red to blue. Record your burette reading (**A** cm³). Ensure that you shake the contents of the flask thoroughly throughout the titration.

Titration 2

To the same flask, add all of the solid NaF given in one vial and shake the contents well for a minute. To this add 20 cm³ of the given standard Mn (II) solution from the other burette. The addition of the Mn (II) solution should be done in small increments (2 – 3 cm³) with thorough shaking. After addition of the total Mn (II) solution, shake the contents for two to three minutes. The colour of the solution will change from blue to wine red. Titrate

the excess of Mn (II) in the solution against the standard Na₂EDTA solution till the colour changes from wine red to blue. Record your burette reading (**B** cm³).

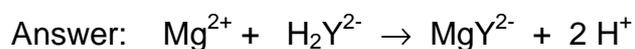
Repeat the same procedure for Trial II.

SOLUTION

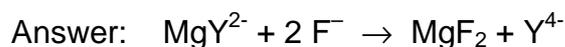
The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

2.2 Give the balanced chemical equation for the reactions of Mg(II) and Mn(II) with Na₂EDTA . (Use the symbol Na₂HY for Na₂EDTA.)



2.3 Give the equation for the release of EDTA by the addition of NaF to the MgEDTA complex.



2.4 Calculate the amount of Mg (II) and Mn (II) in gram for any one of the two trials. (Show the main steps in your calculation.)

2.5 The colour change at the end point (wine red to blue) in Titration 1 is due to

- a) the formation of metal-indicator complex,
- b) the release of free indicator from metal-indicator complex,
- c) the formation of metal-EDTA complex.

[Mark X in the correct box.]

Correct answer is (b).

PROBLEM 3 (Practical)**Determination of the Rate Constant for the Redox Reaction between Ethanol and Chromium (VI)**

The oxidation of alcohols by chromium (VI) forms the basis for analysis of breath samples for measuring alcohol content. A dilute solution of $K_2Cr_2O_7$ in the presence of a strong acid (3.6 M HCl here) is a source of $HCrO_4^-$ which is the oxidant involved in the reaction.

In this experiment, the rate of the reaction between $HCrO_4^-$ and CH_3CH_2OH is determined titrimetrically. Under the given experimental conditions, the rate law reduces to

$$\text{rate} = k[HCrO_4^-]^x$$

where x is the order of the reaction.

At any given time, $[HCrO_4^-]$ is obtained by iodometric titration.

Procedure

You are given 100 cm³ of standard $K_2Cr_2O_7$ solution in HCl in a bottle. Transfer all the absolute ethanol given in a vial into this bottle and stopper it. Mix the contents thoroughly, start the stopwatch immediately and regard this as time $t = 0$. Fill the burette with this solution.

After every 10 minutes, start to draw 10 cm³ of this solution to a clean conical flask containing 4 cm³ of the given KI solution. The solution will turn brown. Titrate this solution with the given standard $Na_2S_2O_3$ solution until the colour changes to pale greenish yellow. Add 2 cm³ of starch indicator and continue the titration until the colour changes from blue to pale green. Record the burette reading in the answer sheet. Repeat this procedure at 10 minutes intervals to obtain four readings.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

3.1 Write down the possible oxidation products in the reaction of HCrO_4^- and $\text{CH}_3\text{CH}_2\text{OH}$.

Solution: Acetic acid, CH_3COOH
Acetaldehyde, CH_3CHO

3.2 Write the chemical equation for the reaction between HCrO_4^- and KI :

Solution: $2 \text{HCrO}_4^- + 6 \text{I}^- + 14 \text{H}^+ \rightarrow 3 \text{I}_2 + 2 \text{Cr}^{3+} + 8 \text{H}_2\text{O}$

3.3 Write down the balanced chemical equation involved in the titration.

Solution: $\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}$

3.4 Give the main steps for the calculation of HCrO_4^- concentration (mol dm^{-3}) for any one titration reading.

3.5 Give concentrations of HCrO_4^- at different times (in a table attached).

3.6 Plot the graph of $\log [\text{HCrO}_4^-]$ vs. time.

3.7 From the nature of the graph determine the order (x) of the reaction with respect to HCrO_4^-

3.8 Determine the rate constant for the reaction.

34th



International Chemistry Olympiad

**10 theoretical problems
3 practical problems**

THE THIRTY-FOURTH INTERNATIONAL CHEMISTRY OLYMPIAD 5–14 JULY 2002, GRONINGEN, THE NETHERLANDS

THEORETICAL PROBLEMS

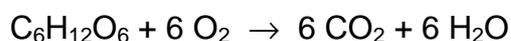
Theme 1 - Chemistry of Life

Life runs on chemistry. Understanding and monitoring life processes receive much attention in chemistry.

PROBLEM 1

OXYGEN IN YOUR LIFE

Oxygen is of vital importance for all of us. Oxygen enters the body via the lungs and is transported to the tissues in our body by blood. There it can deliver energy by the oxidation of sugars:



This reaction releases 400 kJ of energy per mol of oxygen. O₂ uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe²⁺ ion attached to four N atoms of a porphyrin²⁻ ligand. Oxygen can bind at the coordination site of Fe²⁺ giving a Hm·O₂ complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O₂ does. The equilibrium constant K_1 for the reaction:



is 10 000 times larger than the equilibrium constant K_2 for the reaction:



Each Hb molecule can take up four molecules of O₂. Blood in contact with O₂ absorbs a fraction of this amount, depending on the oxygen pressure, as shown in Figure 1 (curve 1). Also shown are the curves (2) and (3) for blood with two kinds of deficient Hb. These occur in patients with certain hereditary diseases.

Relevant data: O₂ pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum

flow of blood through heart and lungs is $4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$. The red cells in blood occupy 40 % of the blood volume; inside the cells the concentration of Hb is 340 kg m^{-3} ; Hb has a molar mass of 64 kg mol^{-1} . $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. $T = 298 \text{ K}$.

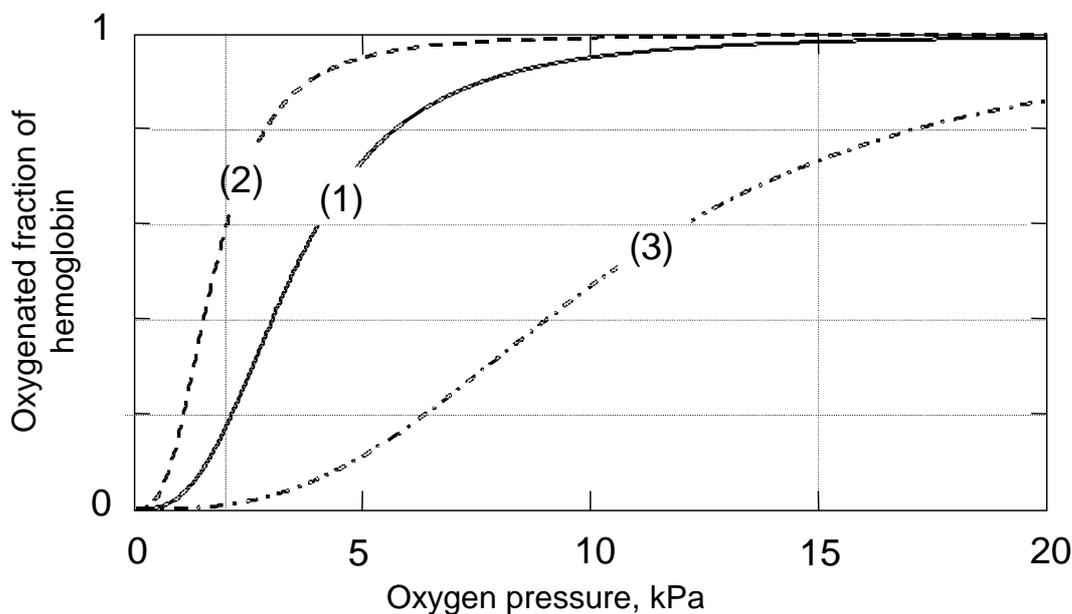


Figure 1

- 1.1 Using the relation between K and the standard Gibbs energy ΔG^0 for a reaction, calculate the difference between the ΔG^0 values for the heme reactions (1) and (2).
- 1.2 Estimate from Figure 1 (to 2 significant figures) how many moles of O_2 are deposited in muscle tissue when one mole of Hb travels from the lungs to the muscles and back again for the three different types of Hb.
- 1.3 The special S-shaped uptake curve 1 is the result of subtle structural features of Hb. The deficient Hb shown in curve 2 is not optimal because:
 - The binding with O_2 is too weak.
 - The binding with O_2 is too strong.
 - The maximum oxygen capacity is too low.
 - The deficiency is caused by carbon monoxide poisoning.
- 1.4 Calculate how much oxygen (in mol s^{-1}) can be deposited in tissue by blood with normal Hb (1).
- 1.5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

SOLUTION

$$1.1 \quad \Delta G_1^0 = -RT \ln K_1 \quad \Delta G_2^0 = -RT \ln K_2$$

$$\Delta G_2^0 - \Delta G_1^0 = RT \ln \frac{K_1}{K_2}$$

$$\Delta G_2^0 - \Delta G_1^0 = (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 10\,000) \text{ J} = 23 \text{ kJ mol}^{-1}$$

$$1.2 \quad \text{Hb-Typ 1: } (0.98 - 0.17) \text{ mol} \times 4 = 3.2 \text{ mol}$$

$$\text{Hb-Typ 2: } (1.00 - 0.60) \text{ mol} \times 4 = 1.6 \text{ mol}$$

$$\text{Hb-Typ 3: } (0.73 - 0.01) \text{ mol} \times 4 = 2.9 \text{ mol}$$

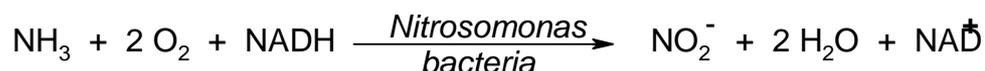
1.3 Correct answer: The binding with O₂ is too strong.

$$1.4 \quad (4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}) \times 0.4 \times (340 \text{ kg m}^{-3}) \times (3.2 \text{ mol O}_2 / \text{mol Hb}) / (64 \text{ kg mol}^{-1}) = \\ = 2.72 \times 10^{-3} \text{ mol s}^{-1}$$

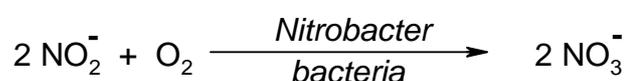
$$1.5 \quad (2.72 \times 10^{-3} \text{ mol s}^{-1}) \times (400 \text{ kJ mol}^{-1}) = 1088 \text{ W}$$

PROBLEM 2**Nitrogen Cycle in Nature**

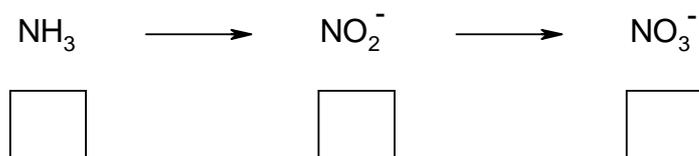
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH_3 first to nitrite and then to nitrate, the storage form of nitrogen in the soil.



NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD), NAD^+ is the oxidized form of the coenzyme NAD.



2.1 Give the oxidation states of N in the following series: (Use the boxes below the compounds)



The spectrophotometric analysis of nitrite is based on a reaction with an indicator. The coloured product then obtained has an absorbance maximum at $\lambda = 543 \text{ nm}$. For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength $\lambda = 543 \text{ nm}$ is plotted against nitrite concentration in a series of standards.

2.2 The measurements are performed at the wavelength with the maximum absorbance because:

- There is no interference of impurities.
- There is no contribution of stray light.
- There is optimal accuracy of the measurement.
- None of these statements.

Mark the correct answer.

The absorption is measured with a single beam spectrophotometer. However 5 % of the light, the so-called stray light I_s , strikes the detector directly (see Figure 2).

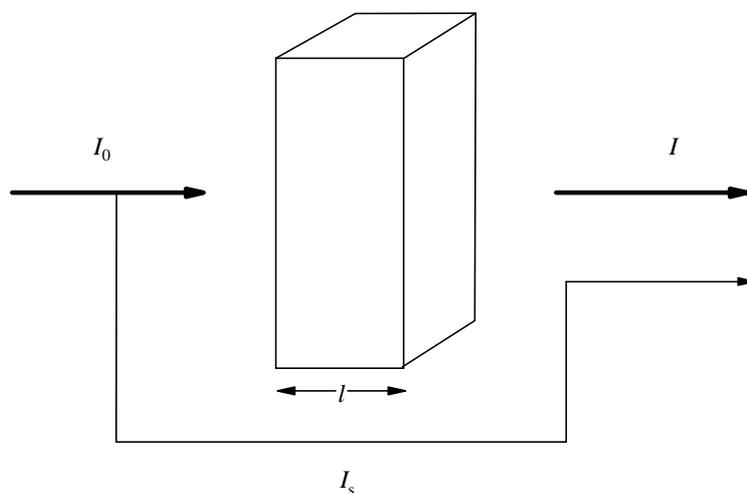


Figure 2

- 2.3** Calculate the value of the absorbance A shown by the spectrophotometer if $\varepsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$, $l = 1 \text{ cm}$ and $c = 1 \times 10^{-4} \text{ M}$

For a nitrite determination in water the following data have been measured.

Table 1

concentration of nitrite nitrogen (ppm)	absorbance at 543 nm (1.000 cm cell)
blank	0.003 (due to impurities in the solvent)
0.915	0.167
1.830	0.328

- 2.4** Determine (show calculation) from the data given above, using the values corrected for the solvent impurities, the slope m and the intercept b of the calibration curve $A = m c + b$.

The duplicate analyses of a water sample are given below. The measurements have been performed at a wavelength of 543 nm and in a 2.000 cm cell.

Table 2

water sample	absorbance
analysis 1	0.562
analysis 2	0.554

For the calculation of the concentration of the nitrite nitrogen (c in ppm) the equation obtained by the method of least squares

$$\text{corrected absorbance} = 0.1769 c + 0.0015 \quad (\text{a})$$

may be applied, using the measurements in a 1.000 cm cell.

2.5 Calculate the average nitrite nitrogen concentration in ppm and $\mu\text{g cm}^{-3}$.

Hint: Take the blank from problem 2.4.

SOLUTION

2.1 NH_3 : -III (-3) NO_2^- : III (3) NO_3^- : V (5)

2.2 Correct answer: There is optimal accuracy of the measurement.

2.3 $I_S = 0.05 \times I_0$ $A = \log \frac{I_0}{I + I_S}$ (see Figure 2)

The absorption of the solution A_{sol} is given by the relation:

$$A_{\text{sol}} = \log 0.95 \times \frac{I_0}{I} = \varepsilon c d$$

$$I = 0.95 \times I_0 \times 10^{-6000 \cdot 0.0001 \cdot 1} = 0.95 I_0 \times 10^{-0.6}$$

$$A = \log \frac{I_0}{0.95 \times I_0 \times 10^{-0.6} + 0.05 \times I_0} = 0.54$$

2.4 The absorbance of the blank solution (see Table): $A = 0.003$.

Slope m of the calibration curve:

$$m = \frac{\Delta A}{\Delta c} = \frac{A_2 - A_1}{c_2 - c_1} = \frac{0.325 - 0.164}{1.830 - 0.915} = \frac{0.161}{0.915 \text{ M}} = 0.176 \text{ M}^{-1}$$

Note: Corrected absorbance values were used in the calculation.

$$A = 0.176 c + b$$

For $c = 0$, $A = 0.003$.

Thus: $b = 0.003$

- 2.5** The average absorption in a 2 cm cell is 0.558; thus, in a 1 cm cell is 0.279.
Regarding the blank value (0.003) the corrected absorption has the value 0.276.
Substituting this value into the equation (a) gives:

$$c = \frac{0.276 - 0.0015}{0.1769} \text{ ppm}$$

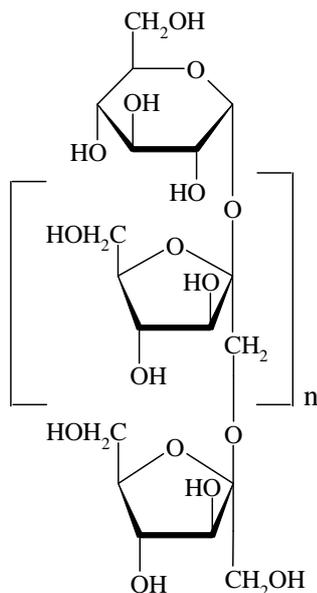
$$c = 1.55 \text{ ppm} = 1.55 \mu\text{g cm}^{-3}$$

Theme II - Chemistry of Industrial Relevance

In our daily life we use many products that are produced on an industrial scale. Mastering the underlying chemistry is at the heart of this business.

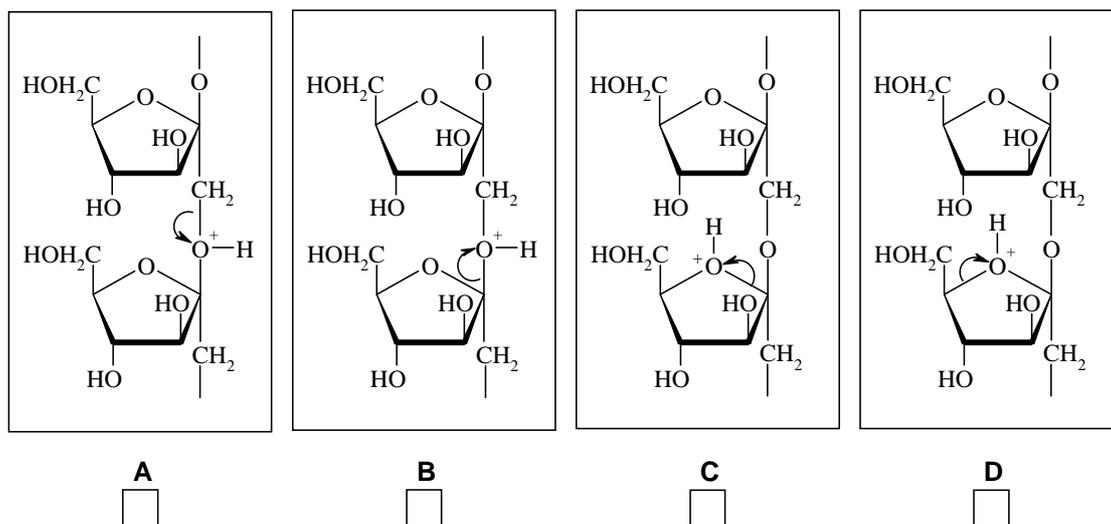
PROBLEM 3

Inulin, a New Renewable Raw Material



Inulin, which is produced from chicory roots in Belgium and The Netherlands, is used as a food additive as it has a beneficial effect on the intestinal flora. It is also used as source of fructose which is 1.9 times sweeter than sucrose, and for the production of mannitol which is used in chewing gum. Inulin is a linear polymer of fructose units with a glucose unit at one end; its Haworth projection formula is shown at the left. In this problem inulin has 10 fructose units ($n = 9$).

3.1 Inulin may be hydrolyzed under H^+ -catalysis conditions. Of the four options below (A, B, C and D) indicate which C-O bond cleavage is most likely to occur.



Mark the correct cleavage mechanism for the most efficient hydrolysis.

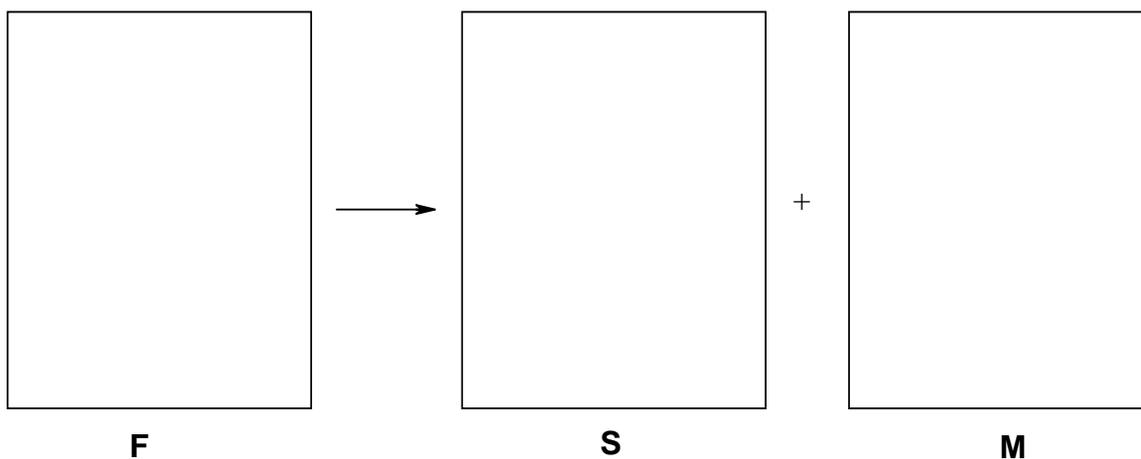
Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can “see” deuterium (^2H) and the oxygen isotope ^{17}O .

3.2 Indicate which labelled water can best be used for this purpose. Mark the correct answer.

- $^2\text{H}_2\text{O}$
 H_2^{17}O
 $^2\text{H}_2^{17}\text{O}$
 None of them.

Upon catalytic hydrogenation glucose gives sorbitol (**S**), whilst fructose (**F**) gives mannitol (**M**) and sorbitol (**S**).

3.3 Draw the Fischer projections of fructose (**F**), sorbitol (**S**) and mannitol (**M**).



1.00 mol of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95 °C in a one step process. The selectivity of the hydrogenation of fructose to mannitol / sorbitol is 7 / 3.

3.4 How many moles of mannitol and sorbitol are obtained?

M:

S:

After completion of the reactions the catalysts are removed and the reaction mixture is cooled to 25 °C. The solubility of **M** is 0.40 mol kg⁻¹ in water at 25 °C and the solubility of **S** is so high that it will not precipitate.

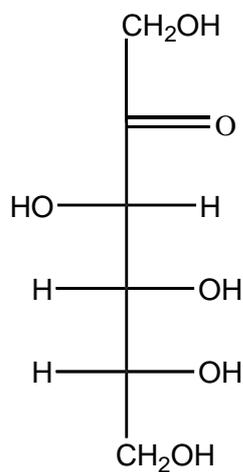
3.5 Calculate how many moles of **M** will precipitate.

SOLUTION

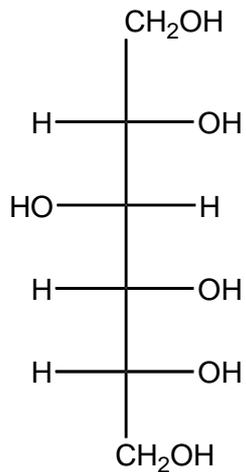
3.1 B is correct.

3.2 H_2^{17}O

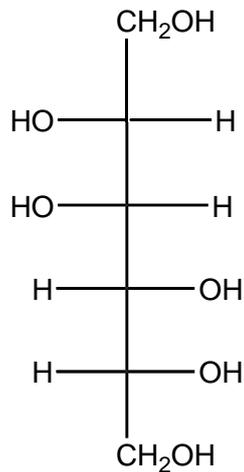
3.3



F



S



M

3.4 $n(\text{M}): 7 \text{ mol}$ $n(\text{S}): 4 \text{ mol}$

3.5 Remaining amount of water:

$$m(\text{H}_2\text{O}) = 2 \text{ kg} - (10 \times 0.018 \text{ kg}) = 1.82 \text{ kg}$$

$$n(\text{M})_{\text{total}} = 7 \text{ mol}$$

$$n(\text{M})_{\text{dissolved}} = 1.82 \times 0.4 \text{ mol} = 0.73 \text{ mol}$$

$$n(\text{M})_{\text{precipitated}} = 7.00 - 0.73 = 6.27 \text{ mol}$$

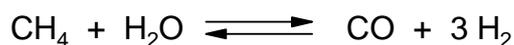
PROBLEM 4

Production of Methanol

Methanol (CH_3OH) is a chemical that is used for the production of additives in gasoline and many common plastics. A factory, producing methanol, is based on the reaction:



Hydrogen and CO are obtained by the reaction:



The three units of the factory, namely, the “reformer” for the hydrogen / carbon monoxide production, the “methanol reactor” and a “separator” to separate methanol from CO and H_2 , are schematically shown in Figure 1. Four positions are indicated by α , β , γ and δ .

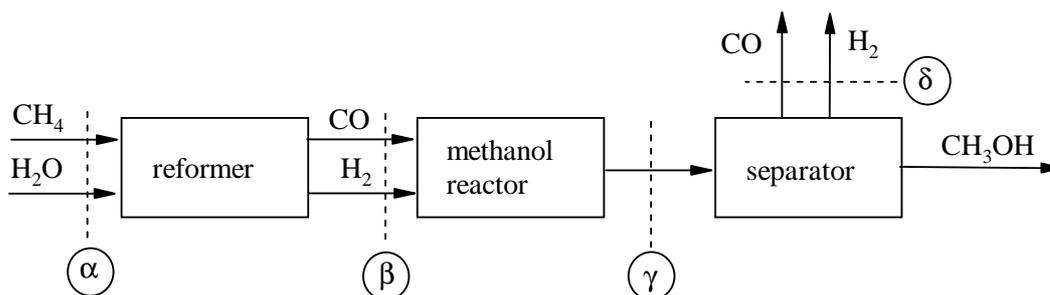


Figure 1

The flow of methanol at position γ is $\eta[\text{CH}_3\text{OH}, \gamma] = 1000 \text{ mol s}^{-1}$. The factory is so designed that $2/3$ of the CO is converted to methanol. Excess CO and H_2 at position δ are used to heat the first reactor. Assume that the reformer reaction goes to completion.

- 4.1 Calculate the flow of CO and H_2 at position β .
- 4.2 Calculate the flow of CO and H_2 at position γ .
- 4.3 Calculate the flows of CH_4 and H_2O needed at position α .
- 4.4 At point γ all species are gases. Calculate the partial pressures in MPa for CO, H_2 and CH_3OH at position γ using the equation:

$$p_i = p \frac{n_i}{n_{\text{tot}}}$$

wherein n_i is the flow and p_i the partial pressure of the compound i , n_{tot} is the total flow at the position considered, and p the total pressure in the system. ($p = 10 \text{ MPa}$)

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures at point γ obey the equation:

$$K_p = \frac{p_{\text{CH}_3\text{OH}} p_0^2}{p_{\text{CO}} p_{\text{H}_2}^2}$$

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in Figure 2 (the vertical scale is logarithmic).

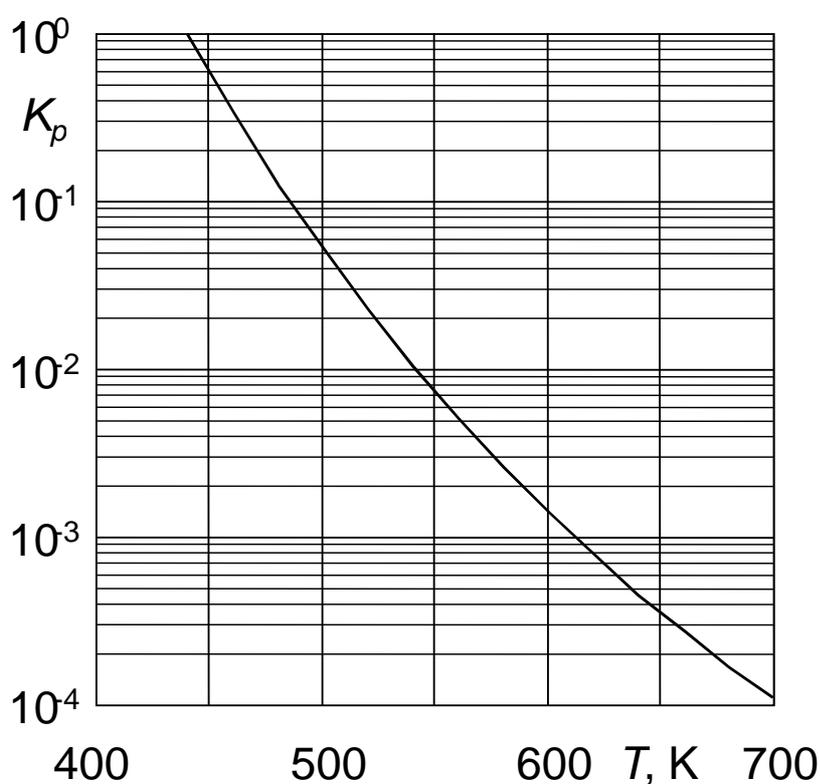


Figure 2

4.5 Calculate K_p and indicate at which temperature T the reaction must be operated to achieve this equilibrium.

SOLUTION

4.1 $n(\text{CO}, \beta) = 3/2 \times n(\text{CH}_3\text{OH}, \gamma) = 1500 \text{ mol s}^{-1}$

$$n(\text{H}_2, \beta) = 3 \times n(\text{CO}, \beta) = 4500 \text{ mol s}^{-1}$$

4.2 $n(\text{CO}, \gamma) = n(\text{CO}, \beta) - n(\text{CH}_3\text{OH}, \gamma) = (1500 - 1000) \text{ mol s}^{-1} = 500 \text{ mol s}^{-1}$
 $n(\text{H}_2, \gamma) = n(\text{H}_2, \beta) - 2 \times n(\text{CH}_3\text{OH}, \gamma) = (4500 - 2 \times 1000) \text{ mol s}^{-1} = 2500 \text{ mol s}^{-1}$

4.3 $n(\text{CH}_4, \alpha) = n(\text{CO}, \beta) = 1500 \text{ mol s}^{-1}$
 $n(\text{H}_2\text{O}, \alpha) = n(\text{CO}, \beta) = 1500 \text{ mol s}^{-1}$

4.4 $n_{\text{tot}} = (1000 + 500 + 2500) \text{ mol s}^{-1} = 4000 \text{ mol s}^{-1}$
 $p_i = p_{\text{tot}} \cdot (n_i/n_{\text{tot}})$
 $p(\text{CO}, \gamma) = 10 \text{ MPa} \times (500/4000) = 1,25 \text{ MPa}$
 $p(\text{H}_2, \gamma) = 10 \text{ MPa} \times (2500/4000) = 6,25 \text{ MPa}$
 $p(\text{CH}_3\text{OH}, \gamma) = 10 \text{ MPa} \times (1000/4000) = 2,50 \text{ MPa}$

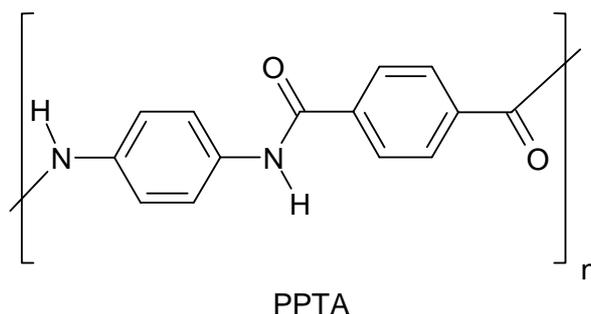
4.5 Calculation of K_p : $K_p = (2.5 \times 0.1^2) / (1.25 \times 6.25^2) = 5.12 \times 10^{-4}$.

The temperature corresponding to this value (see Fig. 2) is $\approx 630 \text{ K}$.

PROBLEM 5

Aramids, High-performance Polymeric Materials

Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north of The Netherlands. The PPTA chains are neatly packed into fibers with a sheet type structure.



5.1 Draw the structure of these sheets (three chains suffice).

For a polymerisation of equimolar amounts of two monomers the average chain length is \bar{P}_n , the degree of conversion is p , which equals the fraction of functional groups that have reacted, the total number of chains is N_t and the total initial number of monomers is U_0 .

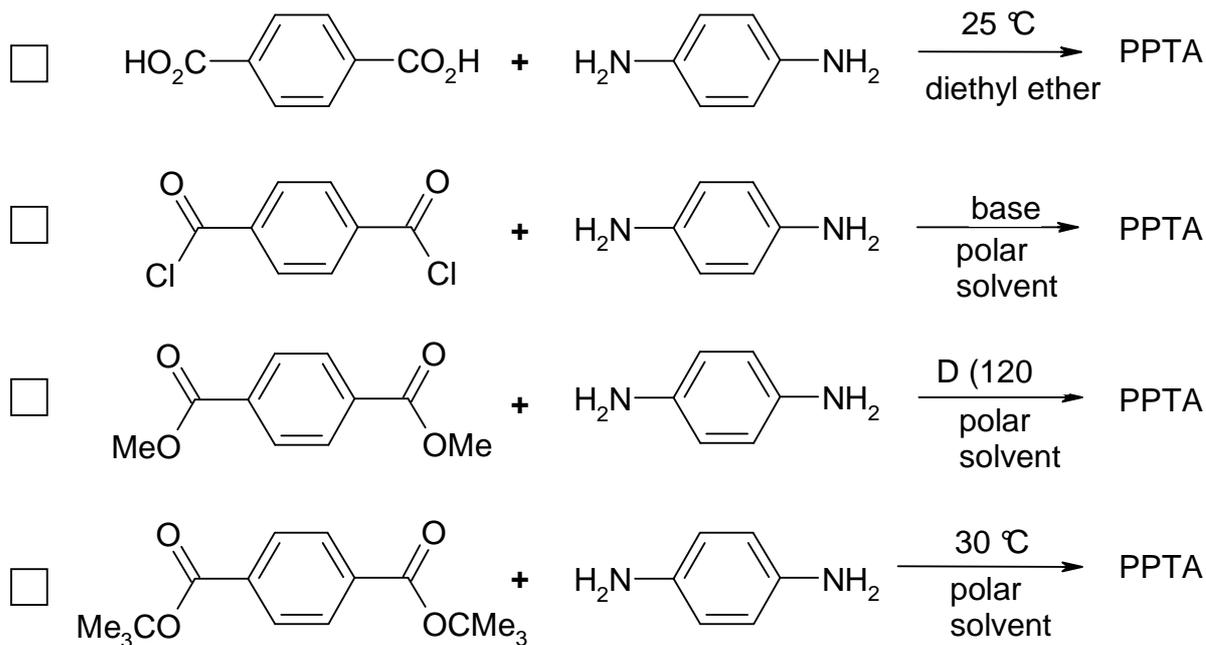
Assuming that the polymerization equilibrium can fully be described by:



where C stands for any $-\text{CO}_2$ group, A stands for any $-\text{NH}_2$ group and Am stands for any amide group.

5.2 Calculate the degree of conversion needed to obtain an average chain length of 500.

5.3 For the synthesis of PPTA the following possibilities are considered. Which of the following reactions will work? Mark the correct answer(s).

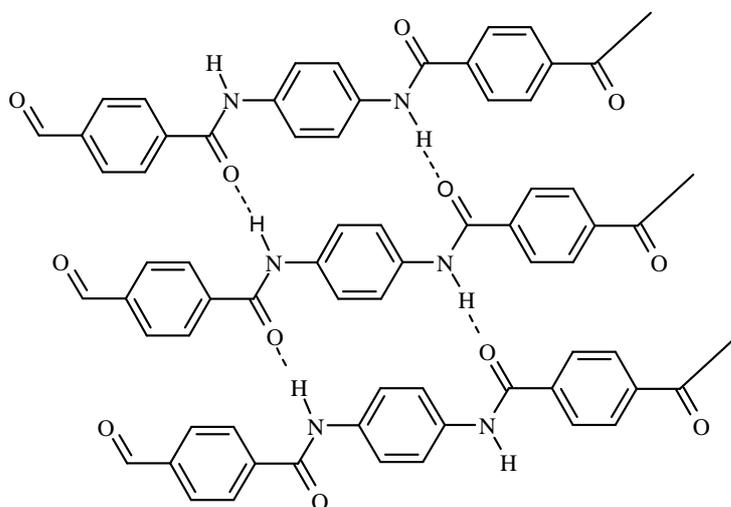


5.4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

- Give the structure of this aramid ($n = 4$)
- Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant $K = 576$.

SOLUTION

5.1



$$5.2 \quad \bar{P}_n = \frac{U_0}{N_t}, \quad p = \frac{U_0 - N_t}{U_0} \rightarrow$$

$$p = 1 - \frac{N_t}{U_0}, \quad \frac{N_t}{U_0} = 1 - p \rightarrow \bar{P}_n = \frac{1}{1-p}$$

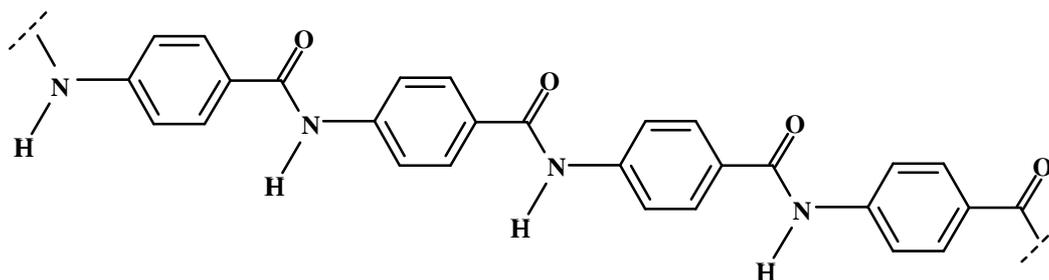
$$500 = \frac{1}{1-p} \quad p = \frac{499}{500} = 0.998$$

5.3

2 and 3

5.4

a)



$$b) \quad K = \frac{[Am] \times [H_2O]}{[C] \times [A]} = \frac{p U_0 \times p U_0}{(1-p)^2 \times U_0^2} = \frac{p^2}{(1-p)^2} = 576 \Rightarrow p = 0.96$$

$$\bar{P}_n = \frac{1}{1-p} = \frac{1}{1-0.96} = 25$$

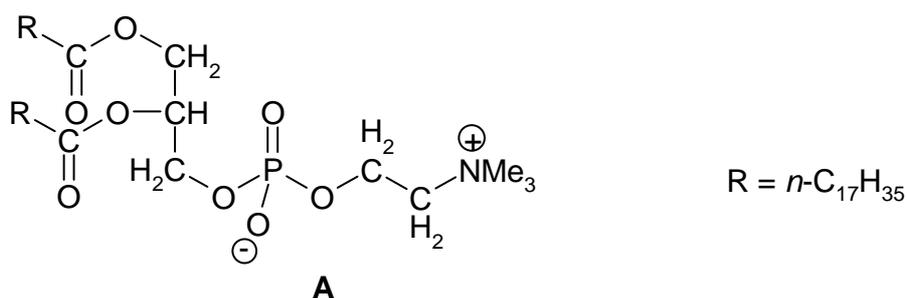
Theme III - Chemistry of Functional Molecules in Nature

A challenge in chemistry is to discover what nature does and how the structures of biologically active molecules are related to what they do.

PROBLEM 6

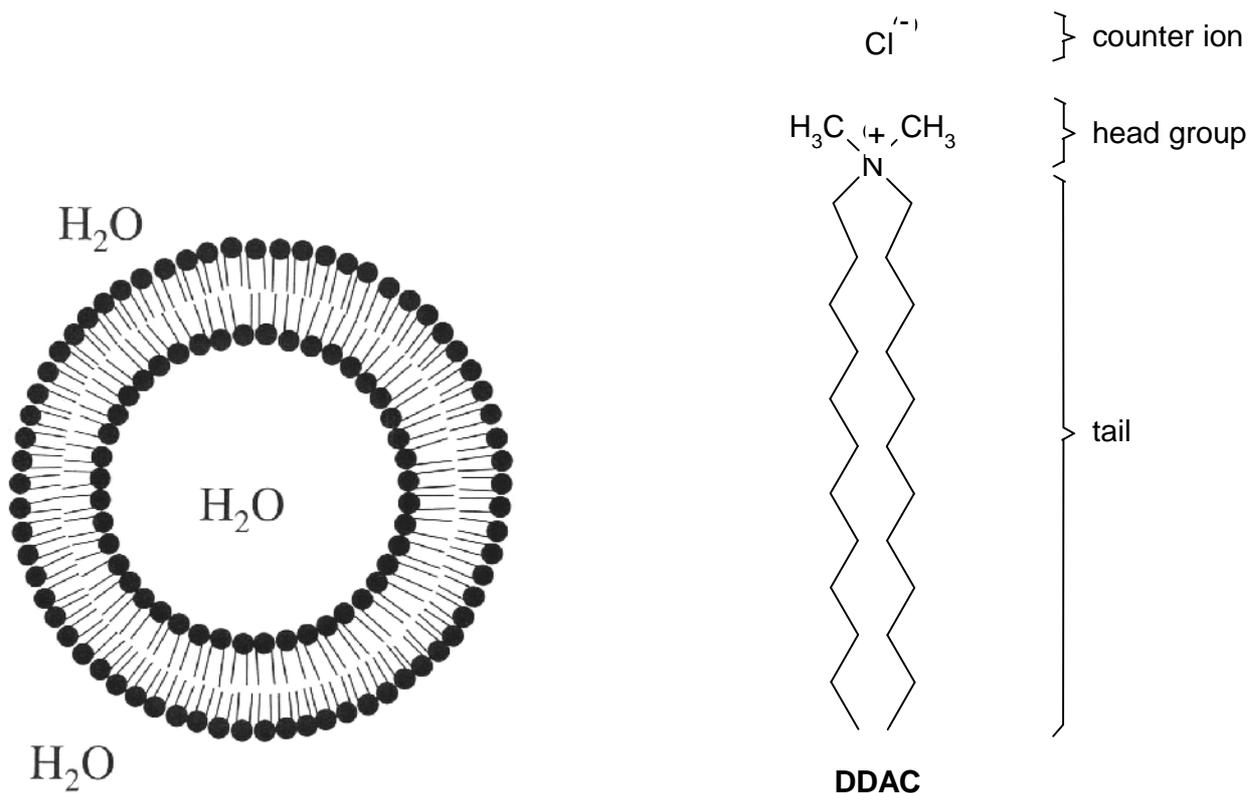
Phospholipids in Membranes

Biological cell membranes are complex, functional, non-covalent molecular assemblies, largely consisting of lipids and proteins. Their function is of vital importance for life processes. They separate the cell from its environment and also determine the specific flow of information between the cell contents and the environment. Phospholipids are among the most important components of cell membranes. An example is compound **A**.

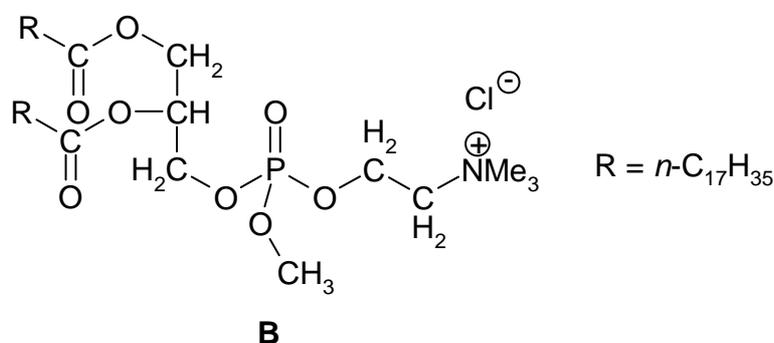


Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or ionic head groups in contact with water and with the alkyl tails sequestered in a hydrophobic core. The bilayer structure encloses an aqueous inner compartment.

Double-tailed *synthetic* surfactants also form closed bilayer assemblies similar to liposomes but now called vesicles. An example is di-*n*-dodecyldimethylammonium chloride (**DDAC**).

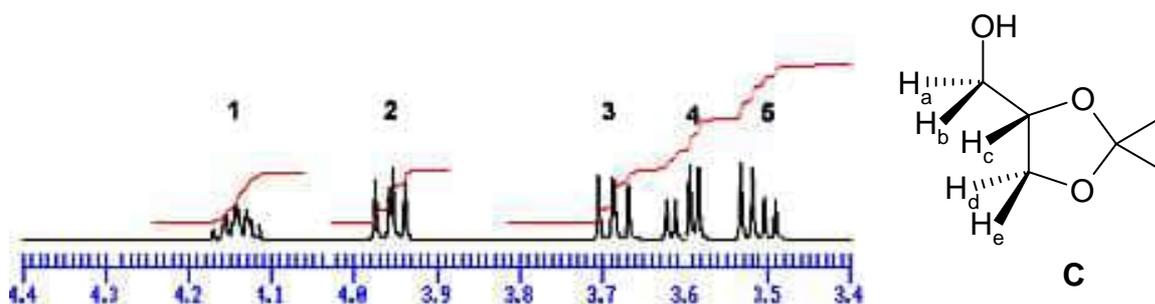


- 6.1 (a)** How many stereoisomers are possible for compound **A**?
- (b)** How many stereoisomers are possible for the trialkylphosphate **B**?



A precursor for the synthesis of compound **A** is the acetone **C** derived from glycerol. Part of the ¹H-NMR spectrum of compound **C** is shown below.

- 6.2** Which signal number in the ¹H-NMR spectrum corresponds to proton **H_c**?



The bilayer of a liposome can be characterized by V (the volume of the hydrocarbon chains), a_0 (optimal cross-sectional surface area of the head groups of the phospholipid in the aggregate) and l_c (the maximum chain length that the alkyl group can assume). A good approximation for unbranched alkyl tails containing n carbon atoms yields:

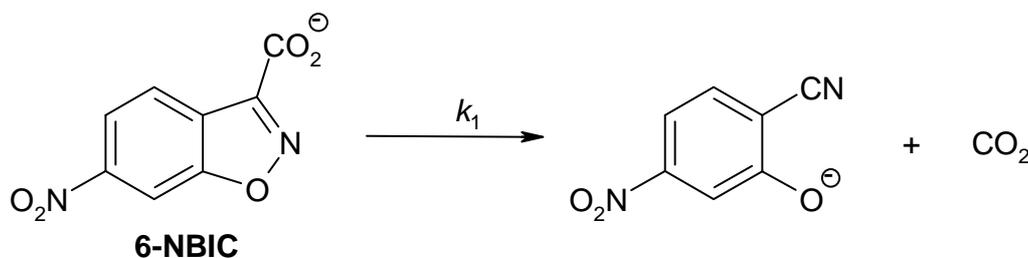
$$V = (27.4 + 26.99 n) \times 10^{-3} \text{ nm}^3$$

$$l_c = (0.154 + 0.1265 n) \text{ nm}$$

For very large n values, the intertail interactions dominate over the head group repulsions.

6.3 Calculate the minimum cross-sectional surface area of the head groups for such very large n values.

Vesicles formed from **DDAC** (above its critical vesicle concentration, c_{vc}) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).



In water at 25 °C $k_1 = 3.1 \times 10^{-6} \text{ s}^{-1}$. At the concentration c_1 of **DDAC** at which **6-NBIC** becomes fully bound to the vesicles, $k_1 = 2.1 \times 10^{-3} \text{ s}^{-1}$.

6.4 Sketch a plot of k_1 vs. $[\text{DDAC}]$ for $[\text{DDAC}] = 0 \rightarrow 3 c_1$.

6.5 The main reason for the efficient catalysis of the decarboxylation of **6-NBIC** by **DDAC** vesicles is:

- The decarboxylation is catalysed by the Cl^- ions bound to the surface of the vesicles.
- Efficient loss of hydration of the carboxylate group of vesicle-bound **6-NBIC**.
- Strong binding of CO_2 in the interior of the vesicle.
- Strong binding of the organic reaction product to the vesicles relative to that of **6-NBIC**.

Mark the correct answer.

SOLUTION

6.1 (a) 2; (b) 4

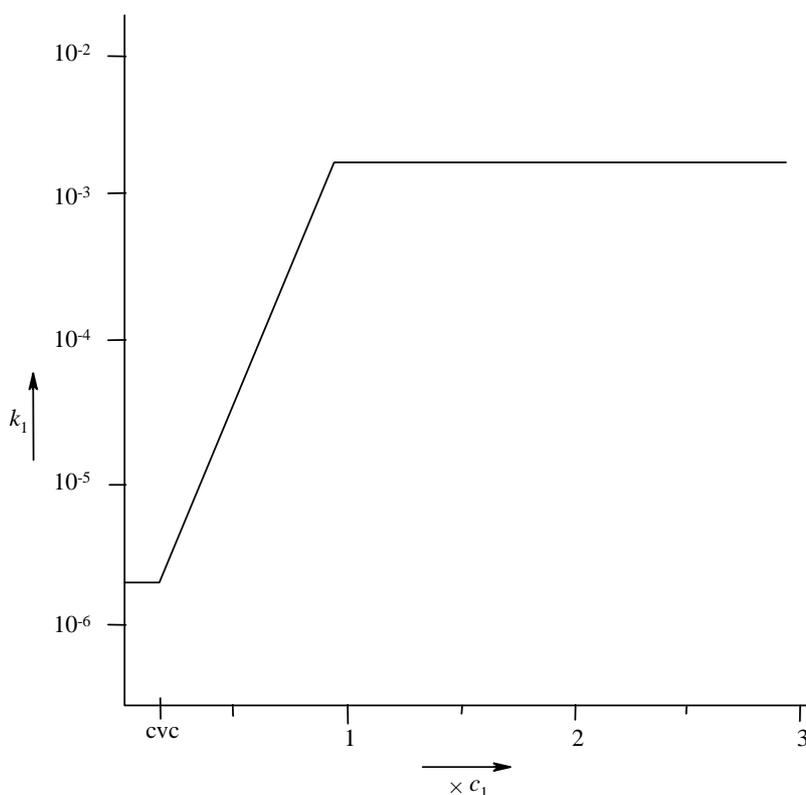
6.2 Signal No 1.

$$6.3 \quad a_0(\text{min}) = \frac{V}{l_c} = \frac{(27.4 + 26.99 n) \times 10^{-3}}{(0.154 + 0.1265 n)} \text{ nm}^2$$

$$\text{For a large value of } n: \quad a_0(\text{min}) = \frac{26.99 \times 10^{-3}}{0.1265} \text{ nm}^2$$

$$a_0(\text{min}) = 0.213 \text{ nm}^2$$

6.4



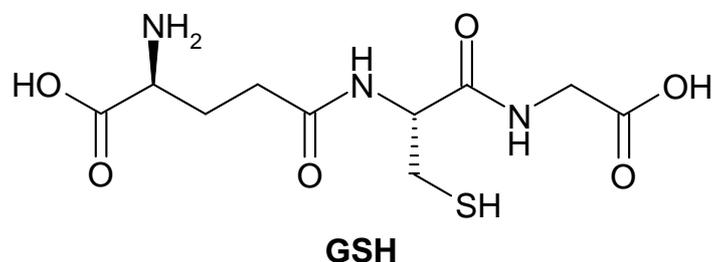
We expect curved bends in the graph, however, sharp corners (see the Figure) are also accepted.

6.5 The second answer is correct: Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.

PROBLEM 7

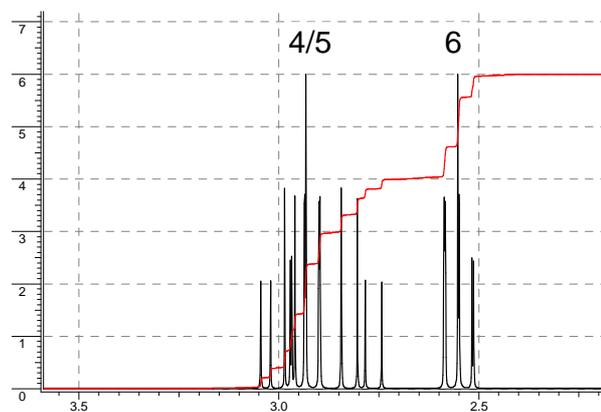
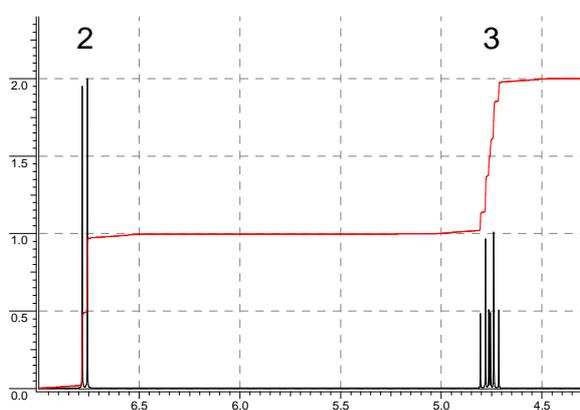
Glutathione, an Essential Mini-Peptide

Glutathione, abbreviated as GSH, is a small peptide that is present in almost all tissues of animals. GSH fulfils important biological functions, such as detoxification of electrophilic chemicals and reduction of (organic) peroxides in blood. An electrophilic compound reacts irreversibly with GSH, especially in the liver, to give a primary product that is converted by a series of biotransformations into a so-called *mercapturic acid*, which is excreted via the urine. Oxidants react with GSH to give the disulfide GSSG, which can be enzymatically reverted to GSH with reductases. The ratio GSH/GSSG in most cells is ≥ 500 .



- 7.1 (a) How many amino acid residues are present in GSH?
- (b) Draw the structures of the corresponding amino acids and mark the chiral centers with an asterisk.

A mercapturic acid **A** isolated from urine of a person who has been exposed to acrylonitrile ($\text{H}_2\text{C}=\text{CH}-\text{CN}$) has the molecular formula $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_3\text{S}$. The ^1H -NMR spectrum of **A** in $(\text{CD}_3)_2\text{SO}$ is shown in Figure 1. When the product is pretreated with D_2O , the signals at δ 12.8 and δ 6.8 are no longer present and the signal 3 is simplified.



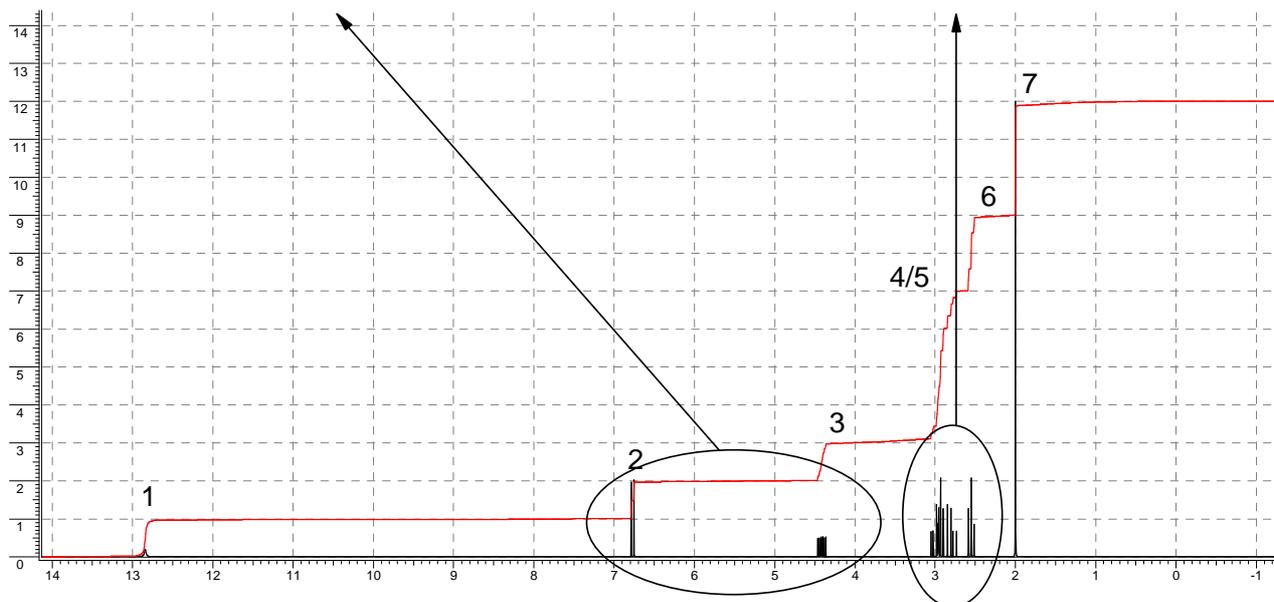


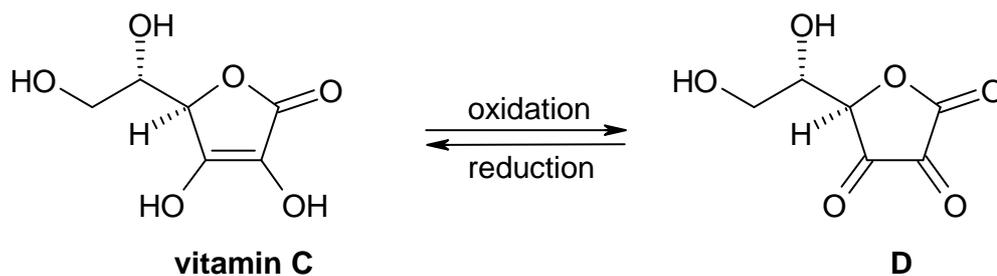
Figure 1

7.2 (a) The NMR-signals correspond with protons in the following groups: CH, CH₂, CH₃, OH and NH. Indicate the appropriate proton group in the boxes for the signals 1 – 7.

Signals	1	2	3	4/5	6	7
Protons	<input type="text"/>					

- (b) How many carbon atoms are present in compound **A** that do not carry any protons?
- (c) Draw the structure of compound **A**.

Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**



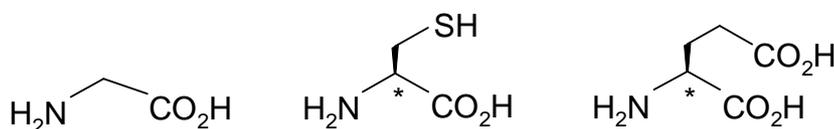
7.3 Eating fresh fruit and vegetables is healthy

- because vitamin C forms a complex with GSH.
- because vitamin C reacts with electrophilic compounds.
- because vitamin C removes oxidants and prevents undesired depletion of GSH.
- for many reasons, but none of them has anything to do with GSH.

SOLUTION

7.1 a) Three amino acid residues.

b)

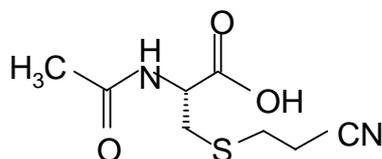


7.2 a)

Signal	1	2	3	4/5	6	7
Group of protons	OH	NH	CH	CH ₂	CH ₂	CH ₃

b) 3

c)



7.3 The third answer is correct: Vitamin C removes oxidants and prevents undesired depletion of GSH.

Theme IV - Chemistry Related to Light and Energy

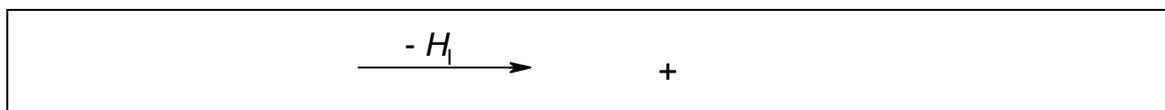
Chemistry plays a major role in meeting our needs of light and energy. Our life is unthinkable without artificial light and energy for mobility.

PROBLEM 8

LIGHTING LAMPS

Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal compounds like CeBr_3 are now included to reach a colour temperature of 6000 K in the lamp. These compounds are ionic solids at room temperature, and upon heating they sublime partially to give a vapour of neutral metal halide molecules. To achieve a high vapour pressure, the sublimation enthalpy should be as low as possible.

- 8.1** Give a thermochemical cycle (Law of Hess) for sublimation of CeBr_3 , via a vapour of mononuclear ions. ($H_l = H_{\text{lattice}}$; $H_e = H_{\text{electrostatic}}$; $H_s = H_{\text{sublimation}}$; H is not absolute, H means ΔH)



+



The lattice energy of the solid can be calculated using the Born–Landé formula:

$$H_l = f \frac{Z_+ Z_- A e^2}{r_+ + r_-} \left(1 - \frac{1}{n}\right)$$

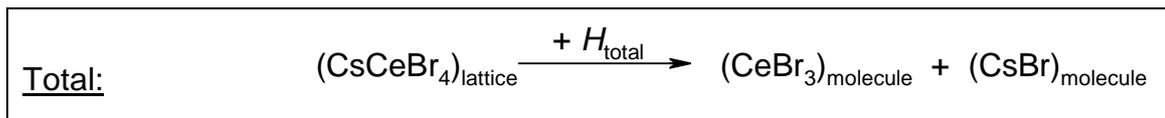
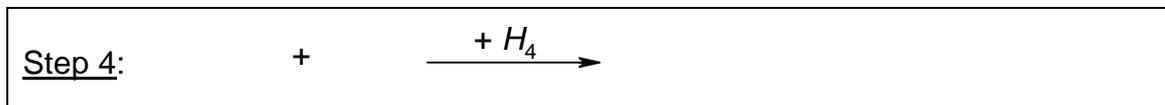
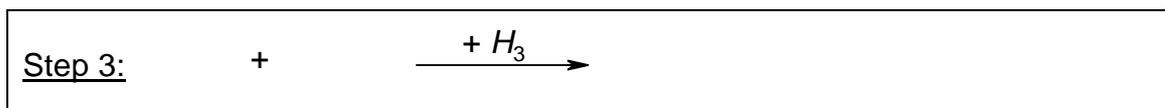
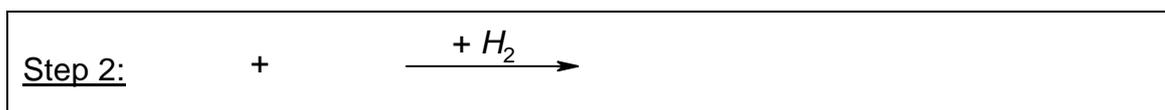
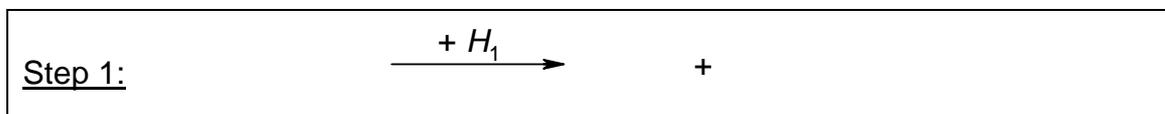
The factor $f e^2$ (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is

2.985. The Born exponent n is 11. The charges of the ions Z_+ and Z_- are integer numbers (Z_- is negative). For the calculation of the energy of gaseous CeBr_3 (when formed from ions) the same Born-Landé formula can be used without A . The structure of CeBr_3 in the gas phase is planar triangular. The radius of Ce^{3+} is 0.115 nm and of Br^- is 0.182 nm.

8.2 Calculate the enthalpy of sublimation of CeBr_3 (in integers; be aware of the signs!)

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of CsBr to the CeBr_3 in the lamp leading at room temperature to solid CsCeBr_4 . When the sublimation temperature decreases the life time of the lamp will increase likewise. The CsCeBr_4 lattice has a NaCl structure with Cs^+ as cations and tetrahedral CeBr_4^- as complex anions. Sublimation of CsCeBr_4 leads to a vapour of CsBr and CeBr_3 molecules.

8.3 Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve CeBr_4^- ions, mononuclear ions and/or neutral molecules in the gas phase.



8.4 Calculate the enthalpy of sublimation of CsCeBr_4 (in integers).

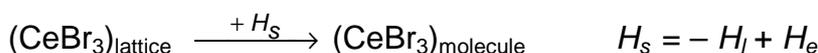
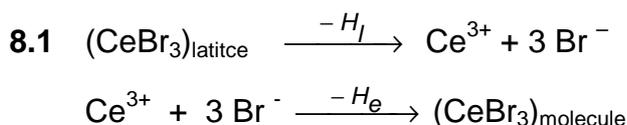
Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The

Cs–Ce distance in the lattice is 0.617 nm. The CeBr_4^- anion is a tetrahedron in which the ratio between the edge and the distance between a corner of the tetrahedron and the centre of gravity (body-radius) amounts to $(2\sqrt{6})/3 = 1.633$. The Born exponent of CsBr is 11. The radius of Cs^+ is 0.181 nm.

8.5 Conclusion in relation to the previous answers: Was adding CsBr a good idea? Mark the correct answer.

- Adding CsBr is counterproductive.
- Adding CsBr has no influence.
- Adding CsBr is advantageous.
- From these data no clear answer can be given.

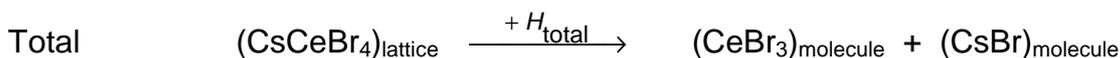
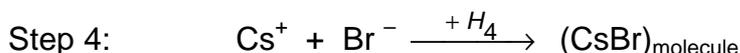
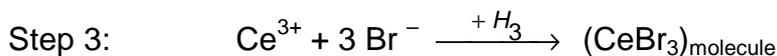
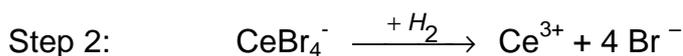
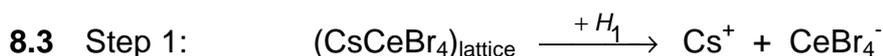
SOLUTION



$$8.2 \quad H_l = -\frac{139 \times 3 \times 1 \times 2.985}{0.297} \times \frac{10}{11} \text{ kJ mol}^{-1} = -3810 \text{ kJ mol}^{-1}$$

$$H_e = \left(-3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11} \right) + \left(3 \times \frac{139 \times 1 \times 1}{0.297 \sqrt{3}} \times \frac{10}{11} \right) \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

$$H_s = 718 \text{ kJ mol}^{-1}$$



8.4 Step 1: The lattice energy of CsCeBr₄ with opposite sign is:

$$H_1 = \frac{139 \times 1 \times 1 \times 1.75}{0.617} \times \frac{10}{11} \text{ kJ mol}^{-1} = 358 \text{ kJ mol}^{-1}$$

Step 2:

$$H_2 = 4 \times \frac{139 \cdot 3 \cdot 1}{0.297} \cdot \frac{10}{11} - 6 \times \frac{139 \times 1 \times 1}{0.297 \times \frac{2}{3} \times \sqrt{6}} \times \frac{10}{11} \text{ kJ mol}^{-1} = 3543 \text{ kJ mol}^{-1}$$

Step 3: The electronic energy in the gas phase of CeBr₃ is (see answer 8.2):

$$H_3 = -3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11} + 3 \times \frac{139 \times 1 \times 1}{0.297 \times \sqrt{3}} \times \frac{10}{11} \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

Step 4: The electrostatic energy in the gas phase of CsBr is

$$H_4 = -\frac{139 \times 1 \times 1}{0.363} \times \frac{10}{11} \text{ kJ mol}^{-1} = -348 \text{ kJ mol}^{-1}$$

Total sum:

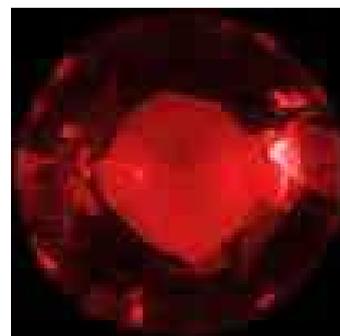
$$H_{\text{total}} = H_1 + H_2 + H_3 + H_4 = 461 \text{ kJ mol}^{-1}$$

8.5 The third answer is correct: Adding CsBr is advantageous.

PROBLEM 9

RED RUBY

Ruby crystals have a deep red colour and are well known for their use in jewellery. Not many people know that the heart of the first laser, built in 1960 by Maiman, was a big ruby crystal. The red colour of ruby originates from the absorption of light by Cr^{3+} ions that are incorporated in colourless aluminium oxide (Al_2O_3) crystals. The Cr^{3+} ion has 3 electrons in the 3d shell and the absorption of light is due to electronic transitions between 3d orbitals of lower and higher energy.



9.1 Indicate which of the four absorption spectra belongs to ruby.

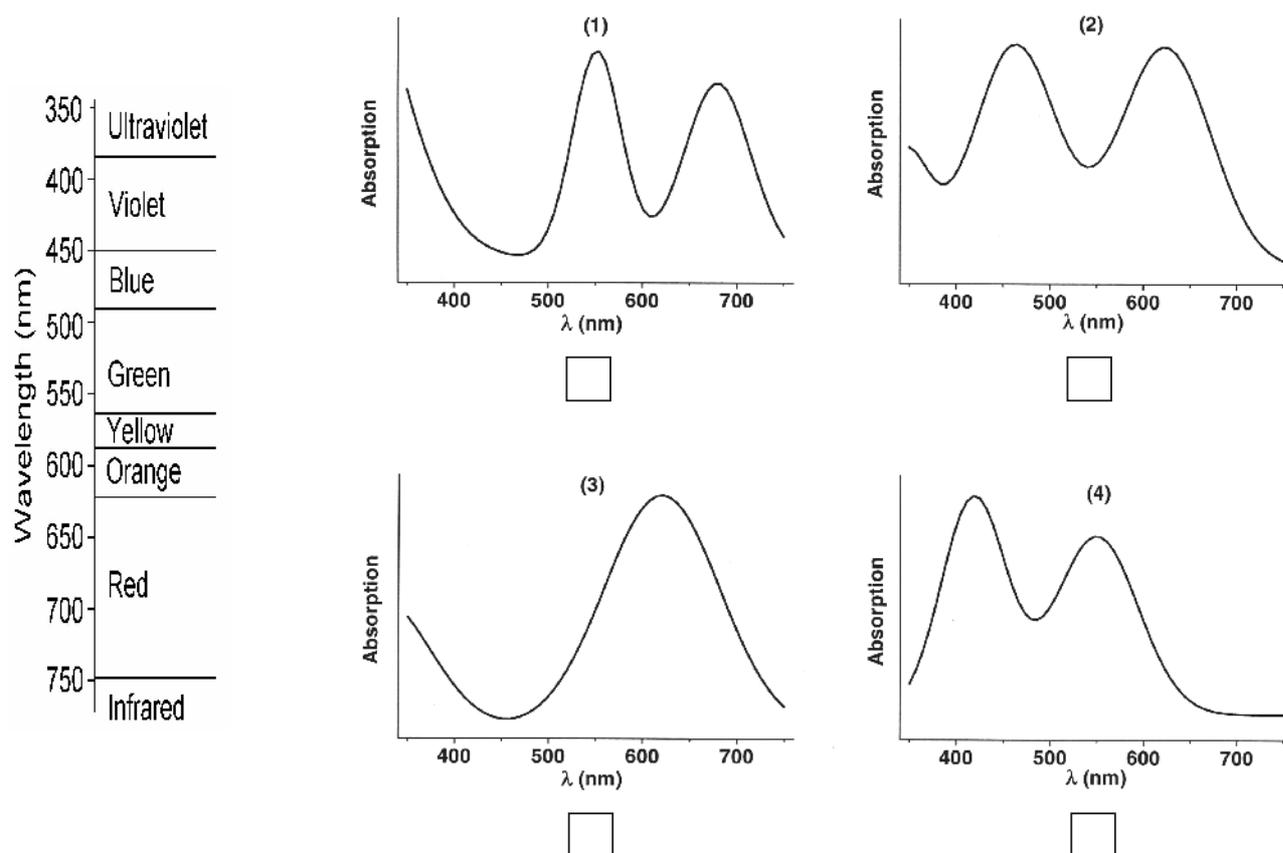


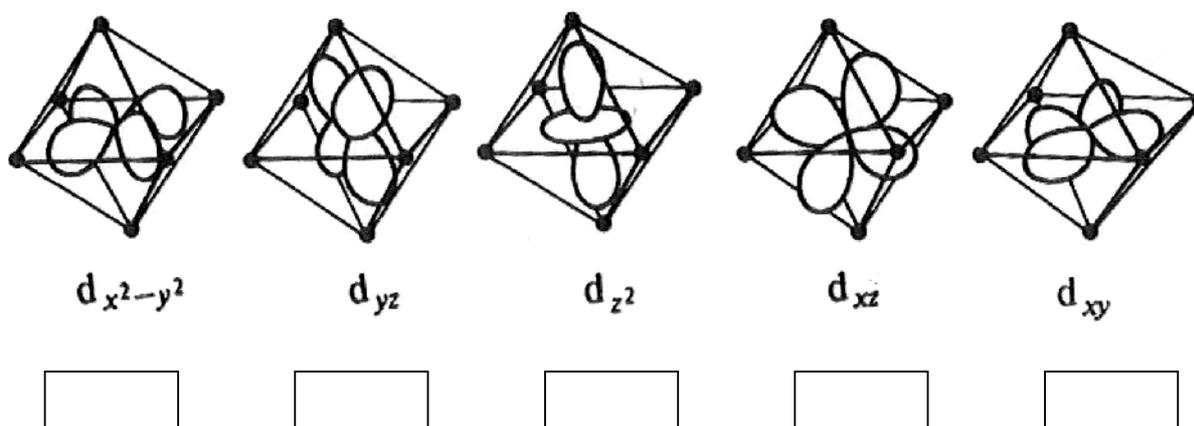
Figure 1

The rod used in ruby lasers is a cylinder with a length of 15.2 cm and a diameter of 1.15 cm. The amount of Cr^{3+} ions is 0.050 mass %. The density of Al_2O_3 is 4.05 g cm^{-3} . The atomic mass of $\text{Cr} = 52\text{u}$. ($1\text{u} = 1.67 \times 10^{-27} \text{ kg}$).

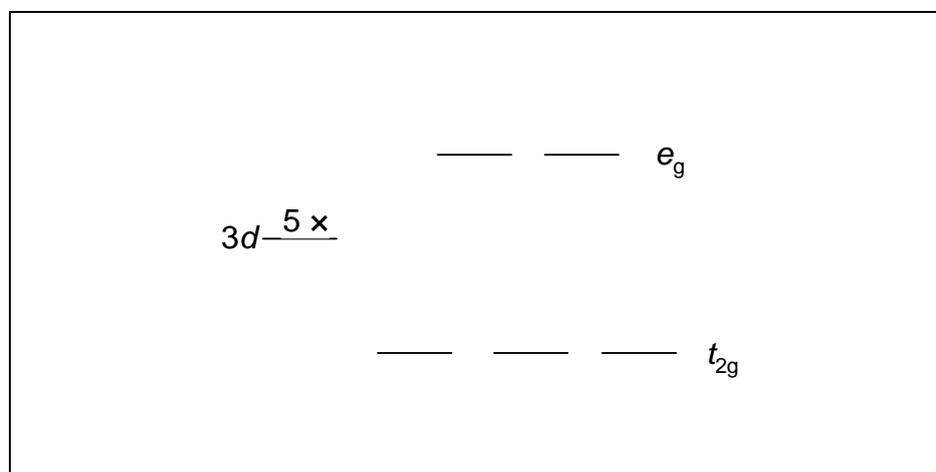
9.2 Calculate how many Cr^{3+} ions are in this laser rod.

In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five $3d$ orbitals is shown below. The box below shows the splitting of the five $3d$ orbitals into a group of three orbitals at lower energy (t_{2g}) and a group of two at higher energy (e_g).

9.3 Indicate in the boxes below which of the $3d$ orbitals (d_z^2 , d_{xy} , d_{yz} , $d_{x^2-y^2}$, d_{xz}) belong to the t_{2g} group and which belong to the e_g group.



9.4 Indicate with arrows the distribution and the direction of the magnetic spin moment of the three $3d$ electrons of Cr^{3+} over the five d orbitals in the lowest energy state of Cr^{3+} .



The ruby is placed on a (non-magnetic) scale. When the scale is in balance (Figure 2) a magnet is placed directly under the side with the ruby.

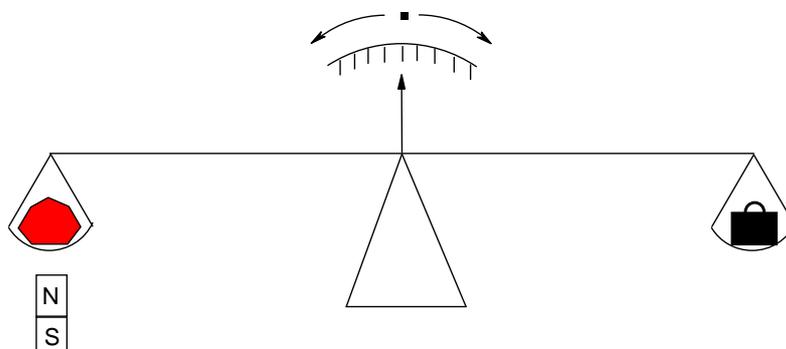


Figure 2

9.5 Indicate what will happen with the ruby (mark the correct answer)

- The magnet attracts the ruby (the ruby moves down)
- The magnet has no influence on the ruby (the ruby does not move)
- The magnet repels the ruby (the ruby moves up)
- The magnet has an oscillating effect on the ruby (the ruby moves up and down)

SOLUTION

9.1 The fourth spectrum is correct.

9.2 Volume of the rod = $\pi \times r^2 \times l$

$$V = \pi \times 0.575^2 \times 15.2 \text{ cm}^3 = 15.79 \text{ cm}^3$$

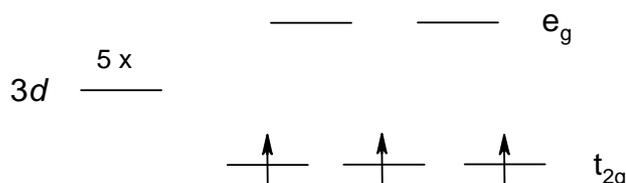
Mass of the rod: $m = 15.79 \times 4.05 \text{ g} = 63.94 \text{ g}$

Mass of chromium in the rod: $m_{\text{Cr}} = 63.94 \text{ g} \times 0.05 / 100 = 0.0319 \text{ g}$

Number of chromium ions: $N = 0.0319 \times 10^{-3} \text{ kg} / (52 \times 1.67 \times 10^{-27}) = 3.68 \times 10^{20}$.

9.3 $d_{x^2-y^2} : e_g$ $d_{yz} : t_{2g}$ $d_{z^2} : e_g$ $d_{xz} : t_{2g}$ $d_{xy} : t_{2g}$

9.4



9.5 The correct answer: The magnet attracts the ruby (the ruby moves down).

PROBLEM 10

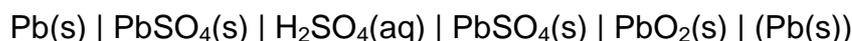
Vehicle Traction Batteries

Battery-powered electric vehicles (EV's) are likely to become increasingly common in the next 50 years because of growing concern over pollution caused by vehicles using combustion engines. The reason for the current meagre commercial success of EV's is that the battery specifications must have a performance and cost profile comparable to conventionally powered vehicles.

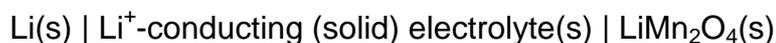
Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

In the current evolution of EV batteries, the most promising long-term solution is the rechargeable light weight lithium-ion battery. Such batteries are under intensive investigation worldwide and hold also promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery. Lithium is used as a negative electrode. It has a high specific capacity and electrode potential. A common positive electrode material is the environmentally benign spinel-type LiMn_2O_4 . The spinel structure comprises a matrix of cubic close-packed oxide ions, stabilised by lithium ions in tetrahedral sites and manganese ions in octahedral sites. In LiMn_2O_4 half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:



A lithium battery is represented by:



Upon discharge the insertion product $\text{Li}_2\text{Mn}_2\text{O}_4$ is formed. Charging the battery leads to the products Li(s) and LiMn_2O_4 .

- 10.1** Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.
- 10.2** Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.

10.3 Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of LiMn_2O_4 .

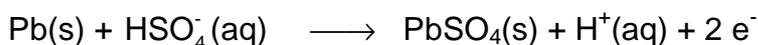
A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1} .

10.4 Calculate the extra weight of the car if the petrol tank is replaced by an equivalent battery in an EV based on (a) lead-acid battery and (b) lithium battery. Assume that in all cases the engine efficiency is the same. Calculate:

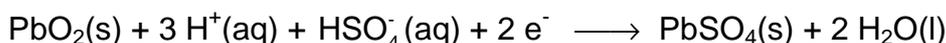
- (a) Extra weight of a lead-acid battery car.
 (b) Extra weight of a lithium battery car.

SOLUTION

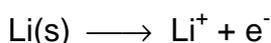
10.1 Reaction at the negative electrode:



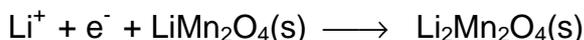
Reaction at the positive electrode:



10.2 Reaction at the negative electrode:



Reaction at the positive electrode:



10.3 Li – ions: coordination number = 4 Mn – ions: coordination number = 6

10.4 Distance of the petrol car = 500 km \Rightarrow 50 kWh

Mass of petrol tank = 10 kg + 50 \times (3.78 / 5) = 47.8 kg

(a) Mass of a lead-acid battery = 50000 Wh / 45 Wh kg^{-1} = 1111.1 kg

Extra weight of a lead-acid battery car = 1111.1 kg – 47.8 kg = 1063.3 kg

(b) Mass of the lithium battery = 1/3 of the mass of a lead-acid battery

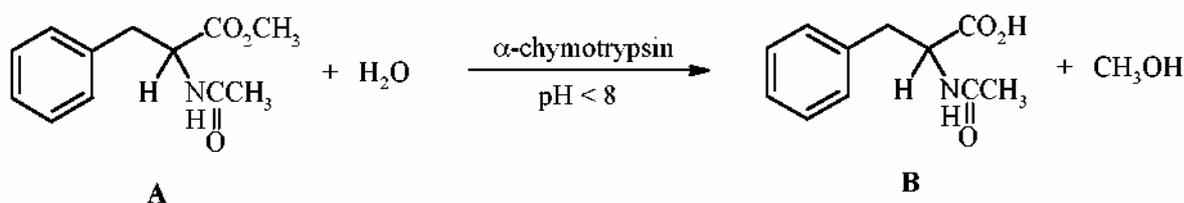
Extra weight of a lithium battery car = 1111.1 kg / 3 – 47.8 kg = 322.6 kg.

PRACTICAL PROBLEMS

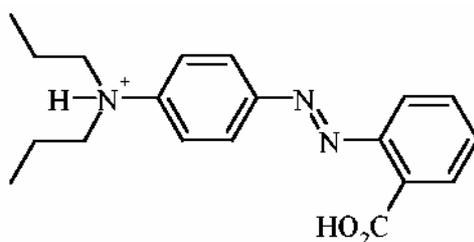
PROBLEM 1 (Practical)

Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

α -Chymotrypsin, a protease enzyme recognizing derivatives of natural α -amino acids, catalyses the hydrolysis of esters. In this experiment the enzymatic hydrolysis of racemic methyl *N*-acetyl-phenylalaninate **A** is investigated (Scheme).



The rate of formation of *N*-acetyl-phenylalanine **B** can be monitored by titration with 0.100 M NaOH in the presence of propyl red as a pH indicator.



Propyl red (protonated form)
At pH < 5: pink; at pH > 6: yellow

Procedure

Note: the required amount of α -chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.

Racemic methyl *N*-acetyl-phenylalaninate **A** [500 mg, the exact mass (± 1 mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 cm³ Erlenmeyer flask and dissolved in methanol (~ 2.5 cm³). Subsequently, propyl red (0.02 % solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α -chymotrypsin (10.0 cm³ of a 0.05 % solution in distilled water) in one portion (*start the stopwatch*).

When the reaction mixture turns pink, it is immediately titrated with 0.100 M NaOH

until the colour changes to yellow. When the pink colour reappears, add just enough titrant to restore the pale yellow colour, swirling the flask continually during the addition. You only need to record the reading on the burette every 5 minutes. (*Note: at the beginning colour changes occur very frequently.*)

Monitor the reaction for 75 minutes. A graph showing the amounts of NaOH consumed in cm³ versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.

SOLUTION

The competitors were expected to show on the answer sheet the following data, tables, graphs or calculations:

1. Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A** (in mg and mmol).
 2. Table with time measured and the total consumption of NaOH in cm³.
 3. A graph of the total consumption of NaOH vs time.
 4. Calculation of the amount of 0.100 M NaOH consumed in this experiment in mmol.
 5. Calculation of the degree of hydrolysis of methyl *N*-acetyl-(*R,S*)-phenylalaninate **A** in mol %.
-
-

of hydrochloric acid (4 M) to pH < 3 with magnetic stirring. Some water is added to the resulting white suspension in order to facilitate stirring.

The white precipitate is then filtered off by suction, washed with ample water (on the filter) and then washed twice with a small amount of di-isopropyl ether to remove most of the adhering water. The urea derivative **B** is left on the filter under suction for at least 3 minutes to remove as much solvent as possible.

A small amount of the obtained urea derivative **B** is retained for TLC-analysis later.

STEP 2

The urea derivative **B** is now transferred into a long-necked round-bottomed flask and hydrochloric acid (4 M, 3 cm³) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 °C on a sand bath. A clear solution is obtained. After a reaction time of 30 minutes, the reaction mixture, which may already contain some precipitate, is cooled to room temperature. The obtained suspension is filtered by suction, washed thoroughly with water and finally washed twice with a small amount of di-isopropyl ether. The product is left on the filter under suction for at least 3 minutes. It is then collected on a filter paper and dried in the air for at least 30 minutes.

The final product **C**, its precursor **B** and starting material **A** (see above) are subjected to TLC-analysis. For this purpose small amounts of either compound are dissolved in a tiny amount of pure acetone. Small samples of these solutions are applied to a TLC plate, using the supplied capillary tubes. The analysis is carried out with two TLC plates in one run. The TLC-plates are developed with a solution of 2% formic acid in ethyl acetate as the eluent. After the elution the TLC-plates are analysed using a UV-lamp. The starting line, solvent front and the UV-active spots are clearly marked with a pencil. Copy the diagram in the box on the answer sheet. The R_f values are determined. Finally, the TLC-plate with the best analysis is wrapped in parafilm and placed in a plastic bag with a sealing strip.

The final product **C** is transferred into a sample vial of which the empty weight has been pre-determined (weight is indicated on the label). Weigh the vial with product and calculate the yield of the product **C**.

The examination committee will check the quality of the benzyhydantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

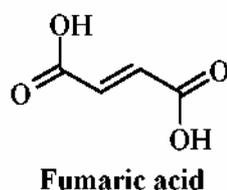
SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations on the answer sheet:

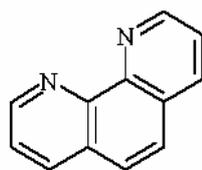
1. Mass of your starting material **A** (see label on the vial) in mg.
 2. Amount of benzylhydantoin **C** obtained.
 3. Calculation of the yield of benzylhydantoin **C** in %.
 4. R_f value of urea derivative **B**.
 5. R_f value of benzylhydantoin **C**.
 6. A copy of the TLC diagram with indication of the front base line of the solvent.
 7. Conclusions from the TLC analysis:
Compound **B**: is pure; contains some **A**; contains several contaminants.
Compound **C**: is pure; contains some **B**; contains some **A** and **B**;
contains several contaminants.
 8. Appearance of benzylhydantoin **C**: white colour, yellowish colour, sticky, crystalline, powder.
 9. Melting point of benzylhydantoin **C** was determined by the examination committee.
 10. The TLC plate was necessary to pack in an envelope and leave it to a laboratory supervisor.
-
-

PROBLEM 3 (Practical)**Determination of Iron in Iron Pills**Introduction

Iron is an essential component of hemoglobin, transporting oxygen in the blood to all parts of the body. It also plays a vital role in many metabolic reactions. Iron deficiency can cause anaemia resulting from low levels of hemoglobin in the blood. Iron deficiency is the most widespread mineral nutritional deficiency worldwide. One way to reduce iron shortage is by treatment with iron pills. The active ingredient in the iron pill to be examined, is iron(II) present as iron(II) fumarate. Besides this organic iron(II) compound the pill contains other compounds such as binding agents. The structure of fumaric acid is:



Iron(II) and 1,10-phenanthroline form an orange/red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The absorbance of this complex, determined at 510 nm in a buffer solution (pH=8) is a measure for the iron content of the iron pill. Since 1,10-phenanthroline only binds to iron(II) and iron(II) is readily oxidized to iron(III), hydroxylammonium chloride is added to reduce all iron(III) to iron(II). A simplified reaction scheme is:



1,10-Phenanthroline

Procedure

The weight of the iron pill is determined with an accuracy of 1 mg using a balance. The pill is carefully pulverized in a mortar and transferred quantitatively into a 100 cm³ beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 cm³, 4 M) is added. The content of the beaker is heated up to approximately 60 °C on a hotplate. The solution turns a yellow colour.

The beaker is then placed in an ultrasonic bath for at least 5 minutes. The beaker is kept in place by styrofoam. The suspension is filtered by suction using a Hirsch funnel containing a small layer of moistened hi-flow filter aid pressed onto the filter. The hi-flow filter aid is washed with ample distilled water. The filtrate is carefully transferred into a volumetric flask (250 cm³) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 cm³ is pipetted from this solution and transferred into a volumetric flask of 100 cm³. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 cm³ is pipetted and transferred into a volumetric flask of 100 cm³. Subsequently, 1,10-phenanthroline solution (10 cm³) and hydroxylammonium chloride solution (1 cm³) are added. Then the volume is adjusted with buffer solution (pH 8).

The absorbance of this solution is measured with a spectrophotometer at 510 nm against water as a blank in a 1.000 cm cell.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient, ϵ) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 M⁻¹cm⁻¹.

Important

In order to eliminate deviations in absorbance typically connected to the spectrophotometer used, a correction factor is denoted on the spectrophotometer you will be using for your experiment. The absorbance observed must be multiplied by this factor in order to obtain the correct absorbance of the solution of the iron complex.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations:

1. Weight of the iron pill in mg.
2. Reading of the spectrophotometer and corrected absorbance.
3. Calculation of the concentration of iron(II)phenanthroline complex in the cell in mmol dm⁻³.
4. Calculation of the total amount of iron(II) in the pill in mg.
5. Calculation of the iron content of the pill in weight %.

35th



International Chemistry Olympiad

**35 theoretical problems
2 practical problems**

THE THIRTY-FIFTH INTERNATIONAL CHEMISTRY OLYMPIAD 5–14 JULY 2003, ATHENS, GREECE

THEORETICAL PROBLEMS

SECTION A: General Chemistry

QUESTION 1

The molar solubility s (mol dm^{-3}) of $\text{Th}(\text{IO}_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

- (a) $s = (K_{\text{sp}} / 128)^{1/4}$
- (b) $s = (K_{\text{sp}} / 256)^{1/5}$
- (c) $s = 256 K_{\text{sp}}^{1/4}$
- (d) $s = (128 K_{\text{sp}})^{1/4}$
- (e) $s = (256 K_{\text{sp}})^{1/5}$
- (f) $s = (K_{\text{sp}} / 128)^{1/5} / 2$

QUESTION 2

Which one of the following equations must be used for the exact calculation of $[\text{H}^+]$ of an aqueous HCl solution at any concentration c_{HCl} ? ($K_{\text{w}} = 1 \times 10^{-14}$).

- (a) $[\text{H}^+] = c_{\text{HCl}}$
- (b) $[\text{H}^+] = c_{\text{HCl}} + K_{\text{w}} / [\text{H}^+]$
- (c) $[\text{H}^+] = c_{\text{HCl}} + K_{\text{w}}$
- (d) $[\text{H}^+] = c_{\text{HCl}} - K_{\text{w}} / [\text{H}^+]$

QUESTION 3

The molar mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 180 g mol^{-1} and N_{A} is the Avogadro constant. Which one of the following statements is not correct?

- (a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 cm³ of solution.
- (b) 1.00 mmol amount of glucose has a mass of 180 mg.
- (c) 0.0100 mol of glucose comprises of 0.0100×24×N_A atoms.
- (d) 90.0 g glucose contain 3×N_A atoms of carbon.
- (e) 100 cm³ of a 0.10 M solution contain 18 g of glucose.

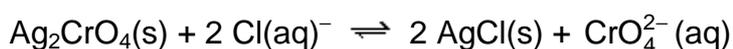
QUESTION 4

If the density of a liquid compound B is ρ (in g cm⁻³), M is the molar mass of B and N_A is the Avogadro constant, then the number of molecules of B in 1 dm³ of this compound is:

- (a) $(1000 \times \rho) / (M \times N_A)$
- (b) $(1000 \times \rho \times N_A) / M$
- (c) $(N_A \times \rho) / (M \times 1000)$
- (d) $(N_A \times \rho \times M) / 1000$

QUESTION 5

The equilibrium constant of the reaction:



is given by the equation:

- (a) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) / K_{sp}(\text{AgCl})^2$
- (b) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) \times K_{sp}(\text{AgCl})^2$
- (c) $K = K_{sp}(\text{AgCl}) / K_{sp}(\text{Ag}_2\text{CrO}_4)$
- (d) $K = K_{sp}(\text{AgCl})^2 / K_{sp}(\text{Ag}_2\text{CrO}_4)$
- (e) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) / K_{sp}(\text{AgCl})$

QUESTION 6

How many cm³ of 1.00 M NaOH solution must be added to 100.0 cm³ of 0.100 M H₃PO₄ solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H₃PO₄ are pK₁ = 2.1, pK₂ = 7.2, pK₃ = 12.0)

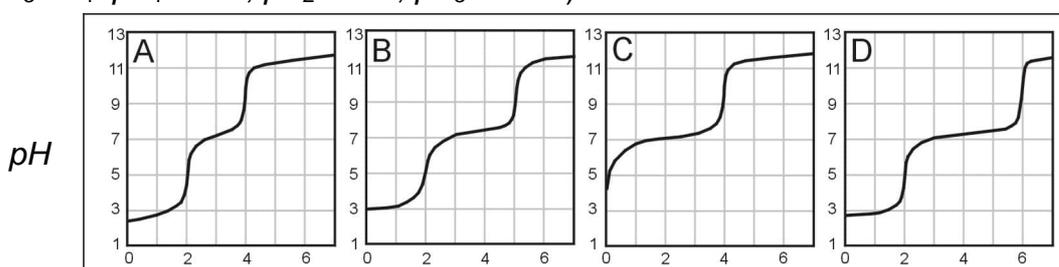
- (a) 5.0 cm³

- (b) 10.0 cm³
- (c) 15.0 mL
- (d) 20.0 mL

QUESTION 7

Solutions containing H₃PO₄ and/or NaH₂PO₄ are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (*pH* vs. volume of titrant) shown in the figure:

(For H₃PO₄: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)



Volume of titrant (cm³)

- a) The sample contains H₃PO₄ only.

Curve A (), Curve B (), Curve C (), Curve D ()

- b) The sample contains both in a mole ratio H₃PO₄ : NaH₂PO₄ = 2 : 1.

Curve A (), Curve B (), Curve C (), Curve D ()

- c) The sample contains both in a mole ratio H₃PO₄ : NaH₂PO₄ = 1 : 1.

Curve A (), Curve B (), Curve C (), Curve D ()

QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine (CH₃)₂NNH₂ and N₂O₄ (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N₂, CO₂ and H₂O are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of (CH₃)₂NNH₂?

- (a) 8
- (b) 9
- (c) 10
- (d) 11
- (e) 12

QUESTION 9

The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

- (a) F
- (b) (4/3) F
- (c) (3/2) F
- (d) 2 F
- (e) 3 F

QUESTION 10

Identify particle X in each of the following nuclear reactions:

- a) ${}_{30}^{68}\text{Zn} + {}_0^1\text{n} \rightarrow {}_{28}^{65}\text{Ni} + \text{X}$
- b) ${}_{52}^{130}\text{Te} + {}_1^2\text{H} \rightarrow {}_{53}^{131}\text{I} + \text{X}$
- c) ${}_{82}^{214}\text{Pb} \rightarrow {}_{83}^{214}\text{Bi} + \text{X}$
- d) ${}_{11}^{23}\text{Na} + {}_0^1\text{n} \rightarrow {}_{11}^{24}\text{Na} + \text{X}$
- e) ${}_{9}^{19}\text{F} + {}_0^1\text{n} \rightarrow {}_{9}^{20}\text{F} + \text{X}$

QUESTION 11

10.0 cm³ of 0.50 M HCl and 10.0 cm³ of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 cm³ of 0.50 M NaOH were used instead of 10.0 cm³. Thermal losses are negligible and the specific heats of both solutions are taken as equal.

- (a) (1/2) ΔT
- (b) (2/3) ΔT
- (c) (3/4) ΔT
- (d) ΔT

QUESTION 12

Natural antimony consists of the following 2 stable isotopes: ^{121}Sb , ^{123}Sb . Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl , ^{37}Cl . Natural hydrogen consists of the following 2 stable isotopes: ^1H , ^2H . How many peaks are expected in a low resolution mass spectrum for the ionic fragment SbHCl^+ ?

- (a) 4
- (b) 5
- (c) 6
- (d) 7
- (e) 8
- (f) 9

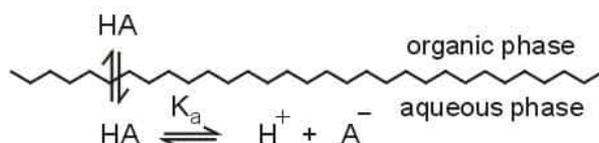
QUESTION 13

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5° . Based on this we must expect a beam of X-rays diffracted at:

- (a) 22.0 degrees
- (b) 22.5 degrees
- (c) 23.0 degrees
- (d) 23.5 degrees
- (e) 24.0 degrees
- (f) 24.5 degrees

QUESTION 14

The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

- (a) The distribution constant (K_D) of the acid HA depends on the pH of the aqueous phase. (Y) (N)
- (b) HA can be efficiently extracted only from acidic aqueous solutions. (Y) (N)

- (c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. (Y) (N)
- (d) The distribution ratio (D) of the acid HA depends mainly on its concentration. (Y) (N)

QUESTION 15

Regarding Beer's law, are the following statements correct (Y) or not (N)?

- (a) The absorbance is proportional to the concentration of the absorbing compound. (Y) (N)
- (b) The absorbance is linearly related to the wavelength of the incident light. (Y) (N)
- (c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. (Y) (N)
- (d) The transmittance is inversely proportional to the logarithm of absorbance. (Y) (N)
- (e) The transmittance is inversely proportional to the concentration of the absorbing compound. (Y) (N)

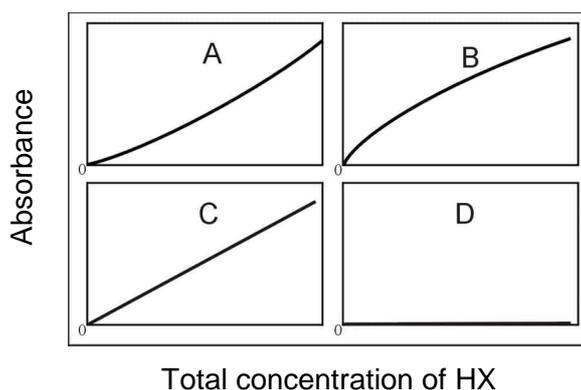
QUESTION 16

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics:

- a) 3000 Å 150 nm (), 300 nm (), 600 nm (), 5000 nm ()
- b) 5×10^{14} Hz 150 nm (), 300 nm (), 600 nm (), 5000 nm ()
- c) 2000 cm^{-1} 150 nm (), 300 nm (), 600 nm (), 5000 nm ()
- d) 2×10^6 GHz 150 nm (), 300 nm (), 600 nm (), 5000 nm ()

QUESTION 17

The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:



- a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb. Curve A (), Curve B (), Curve C (), Curve D ()
- b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb. Curve A (), Curve B (), Curve C (), Curve D ()
- c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb. Curve A (), Curve B (), Curve C (), Curve D ()
- d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb. Curve A (), Curve B (), Curve C (), Curve D ()
- e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero. Curve A (), Curve B (), Curve C (), Curve D ()

QUESTION 18

Which of the following acids is the strongest?

- a) perchloric acid, HClO_4
- b) chloric acid, HClO_3
- c) chlorous acid, HClO_2
- d) hypochlorous, HClO
- (e) All of them are equally strong because they all contain chlorine

QUESTION 19

Which structure describes best the crystal system of iron in which the coordination number is 8?

- a) simple cubic
- b) body-centered cubic
- c) cubic closest packed
- d) hexagonal closest packed
- e) none of the above

QUESTION 20

Which of the following elements has the largest third ionization energy?

- a) B
- b) C
- c) N
- d) Mg
- e) Al

QUESTION 21

Which second period (row) element has the first six ionization energies (IE in electron volts, eV) listed below?

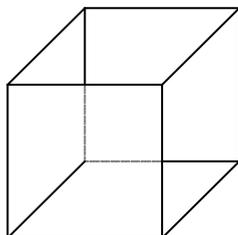
IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

- a) B
- b) C
- c) N
- d) O
- e) F

QUESTION 22

Silver metal exists as a face-centered cubic (fcc) packed solid.

- a) Draw an fcc unit cell.



- b) How many atoms are present in the fcc unit cell?
 c) The density of silver has been determined to be 10.5 g cm^{-3} . What is the length of each edge of the unit cell?
 d) What is the atomic radius of the silver atoms in the crystal?

QUESTION 23

Are the following statements correct (Y) or not (N)?

- a) HF boils at a higher temperature than HCl. (Y) (N)
 b) HBr boils at a lower temperature than HI (Y) (N)
 c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. (Y) (N)
 d) Ammonia solutions are buffer solutions because they contain the conjugate pair $\text{NH}_3 - \text{NH}_4^+$. (Y) (N)
 e) Pure water at $80 \text{ }^\circ\text{C}$ is acidic. (Y) (N)
 f) During electrolysis of an aqueous KI solution with graphite electrodes, the *pH* near the cathode is below 7. (Y) (N)

QUESTION 24

Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1 : 3. How many moles of HNO_3 are consumed by 1 mol of Zn?

- | | | | | | |
|----|-----|--------------------------|----|-----|--------------------------|
| a) | 2.2 | <input type="checkbox"/> | d) | 2.8 | <input type="checkbox"/> |
| b) | 2.4 | <input type="checkbox"/> | e) | 3.0 | <input type="checkbox"/> |
| c) | 2.6 | <input type="checkbox"/> | f) | 3.2 | <input type="checkbox"/> |

SOLUTIONS FOR SECTION A

1: (b); :

2: (b);

3: (e) is not correct;

4: (b);

5: (a);

6: (c);

7: **a)** curve A;

b) curve B;

c) curve D;

8: (b);

9: (d);

10: **a)** alpha;

b) neutron;

c) beta;

d) gamma;

e) gamma;

11: (b);

12: (c);

13: (d);

14: **a)** N;

b) Y;

c) Y;

d) N;

15: **a)** Y;

b) N;

c) Y;

d) N;

e) N;

16: **a)** 300 nm;

b) 600 nm;

c) 5000 nm;

d) 150 nm;

17: **a)** Curve A;

b) Curve B;

c) Curve D;

d) Curve C;

e) Curve C;

18: (a);

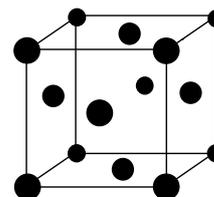
19: (b);

20: (d);

21: (b);

22:

a)



b) 4 atoms,

c) The length of each edge of the unit cell is 0.409 nm,

d) The atomic radius of the silver atoms in the crystal is 0.145 nm.

23: **a)** Y;

b) Y;

c) N;

d) N;

e) N;

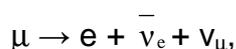
f) N;

24: (d)

SECTION B: PHYSICAL CHEMISTRY**PROBLEM 25 Muon**

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

- a) The most common spontaneous disintegration reaction for the muon is:



where $\bar{\nu}_e$ is the electron antineutrino, and ν_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + \nu_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of 1.4846×10^{-11} J. Determine the mass of the muon.

- b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^1H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

SOLUTION

- a) Energy of a stationary muon:

$$E_\mu = m_\mu c^2 = E_e + E_{\nu,\nu}$$

$$m_\mu c^2 = m_e c^2 + (T_e + E_{\nu,\nu})$$

$$m_\mu = \frac{m_e + (T_e + E_{\nu,\nu})}{c^2} = \frac{9.109 \times 10^{-31} + (1.4846 \times 10^{-11} + 2.000 \times 10^{-12})}{(2.998 \times 10^8)^2} = 1.883 \times 10^{-28} \text{ kg}$$

- b) From Bohr theory:

$$E_n = -\frac{m e^4}{2 n^2 h^2} = -109700 \text{ cm}^{-1} \times \frac{1}{n^2} \times \left(\frac{m}{m_e} \right),$$

where

$$m = \frac{m_{\mu} m_{\text{H}}}{m_{\mu} + m_{\text{H}}}$$

$$\lambda = \frac{1}{E_4 - E_2} = \frac{1}{109700 \left(\frac{m}{m_e} \right) \left(\frac{1}{4} - \frac{1}{16} \right)} = 2.615 \times 10^{-7} \text{ cm}$$

$$\frac{m}{m_e} = 185.9$$

$$m = 185.9 \times 9.109 \times 10^{-31} = 1.693 \times 10^{-28} \text{ kg}$$

The mass of a proton from Tables attached :

$$m_{\text{H}} = 1.673 \times 10^{-27} \text{ kg}$$

$$m_{\mu} = \frac{m m_{\text{H}}}{m_{\text{H}} - m} = \frac{1.693 \times 10^{-28} \times 1.673 \times 10^{-27}}{1.673 \times 10^{-27} - 1.693 \times 10^{-28}} = 1.884 \times 10^{-28} \text{ kg}$$

PROBLEM 26 **Spectrum of CO**

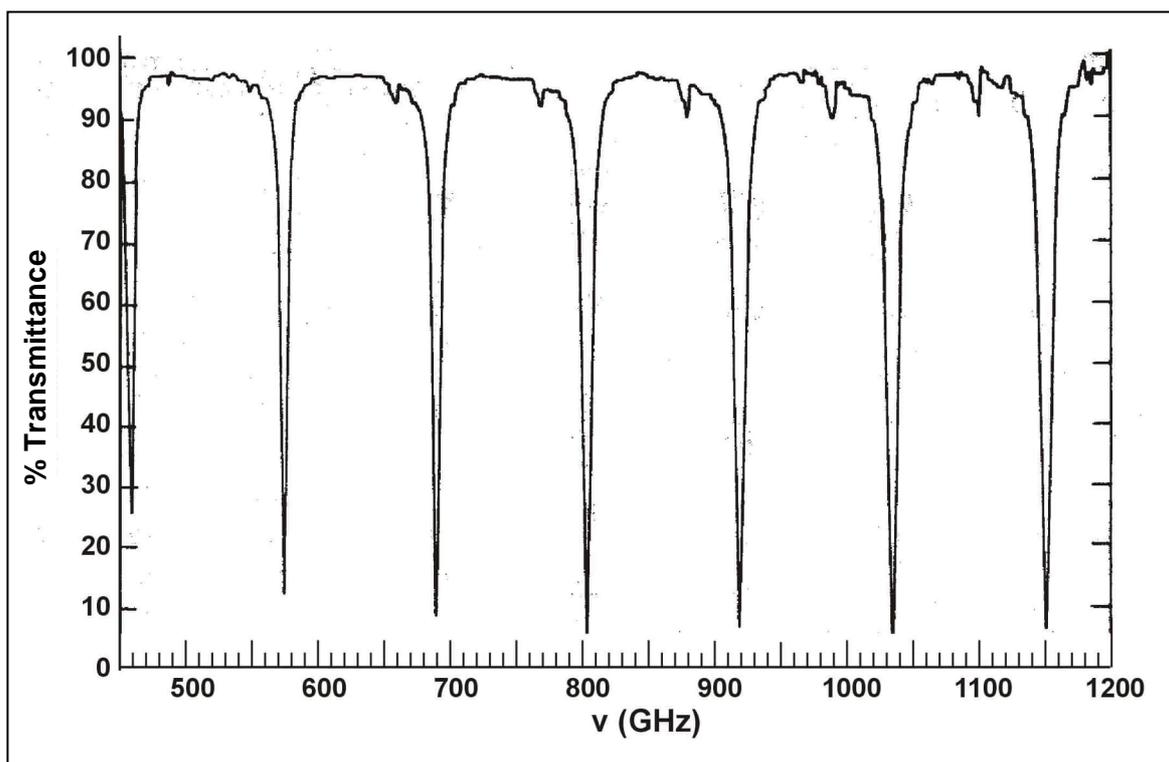
Rotational energy levels of diatomic molecules are well described by the formula $E_J = B J(J+1)$, where J is the rotational quantum number of the molecule and B its rotational constant. Constant B is related to the reduced mass μ and the bond length R of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}$$

In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h \nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2 B (J+1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h (\Delta \nu) = 2 B$.

By inspecting the spectrum provided, determine the following quantities for $^{12}\text{C}^{16}\text{O}$ with appropriate units:

- $\Delta \nu$
- B
- R



SOLUTION

a) For example: $\Delta\nu = 1150 - 1035 = 115 \text{ GHz}$

b)
$$B = \frac{h \Delta\nu}{2} = \frac{6.63 \times 10^{-34} \times 115 \times 10^9}{2} = 3.81 \times 10^{-23} \text{ J}$$

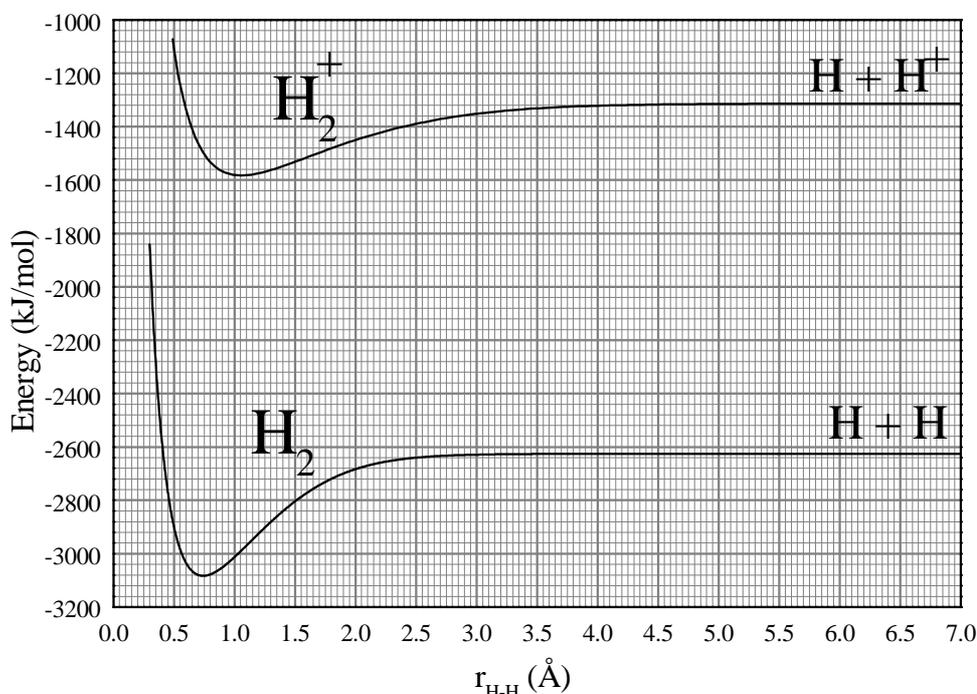
c)
$$\mu = \frac{m(\text{C}) \times m(\text{O})}{m(\text{CO})} = \frac{12 \times 16}{28} = 6.86 \text{ a.u.} = 1.14 \times 10^{-26} \text{ kg}$$

For interatomic distance R :

$$R = \frac{h}{2\pi \sqrt{2\mu B}} = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \sqrt{2 \times 1.14 \times 10^{-26} \times 3.81 \times 10^{-23}}} = 1.13 \times 10^{-10} \text{ m} = 1.13 \text{ \AA}$$

PROBLEM 27 Hydrogen molecule

Using the information provided on this graph, give numerical answers with appropriate units to the following questions:



1. What are the equilibrium bond lengths of H₂ and H₂⁺?
2. What are the binding energies of H₂ and H₂⁺?
3. What is the ionisation energy of the H₂ molecule?
4. What is the ionisation energy of the H atom?
5. If we use electromagnetic radiation of frequency 3.9×10^{15} Hz in order to ionise H₂, what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

SOLUTION

1. The equilibrium bond lengths of H₂ and H₂⁺ can be read from the minimum of the curves: $r(\text{H}_2) = 0.75 \text{ \AA}$; $r(\text{H}_2^+) = 1.05 \text{ \AA}$
2. The binding energies of H₂ and H₂⁺ can be calculated as the differences in the values for infinitive bond lengths and those for minima of the particular curves:

$$E_{\text{bond}}(\text{H}_2) = -2620 - (-3080) = 460 \text{ kJ mol}^{-1}$$

$$E_{\text{bond}}(\text{H}_2^+) = -1310 - (-1580) = 270 \text{ kJ mol}^{-1}$$

3. The ionization energy $E_{\text{ion}}(\text{H}_2)$:

$$E_{\text{ion}}(\text{H}_2) = -1580 - (-3080) = 1500 \text{ kJ mol}^{-1}$$

4. $E_{\text{ion}}(\text{H}) = -1310 - (-2620) = 1310 \text{ kJ mol}^{-1}$

5. $\text{H}_2 + h\nu \rightarrow \text{H}_2^+ + \text{e}^-$

$$E(\text{H}_2) + h\nu \rightarrow E(\text{H}_2^+) + \frac{m_e v_e^2}{2}$$

$$v_e = \sqrt{\frac{2(E(\text{H}_2) - E(\text{H}_2^+) + h\nu)}{m_e}} =$$

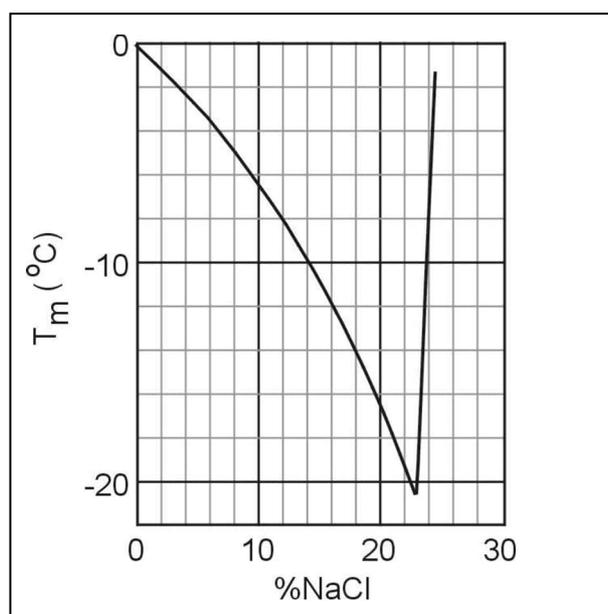
$$= \sqrt{\frac{2\left(\frac{-3080 \times 10^3 - (-1510 \times 10^3)}{6.02 \times 10^{23}}\right) + 6.63 \times 10^{-34} \times 4.1 \times 10^{15}}{9.11 \times 10^{-31}}} = 492 \times 10^3 \text{ ms}^{-1}$$

PROBLEM 28 Cryoscopy

Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 °C) and well above the CO₂ sublimation point (–78 °C) this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as –20 °C can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 °C with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

- a) The mixing process is spontaneous. (Y) (N)
- b) The change of entropy during the mixing process is negative. (Y) (N)
- c) The following diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is the freezing point of the bath based on the diagram?



- d) If an equal mass of MgCl₂ were used instead of NaCl, would the freezing point be higher? (Y) (N)

SOLUTION

The correct answers are as follows:

- a) Y (Yes)
- b) N (No)
- c) The freezing point of the bath is –9 °C.
- d) Y (Yes)

PROBLEM 29 Pool

A very large swimming pool filled with water of temperature equal to 20 °C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine:

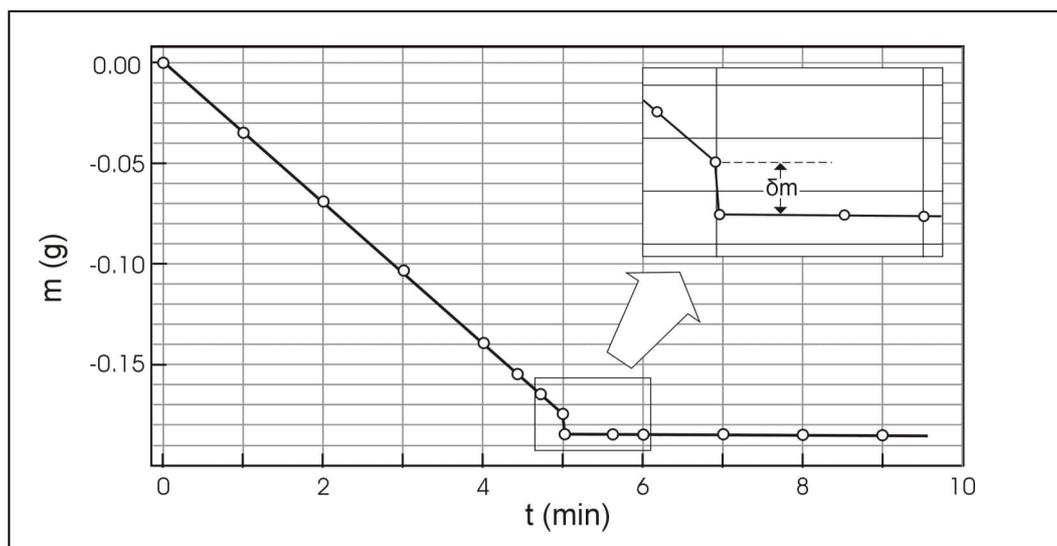
- a) The heat delivered to the water.
- b) Is the change of entropy of the resistor positive, negative, or zero?
- (i) $\Delta S_{\text{res}} > 0$
- (ii) $\Delta S_{\text{res}} = 0$
- (iii) $\Delta S_{\text{res}} < 0$
- c) Is the change of entropy of the water positive, negative, or zero?
- i) $\Delta S_{\text{pool}} > 0$
- (ii) $\Delta S_{\text{pool}} = 0$
- (iii) $\Delta S_{\text{pool}} < 0$
- d) Is the change of entropy of the system positive, negative, or zero?
- (i) $\Delta S_{\text{total}} > 0$
- (ii) $\Delta S_{\text{total}} = 0$
- (iii) $\Delta S_{\text{total}} < 0$
- e) Is the process reversible? (Y) (N)

SOLUTION

- a) $Q = 500 \text{ W} \times 20 \text{ min} \times 60 = 600 \text{ kJ}$
- b) $\Delta S_{\text{res}} = 0$
- c) $\Delta S_{\text{pool}} > 0$
- d) $\Delta S_{\text{total}} > 0$
- e) The answer is No (N).

PROBLEM 30 Gas velocity

The experiment described here gives a simple way to determine the mean velocity u of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time $t = 0$. Balance readings are recorded as shown on the diagram.



At $t = 5$ min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δm . Therefore, the force exerted on the lid is $f = \delta m g$. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., $f = \frac{1}{2} u \frac{dm}{dt}$. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume $g = 9.8 \text{ m s}^{-2}$.

SOLUTION

$$\frac{dm}{dt} = \frac{\Delta m}{\Delta t} = \frac{0.14 \text{ g}}{4 \text{ min}} = 0.035 \text{ g min}^{-1} = 5.8 \times 10^{-4} \text{ g s}^{-1}$$

$$\delta m g = \frac{1}{2} u \frac{dm}{dt}$$

$$u = \frac{0.01 \times 9.81 \times 2}{5.8 \times 10^{-4}} = 338 \text{ m s}^{-1}$$

SECTION C: Organic Chemistry**PROBLEM 31 Ester identification**

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 cm³ of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 cm³ of a 1.00 M HCl solution to titrate the unused NaOH only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with I₂/NaOH to give a yellow precipitate and C₆H₅COONa. The diacid **B** reacted with Br₂ in CCl₄ to give a single, optically inactive product (compound **D**). Ozonolysis of **B** gave only one product.

- Determine the molecular mass of compound **A**.
- Give the structural formulas of **A**, **B**, and **C** without stereochemical information.
- Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.
- Give the stereochemical formula for **D**, using a Fischer projection.
- Give the stereochemical formula for **B**.

The diester **A** also reacted with Br₂ in CCl₄ and was converted to a mixture of two compounds (**E**, **F**) both optically active.

- Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

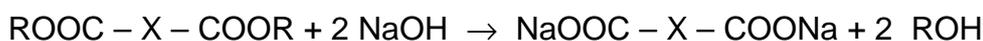
If we use Na¹⁸OH for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

- Mark the correct answer:
 - Only **B**
 - Only **C**
 - Both **B** and **C**

SOLUTION

- For reaction with diester **A** $30 - 6 = 24$ cm³ of 1.00 M NaOH (0.024 mol NaOH)

Reaction:

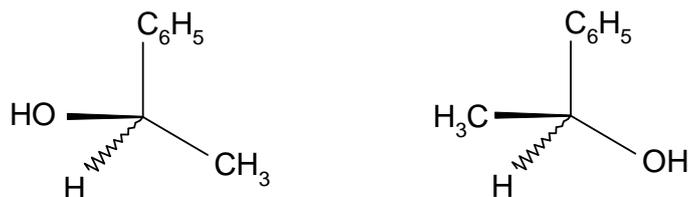


The amount of diester: $0.024 \text{ mol} / 2 = 0.012 \text{ mol}$

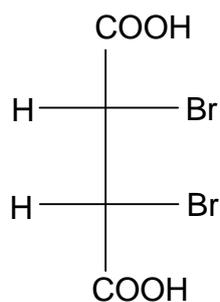
$$M(A) = 2.81 \text{ g} / 0.012 \text{ mol} = 234 \text{ g mol}^{-1}$$

- b) **A:** $\text{H}_3\text{COCO-CH=CH-COO}(\text{CH}_3)\text{C}_6\text{H}_5$
B: HOOC-CH=CH-COOH
C: $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$

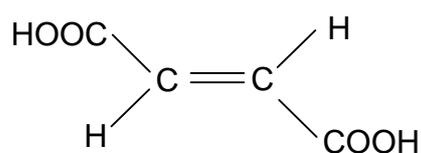
- c) Possible stereochemical formulas for **C**:



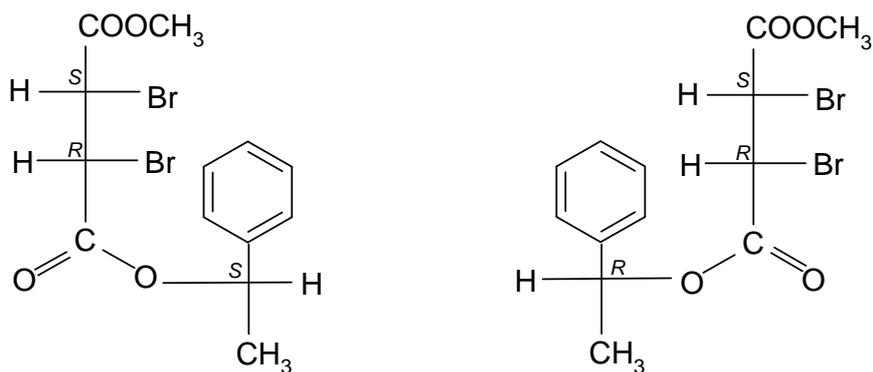
- d) Stereochemical formula for **D**:



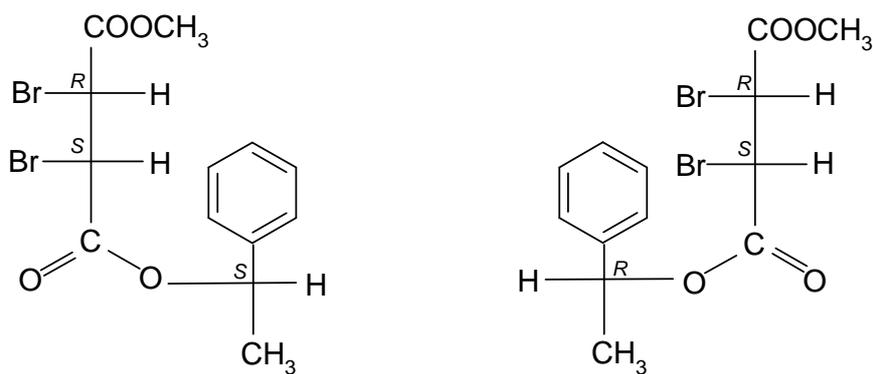
- e) Stereochemical formula for **B**:



- f) Possible stereochemical formula(s) for **E**:



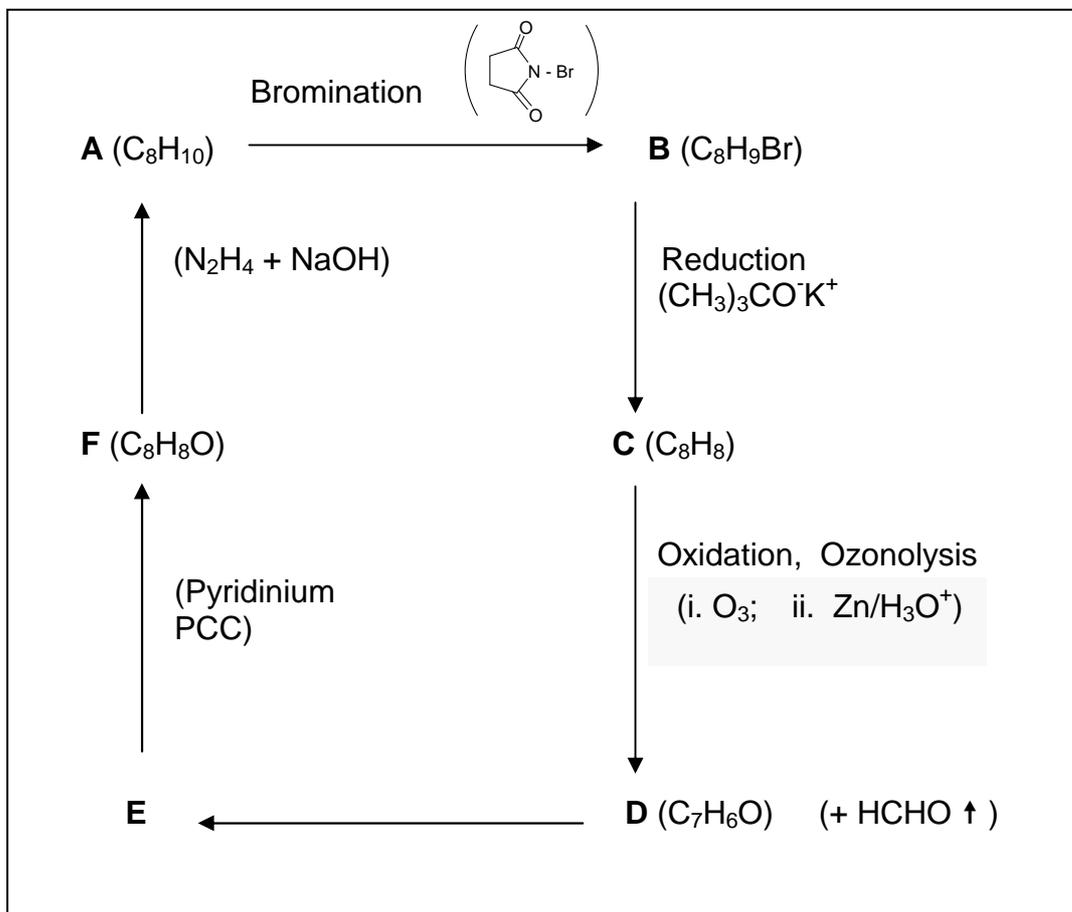
Possible stereochemical formula(s) for F:



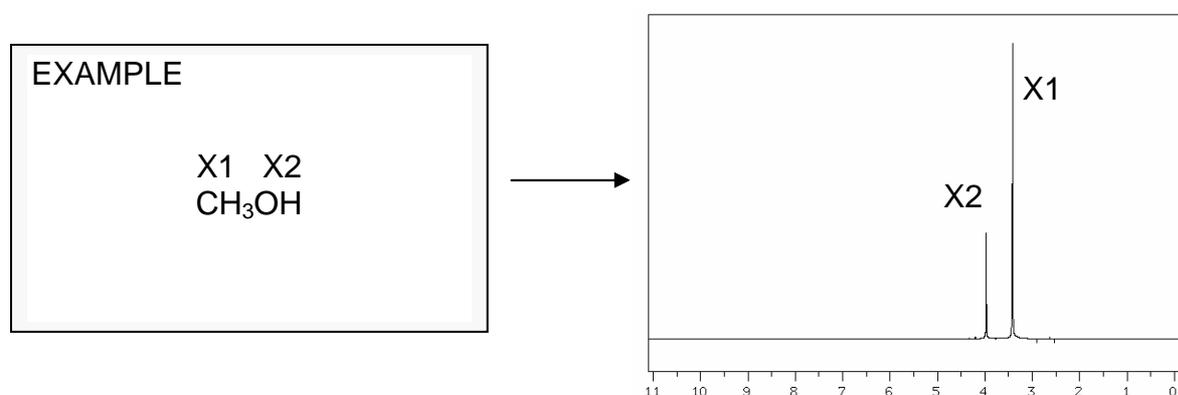
g) Correct answer is ii).

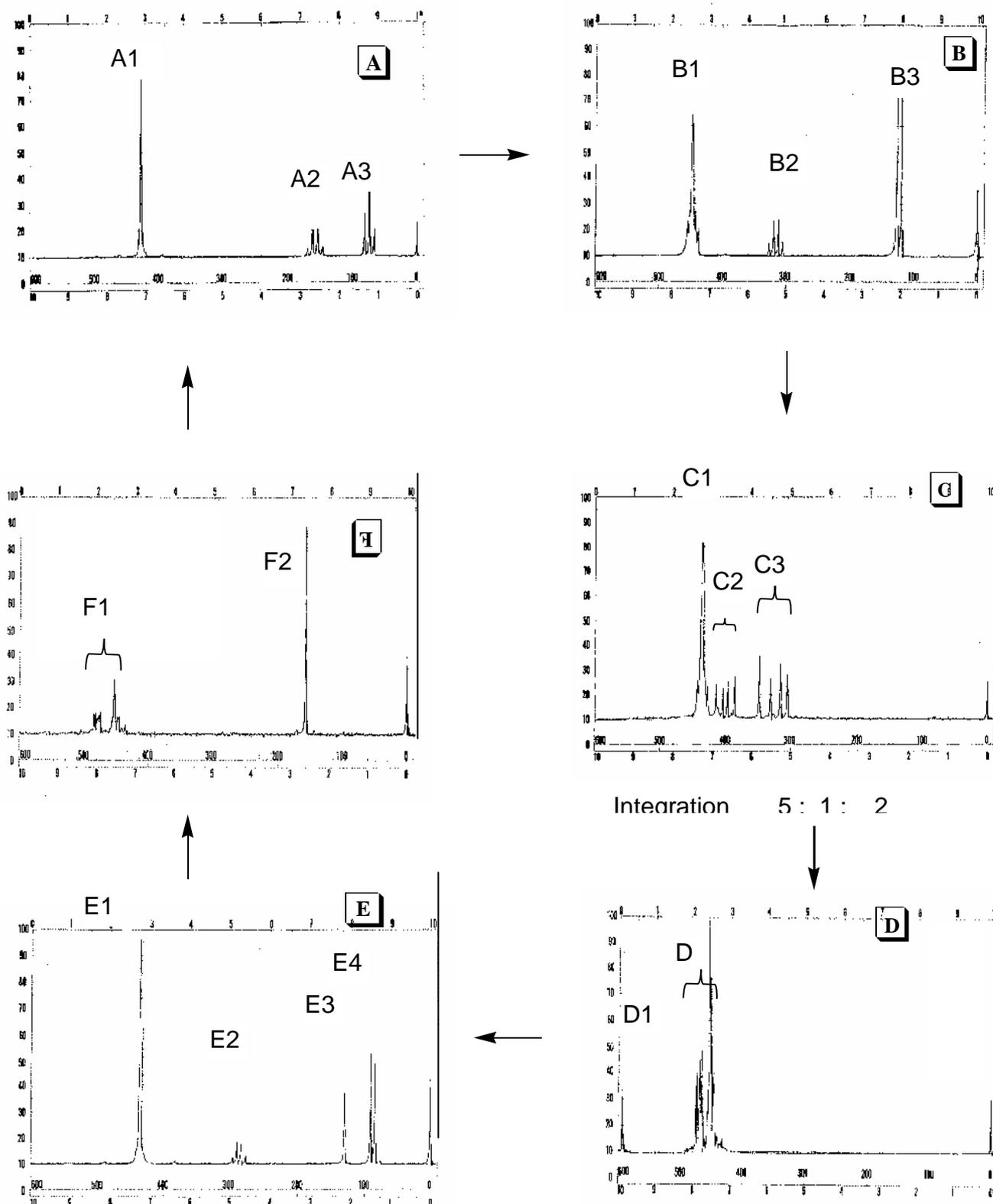
PROBLEM 32 NMR puzzle

An organic compound **A** (C_8H_{10}) gives the following chain of reactions:

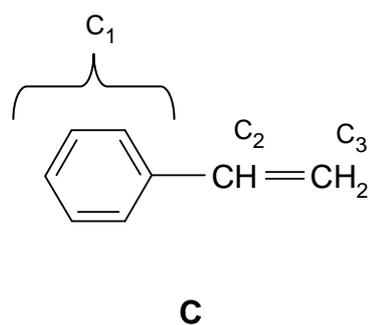
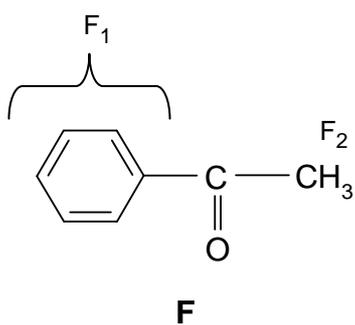
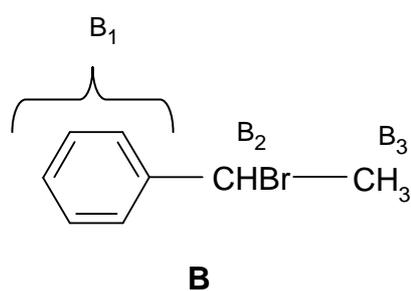
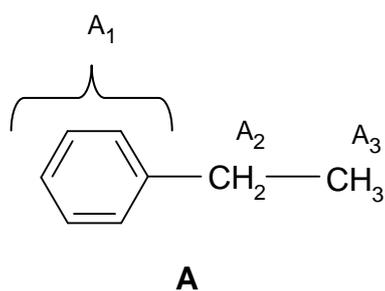
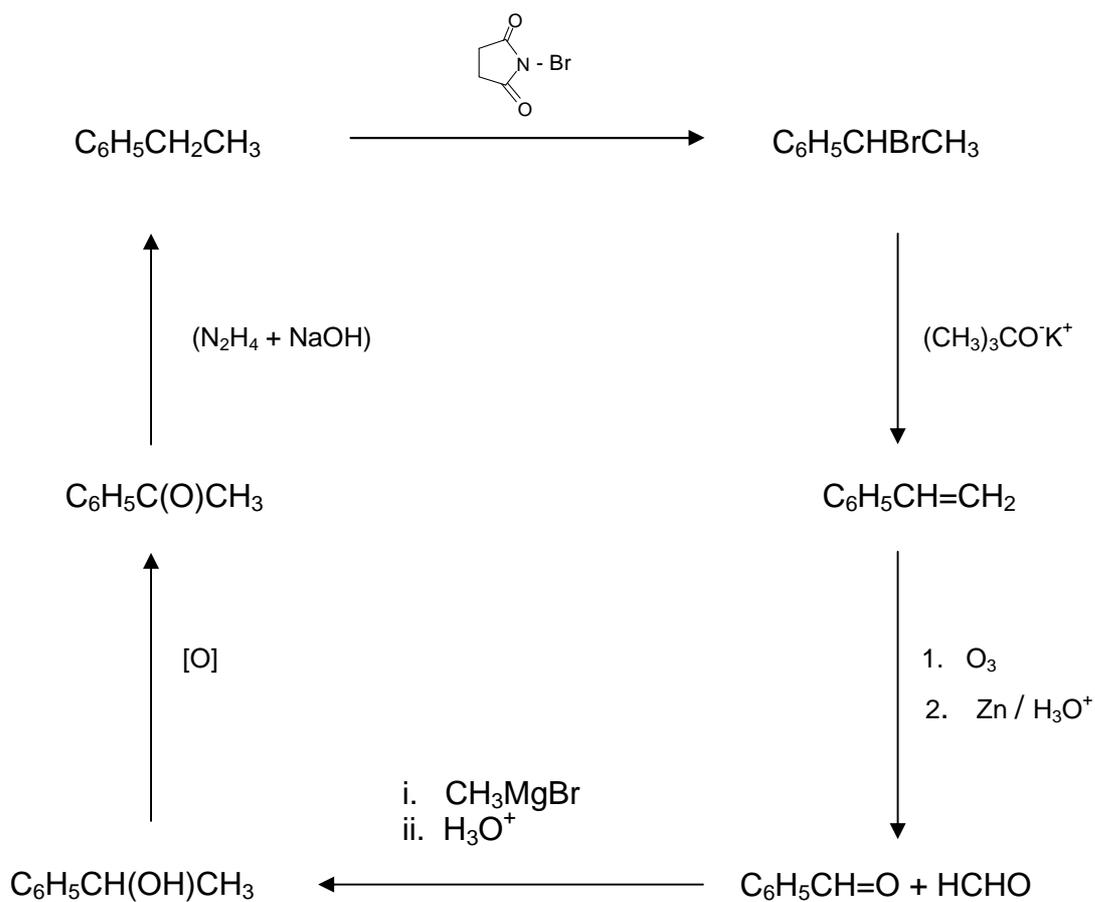


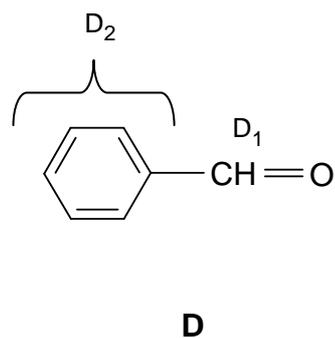
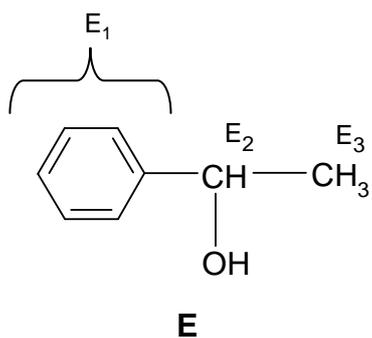
Based on the $^1\text{H-NMR}$ spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding $^1\text{H-NMR}$ peaks, as shown in the example.





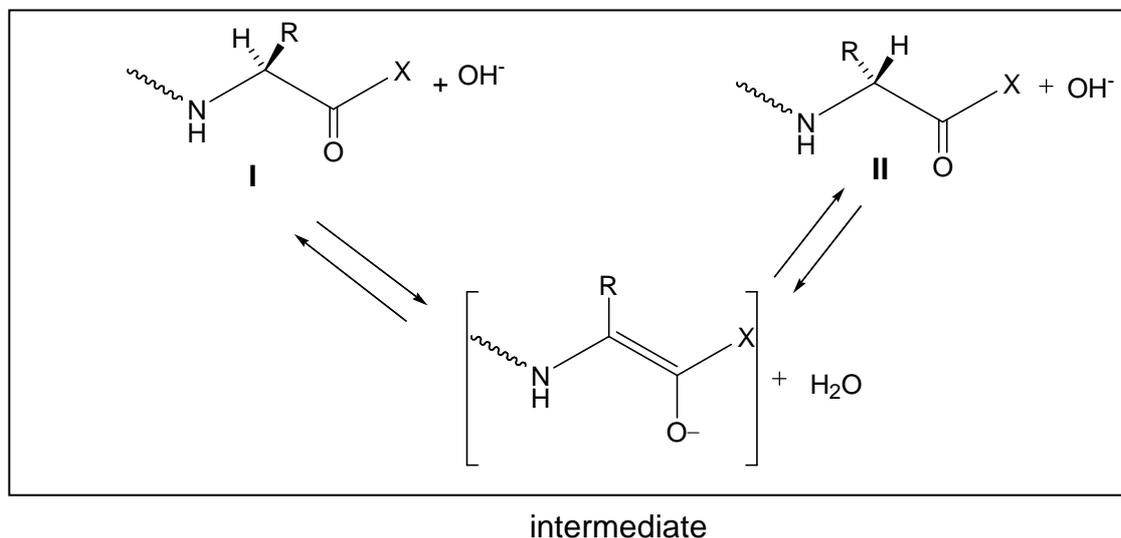
General remarks: NMR spectra were recorded in CDCl_3 on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in CDCl_3 solutions and catalyse rapid exchange of some particular protons.

SOLUTION




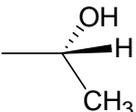
PROBLEM 33 Peptides

Racemization of α -aminoacids and peptides can occur by an α -enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:



1. Draw stereochemical formulas **I** and **II** (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α -enolization mechanism described above operating on each of the following hydroxyaminoacids **A** and **B**:

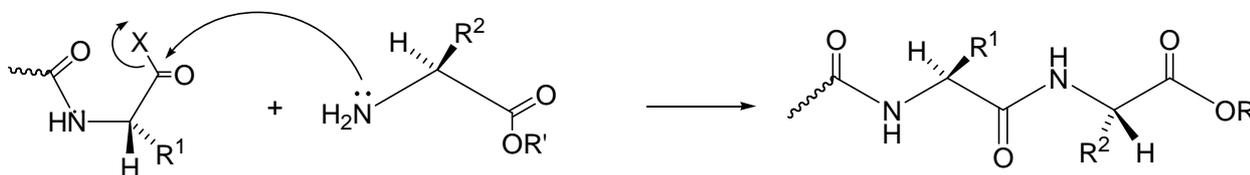
A: serine ($R = -\text{CH}_2\text{OH}$)

B: ($2S,3R$)-threonine ($R =$ )

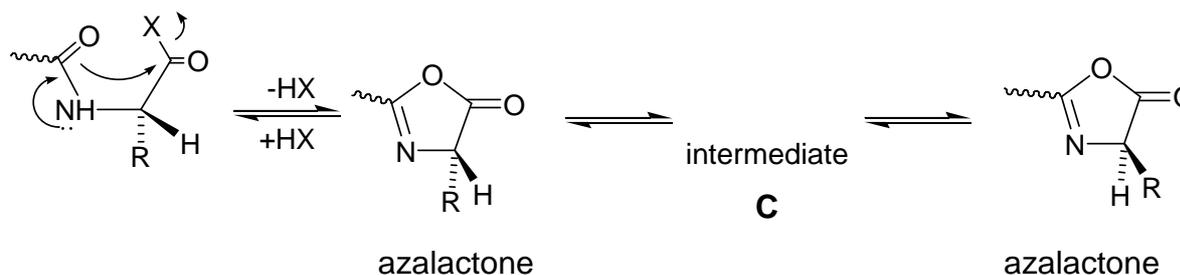
2. Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

	enantiomers	diastereomers
A _{I, II}	<input type="checkbox"/>	<input type="checkbox"/>
	enantiomers	diastereomers
B _{I, II}	<input type="checkbox"/>	<input type="checkbox"/>

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:



It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:



3. Write the structural formula for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center.

Azalactones are very reactive substances that can still react with the amino group of an amino acid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

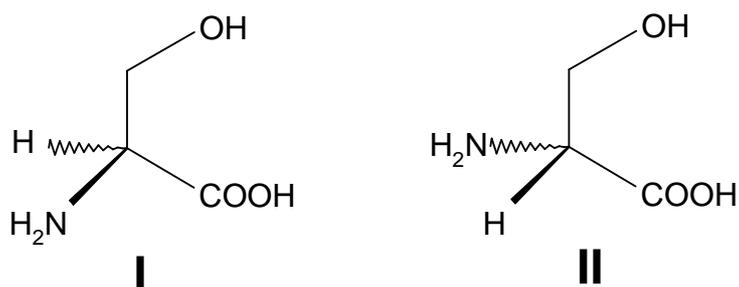
4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40 °C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$ (**P**₁).
- Propose a structure for substance **P**₁.
 - Write the reaction product(s) of the substance **P**₁ with *S*-alanine ethyl ester (**P**₂) (the side chain R of the amino acid alanine is a methyl group) using

stereochemical formulas (with bold and dashed bonds) for both reactants and product.

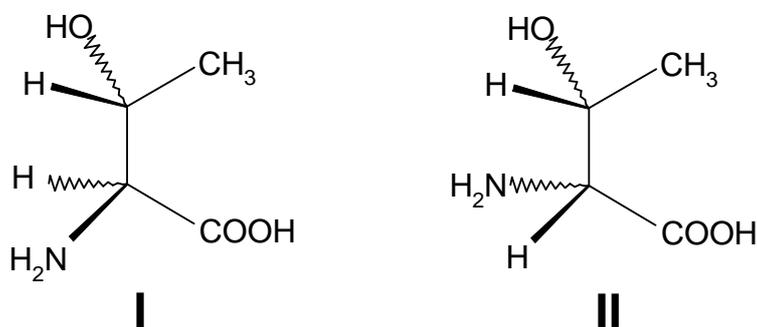
SOLUTION

1.

A:

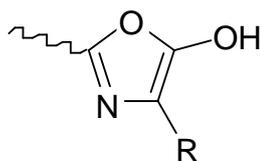


B:

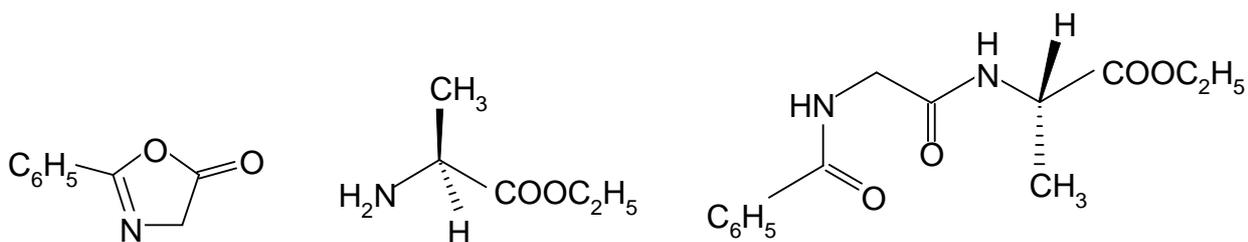


2. **A(I)** and **A(II)** are enantiomers.
B(I) and **B(II)** are diastereomers.

3. Intermediate **C**



4.

Substance P₁Ester P₂

Product

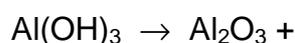
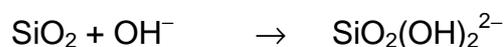
SECTION D: Inorganic Chemistry**PROBLEM 34 Aluminium**

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al_2O_3) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $\text{AlO}_x(\text{OH})_{3-2x}$ where $0 < x < 1$.

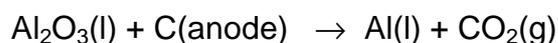
Production of Al metal follows a two-stage process:

- (i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al_2O_3 40 – 60 %, H_2O 12 – 30 %, SiO_2 free and combined 1 – 15 %, Fe_2O_3 7 – 30 %, TiO_2 3 – 4 %, F, P_2O_5 , V_2O_5 , etc., 0.05 – 0.2 %). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200 °C.

Complete and balance the following chemical reactions:



- ii) Hérault-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6 . Typical electrolyte composition ranges are Na_3AlF_6 (80 – 85 %), CaF_2 (5 – 7 %), AlF_3 (5 – 7 %), Al_2O_3 (2 – 8 % intermittently recharged). Electrolysis is carried out at 940°C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:



Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:



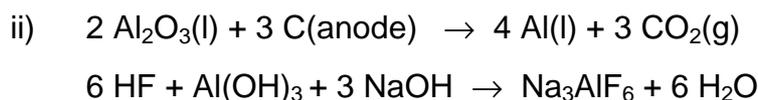
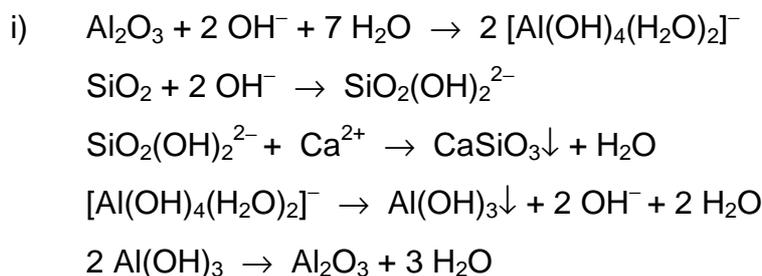
During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

- iii) By using the thermodynamic data given below, which are taken to be independent on temperature, determine the thermodynamic quantities ΔH , ΔS and ΔG at 940 °C for the reaction:



	Al(s)	Al ₂ O ₃ (s)	C (graphite)	CO(g)	CO ₂ (g)	O ₂ (g)
$\Delta_f H^\circ$ (kJ mol ⁻¹)	0	-1676	0	-111	-394	
S° (J.K ⁻¹ mol ⁻¹)	28	51	6	198	214	205
$\Delta_{fus} H$ (kJ mol ⁻¹)	11	109				

- iv) At the same temperature and using the data from the table in part (iii) determine the quantities ΔH and ΔG for the reaction
- $$2 \text{Al}(\text{l}) + 3 \text{CO}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{l}) + 3 \text{CO}(\text{g})$$
- given that $\Delta S = -126 \text{ J K}^{-1} \text{ mol}^{-1}$. (Show your calculations)
- v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[\text{Al}(\text{OH})_4]^{-}(\text{aq})$. In both cases liberation of H₂ occurs. AlF₃ is made by treating Al₂O₃ with HF gas at 700 °C, while the other trihalides, AlX₃, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.
- vi) The AlCl₃ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4°C) the structure changes to a 4-coordinate molecular dimer, Al₂Cl₆. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar AlCl₃ molecules.
- For the molecular dimer Al₂Cl₆, in the gas phase, two different Al–Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al–Cl distances.
- vii) What is the hybridization of the Al atom(s) in Al₂Cl₆ and AlCl₃?

SOLUTION

iii) $\Delta_r H_{1213}^0 = 2\Delta_f H_{1213}^0(\text{CO}) - \Delta_f H_{1213}^0(\text{CO}_2) = 2 \times (-111) - (-394) = 172 \text{ kJ}$
 $\Delta_r S_{1213}^0 = 2S_{1213}^0(\text{CO}) - S_{1213}^0(\text{CO}_2) - S_{1213}^0(\text{C}) = 2 \times (-198) - 214 - 6 = 176 \text{ JK}^{-1}$
 $\Delta_r G_{1213}^0 = \Delta_r H_{1213}^0 - T\Delta S_{1213}^0 = 172 - 1213 \times 0.176 = -41.5 \text{ kJ K}^{-1}$

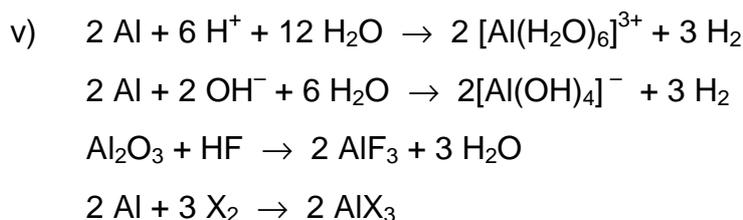
iv)

$$\Delta_r H_{1213}^0 = 3\Delta_f H_{1213}^0(\text{CO}) + \Delta_f H_{298}^0(\text{Al}_2\text{O}_3) + \Delta_{\text{melt}} H(\text{Al}_2\text{O}_3) - 3\Delta_f H_{1213}^0(\text{CO}_2) - 2\Delta H_{\text{melt}} H(\text{Al}) =$$

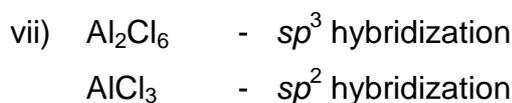
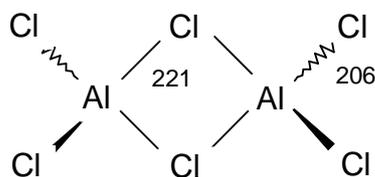
$$= 3 \times (-111) - (-1676) + 109 - 3 \times (-394) - 2 \times 11 = -740 \text{ kJ}$$

$$\Delta_r H_{1213}^0 = 3\Delta_f H_{1213}^0(\text{CO}) + \Delta_f H_{298}^0(\text{Al}_2\text{O}_3) + \Delta_{\text{melt}} H(\text{Al}_2\text{O}_3) - 3\Delta_f H_{1213}^0(\text{CO}_2) - 2\Delta H_{\text{melt}} H(\text{Al}) =$$

$$= 3 \times (-111) - (-1676) + 109 - 3 \times (-394) - 2 \times 11 = -740 \text{ kJ}$$



vi)



PROBLEM 35 Kinetics

The acid-catalyzed reaction $\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ was found to be of first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by $0.010 \text{ mol dm}^{-3}$ was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

$[\text{CH}_3\text{COCH}_3]$ (mol dm^{-3})	$[\text{I}_2]$ (mol dm^{-3})	Time (min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	...
1.50
...	...	0.36

- Derive the rate law for the reaction and calculate the rate constant.
- Calculate the time needed for 75 % of CH_3COCH_3 to react in excess I_2 .
- Show graphically the dependence of the rate on $[\text{CH}_3\text{COCH}_3]$ and on $[\text{I}_2]$, for fixed initial concentration of the other reagents.
- If the rate is doubled by raising the temperature by $10 \text{ }^\circ\text{C}$ from 298 K , calculate the activation energy for this reaction.

SOLUTION

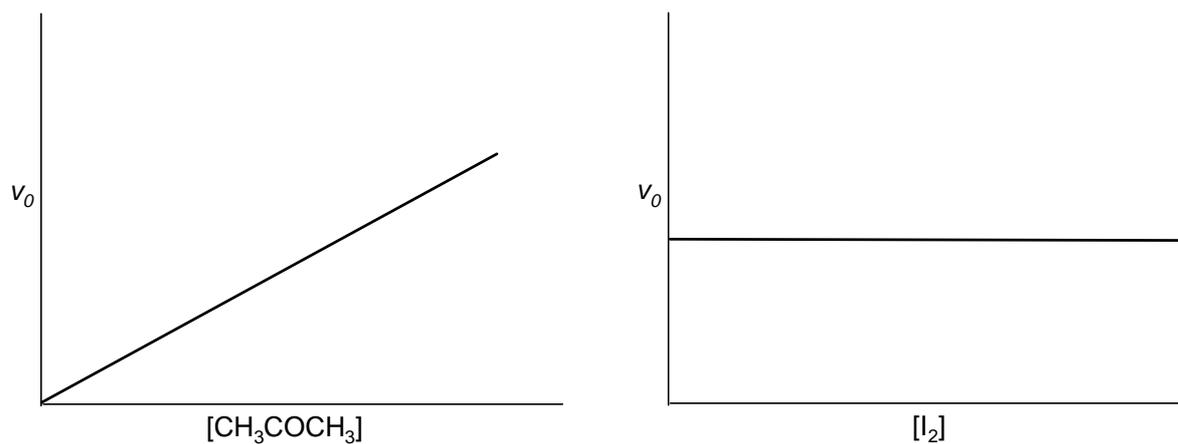
a) $v = k [\text{CH}_3\text{COCH}_3]$

$$k = \frac{v}{[\text{CH}_3\text{COCH}_3]} = \frac{0.010}{0.25 \cdot 7.2} = 5.56 \times 10^{-3} \text{ min}^{-1} = 9.26 \times 10^{-5} \text{ s}^{-1}$$

b) $\tau = \ln 2 / k = 125 \text{ min}$

$$t = 2 \tau = 250 \text{ min}$$

c)



d)

$$k = A \exp\left(-\frac{E_A}{RT}\right)$$

$$\frac{v_2}{v_1} = \frac{k_2}{k_1} = \frac{\exp\left(-\frac{E_A}{RT_2}\right)}{\exp\left(-\frac{E_A}{RT_1}\right)} = \exp\left(-\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\ln \frac{v_2}{v_1} = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_A = -R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} \ln \frac{v_2}{v_1}$$

$$E_A = -8.314\left(\frac{1}{308} - \frac{1}{298}\right)^{-1} \ln \frac{2}{1} = 52.9 \text{ kJ mol}^{-1}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of the Dipeptide *N*-acetyl-*L*-prolinyl-*L*-phenylalanine Methyl Ester (Ac-*L*-Pro-*L*-Phe-OCH₃)

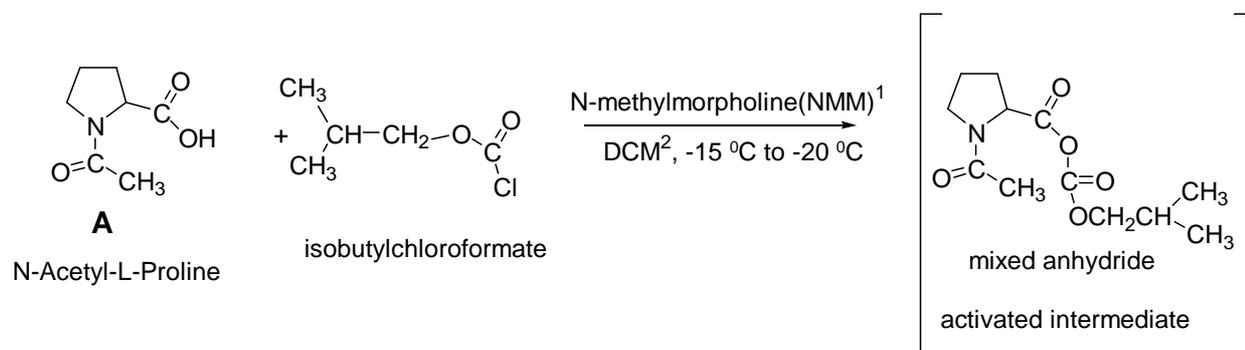
Introduction

Peptide synthesis is now a well-refined art and many of their synthetic procedures can be readily adapted to the elementary laboratory. Interest in peptides, always high, has heightened even more with the recent discovery of the importance of the so-called "opiate" peptides as well as of other biological active peptides.

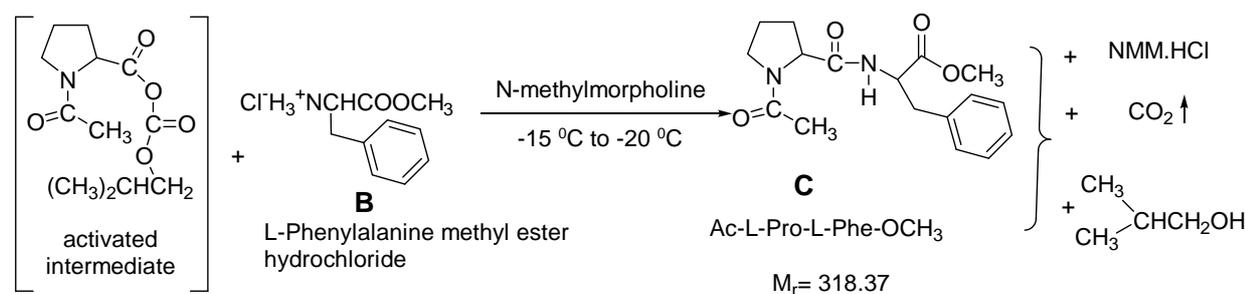
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

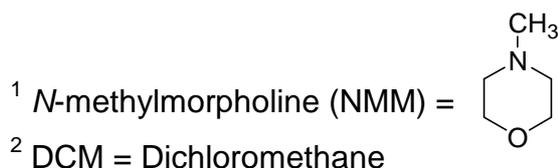
Reactions

STEP 1



STEP 2





Procedure

STEP 1

Place the 1.50 g (0.0095 mol) sample of *N*-acetyl-*L*-proline (labelled AcPro), which you have been given, into a 50-cm³ round-bottom flask. Add 20 cm³ dichloromethane (labelled DCM) in the graduated cylinder. Use some of the 20 cm³ DCM to wash out the AcPro vial and add the remaining DCM also into the round-bottomed flask. Plug the flask with a septum, clamp it loosely to a support stand and cool it to $-15\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$ in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 cm³ (0.0109 mol) of *N*-methylmorpholine (labelled NMM) to the flask, by means of a syringe. Then, slowly add 1.5 cm³ (0.0116 mol) isobutyl-chloroformate (labelled IBCF) to the flask by means of a second syringe. During the addition, swirl the reaction mixture gently by hand, and continue swirling for another 10 min. The temperature should remain in the range -20 ° to $-15\text{ }^{\circ}\text{C}$.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled HCl-H₂NPheOCH₃) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 cm³ (0.0109 mol) of *N*-methylmorpholine (labelled NMM) using a third syringe, while the reaction mixture is swirled by hand. ***ATTENTION:*** *Leave the needle part of the syringe in the septum for the remainder of the reaction.* Allow the reaction to proceed for 60 min at $-15\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$, swirling periodically by hand.

During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.

After 60 min at $-20\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$, remove the 50 cm³ round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 cm³ beaker and let it warm up to

room temperature. Transfer the contents of the flask into the 50 cm³ separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3 – 5 cm³), which is in a vial (labelled DCM). Wash the organic layer successively with two 20 cm³ portions of 0.2 M aqueous HCl solution, two 20 cm³ portions of 1 % aqueous

NaHCO₃ solution (read caution comment in next paragraph) and finally one 10 cm³ portion of saturated solution of sodium chloride (labelled brine).

Important

After each washing allow the separating funnel to stand for enough time, so that the two phases separate completely. Also, take into consideration that the organic phase (DCM) is always the lower layer and contains the product. All the aqueous washings are collected in the same Erlenmeyer flask (empty if necessary).

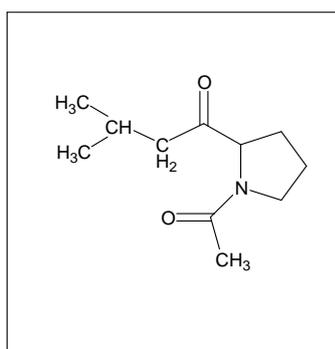
CAUTION: Keep in mind, also, that during washing with 1 % NaHCO₃, the CO₂ liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.

Before continuing, wash the glass funnel, the 50 cm³ cylinder and the 50 cm³ round-bottom flask with water and then dry them with acetone. Your supervisor will show you where to dispose of the water and the acetone.

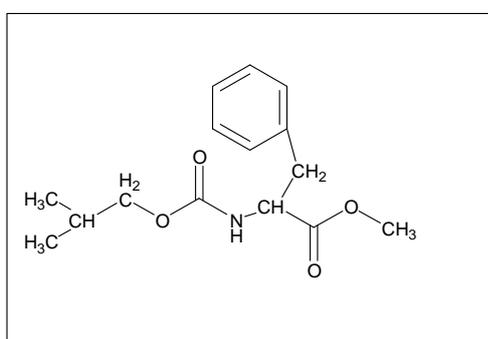
Pour the organic layer into a clean 50 cm³ Erlenmeyer flask. Add the anhydrous sodium sulphate, which is in a vial labelled Na₂SO₄, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm³ round-bottom flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3 – 5 cm³). Removal of the organic solvent is done under reduced pressure, using a rotary evaporator apparatus. This will be done for you by a laboratory supervisor, who will add 20 cm³ of diethylether to the residue in your flask, which will cause precipitation of your product. After cooling for 5 minutes in the ice bath, scrape the walls of the flask with a spatula, filter by suction the crystallized dipeptide through a fritted glass funnel. Wash twice with diethylether (5 cm³ each time).

Leave the product on the filter under suction for at least 3 minutes. Then collect it on weighing paper, weigh it in the presence of a supervisor and then transfer it into a sample vial and label it with your student code. Write the mass of your product (**C**) on the label and on your answer sheet (on the next page).

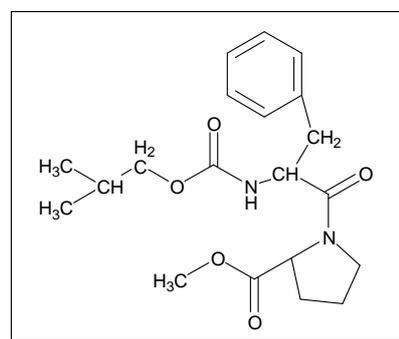
During the reaction between the phenylalanine methylester **B** and the activated mixed anhydride intermediate (step 2) the formation of the desired dipeptide product **C** is usually accompanied by a by-product the correct structure of which is one of the three structures **I**, **II**, **III** given below. Circle the Roman numeral corresponding to the correct structure.



I



II



III

TLC- Analysis

You have two Eppendorfs, one empty and one with a tiny amount of substance **B**. Put a small amount of **C** into the empty Eppendorf, and dissolve both **B** and **C** in a few drops of methanol. Use the supplied capillary tubes to apply small samples of these solutions to the TLC plate. Develop the TLC plate with a solution of chloroform-methanol-acetic acid (7 : 0.2 : 0.2) as eluant. The appropriate amount of eluant has been placed in the proper vial by the supervisor.

After the elution, analyze the TLC-plate using a UV-lamp. Clearly mark the starting line, solvent front and the UV-active spots.

Draw the diagram in the box on the answer sheet. Determine the R_f values. Finally place the TLC-plate in a small plastic bag with a sealing strip and put it in an envelope provided by the supervisor. Write your student code on the envelope.

The examination committee will check the quality of the *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester that you have prepared by determining its angle of optical rotation and consequently its specific rotation, $[\alpha]_D^t$, using an accurate polarimeter apparatus.

SOLUTION

The following values were required to be written in the Answer Sheet

- Mass of Ac-L-Pro-L-Phe-OCH₃ obtained (product **C**).
 - The yield of Ac-L-Pro-L-Phe-OCH₃ **C**.
 - The TLC diagram with indication of the base line and the front of the solvent.
 - R_f value of L-phenylalanine methyl ester hydrochloride (material B) and that of R_f value of Ac-L-Pro-L-Phe-OCH₃ (product C).

 - Conclusions from the TLC analysis:
Compound **C**:
 - Is pure,
 - Contains some **B**,
 - Contains several contaminants,
 - No conclusion.

 - Specific rotation of the dipeptide Ac-L-Pro-L-Phe-OCH₃ C (to be measured later by the examination committee)
$$[\alpha]_D^{25} = 45^\circ$$

 - The correct structure of the by-product: **II**.
-
-

36th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 18–27 JULY 2004, KIEL, GERMANY

THEORETICAL PROBLEMS

PROBLEM 1

Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0 °C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

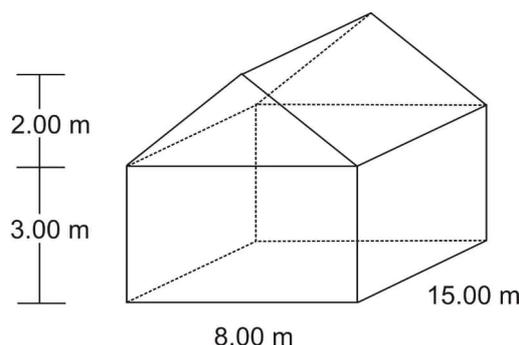
The thermodynamic properties and the composition of natural gas can be found in Table 1.

1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

- Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).
- Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m³ of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00 °C and the air temperature in the house (dimensions given in the figure below) is 10.0 °C. Assume a water density of $\rho = 1.00 \text{ kg dm}^{-3}$ and air behaving like an ideal gas.



- 1.3** Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0 °C and the energy which is required to heat the initial amount of air (21.0 % of O₂, 79.0 % of N₂) to 30.0 °C at a pressure of $1.013 \times 10^5 \text{ Pa}$.

In February, the outside temperature is about 5 °C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is $1.00 \text{ W K}^{-1} \text{ m}^{-1}$.

- 1.4** Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0 °C during the party (12 hours).

1.00 m³ of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

- 1.5** What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0 %? What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100 % efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	$\Delta_f H^0$ (kJ mol ⁻¹) ⁻¹	S^0 (J mol ⁻¹ K ⁻¹) ⁻¹	C_p^0 (J mol ⁻¹ K ⁻¹) ⁻¹
CO ₂ (g)	0.0024	-393.5	213.8	37.1
N ₂ (g)	0.0134	0.0	191.6	29.1
CH ₄ (g)	0.9732	-74.6	186.3	35.7
C ₂ H ₆ (g)	0.0110	-84.0	229.2	52.5
H ₂ O (l)	-	-285.8	70.0	75.3
H ₂ O (g)	-	-241.8	188.8	33.6
O ₂ (g)	-	0.0	205.2	29.4

Equation:

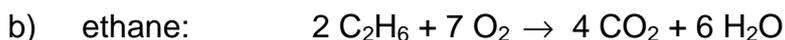
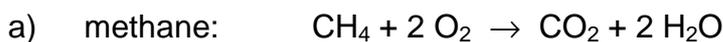
$$J = E \times (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \times \Delta T \times d^{-1}$$

J energy flow E along a temperature gradient (wall direction z) per area A and time Δt

d wall thickness

λ_{wall} heat conductivity

ΔT difference in temperature between the inside and the outside of the house

SOLUTION**1.1** Chemical equations:

Thermodynamic data for the equations:

$$\Delta H^0 = [2 \times (-241.8) - 393.5 - (-74.6)] \text{ kJ mol}^{-1} = -802.5 \text{ kJ mol}^{-1}$$

$$\Delta S^0 = [2 \times (188.8) + 213.8 - 186.3 - 2 \times 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^0 = -802.5 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (-5.3 \text{ J mol}^{-1} \text{ K}^{-1}) = -800.9 \text{ kJ mol}^{-1}$$

$$\text{Methane: } \Delta H^0 = -802.5 \text{ kJ mol}^{-1}; \Delta S^0 = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}; \Delta G^0 = -800.9 \text{ kJ mol}^{-1}$$

$$\Delta H^0 = [6 \times (-241.8) - 4 \times 393.5 - 2 \times (-84.0)] \text{ kJ mol}^{-1} = -2856.8 \text{ kJ mol}^{-1}$$

$$\Delta S^0 = [6 \times 188.8 + 4 \times 213.8 - 2 \times 229.2 - 7 \times 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^0 = -2856.8 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (93.2 \text{ J mol}^{-1} \text{ K}^{-1}) = -2884.6 \text{ kJ mol}^{-1}$$

$$\text{Ethane: } \Delta H^0 = -2856.8 \text{ kJ mol}^{-1}; \Delta S^0 = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}; \Delta G^0 = -2884.6 \text{ kJ mol}^{-1}$$

1.2 a) Amount of methane and ethane in 1 m³ natural gas:

$$m = \rho \times V = 0.740 \text{ g dm}^{-3} \times 1000 \text{ dm}^3 = 740 \text{ g}$$

$$M_{\text{av}} = \sum_i x(i)M(i) = (0.0024 \times 44.01 \text{ g mol}^{-1}) + (0.0134 \times 28.02 \text{ g mol}^{-1}) \\ + (0.9732 \times 16.05 \text{ g mol}^{-1}) + (0.011 \times 30.08 \text{ g mol}^{-1}) = 16.43 \text{ g mol}^{-1}$$

$$n_{\text{tot}} = m (M_{\text{av}})^{-1} = 740 \text{ g} \times (16.43 \text{ g/mol})^{-1} = 45.04 \text{ mol}$$

$$n(i) = x(i) \cdot n_{\text{tot}}$$

$$n(\text{CH}_4) = x(\text{CH}_4) \times n_{\text{tot}} = 0.9732 \times 45.04 \text{ mol} = 43.83 \text{ mol}$$

$$n(\text{C}_2\text{H}_6) = x(\text{C}_2\text{H}_6) \times n_{\text{tot}} = 0.0110 \times 45.04 \text{ mol} = 0.495 \text{ mol}$$

b) Energy of combustion, deviation:

$$E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) = \sum_i n(i)\Delta_c H^0(i) = \\ = 43.83 \text{ mol} \times (-802.5 \text{ kJ mol}^{-1}) + 0.495 \text{ mol} \times 0.5 \times (-2856.8 \text{ kJ mol}^{-1}) \\ = -35881 \text{ kJ}$$

$$E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) = -35881 \text{ kJ}$$

Deviation from PUC

$$E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) = 9.981 \text{ kWh m}^{-3} \times 1 \text{ m}^3 \times 3600 \text{ kJ (kWh)}^{-1} = 35932 \text{ kJ}$$

$$\text{Deviation: } \Delta^E = (E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) - E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) \times 100 \% \times [E_{\text{comb.}}(\text{H}_2\text{O}(\text{g}))]^{-1} \\ = (35881 \text{ kJ} - 35932 \text{ kJ}) \times 100 \% \times (35881 \text{ kJ})^{-1} = -0.14\%$$

1.3 Energy for heating the water:

$$\text{Volume of water: } V_{\text{water}} = 22.5 \text{ m}^3$$

$$n_{\text{water}} = V_{\text{water}} \rho_{\text{water}} (M_{\text{water}})^{-1} = 22.5 \text{ m}^3 \times 10^6 \text{ g m}^{-3} \times (18.02 \text{ g mol}^{-1})^{-1} = 1.249 \times 10^6 \text{ mol}$$

$$E_{\text{water}} = n_{\text{water}} \times C_p \times \Delta T = 1.249 \times 10^6 \text{ mol} \times 75.30 \text{ J K}^{-1} \text{ mol}^{-1} \times 14 \text{ K} = 1316 \text{ MJ}$$

Energy for heating the air:

Volume of the house is:

$$V_{\text{air}} = (15 \text{ m} \times 8 \text{ m} \times 3 \text{ m}) + 0.5 \times (15 \text{ m} \times 8 \text{ m} \times 2 \text{ m}) = 480 \text{ m}^3$$

$$n_{\text{air}} = pV(RT)^{-1} = 1.013 \times 10^5 \text{ Pa} \times 480 \text{ m}^3 \times (8.314 \text{ J (K mol)}^{-1} \times 283.15 \text{ K})^{-1} = \\ = 2.065 \times 10^4 \text{ mol}$$

$$C_p(\text{air}) = 0.21 \times 29.4 \text{ J (K mol)}^{-1} + 0.79 \times 29.1 \text{ J (K mol)}^{-1} = 29.16 \text{ J (K mol)}^{-1}$$

$$E_{\text{air}} = n_{\text{air}} \times C_p(\text{air}) \times \Delta T = 2.065 \times 10^4 \text{ mol} \times 29.17 \text{ J (K mol)}^{-1} \times 20 \text{ K} = 12.05 \text{ MJ}$$

1.4 Energy for maintaining the temperature:

Surface area of the house:

$$A_{\text{house}} = 3 \text{ m} \times 46 \text{ m} + 8 \text{ m} \times 2 \text{ m} + ((2 \text{ m})^2 + (4 \text{ m})^2)^{1/2} \times 2 \times 15 \text{ m} = 288.16 \text{ m}^2$$

Heat conductivity: $\lambda_{\text{wall}} = 1 \text{ J (s K m)}^{-1}$

Energy flux along a temperature gradient (wall thickness $d = 0.2 \text{ m}$)

$$J = E_{\text{loss}} (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \Delta T d^{-1}$$

$$E_{\text{loss}} = 288.16 \text{ m}^2 \times (12 \cdot 60 \cdot 60 \text{ s}) \times 1 \text{ J (s K m)}^{-1} \times 25 \text{ K} \times (0.2 \text{ m})^{-1} = 1556 \text{ MJ}$$

$$E_{\text{loss}} = 1556 \text{ MJ}$$

1.5 Total energy and costs:

$$\text{Total energy: } E_{\text{tot}} = E_{\text{water}} + E_{\text{air}} + E_{\text{loss}} = 1316 \text{ MJ} + 12 \text{ MJ} + 1556 \text{ MJ} = 2884 \text{ MJ}$$

$$2884 \text{ MJ corresponds to } 2.884 \times 10^6 \text{ kJ} \times (3600 \text{ s h}^{-1} \times 9.981 \text{ kJ s}^{-1} \text{ m}^{-3} \times 0.9)^{-1} = \\ 89.18 \text{ m}^3$$

$$\text{Volume of gas: } V = 89.18 \text{ m}^3$$

2884 MJ correspond to a cost of:

$$0.40 \text{ € m}^{-3} \times 89.18 \text{ m}^3 = 35.67 \text{ €}$$

Rent for equipment: 150.00 €

Total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

$$2.884 \cdot 10^6 \text{ kJ} \times 0.137 \text{ €} \times (3600 \text{ s h}^{-1} \times 1 \text{ kJ s}^{-1} \text{ h})^{-1} = 109.75 \text{ €}$$

Rent for equipment: 100.00 €

Total cost of electric heating: 209.75 €

PROBLEM 2

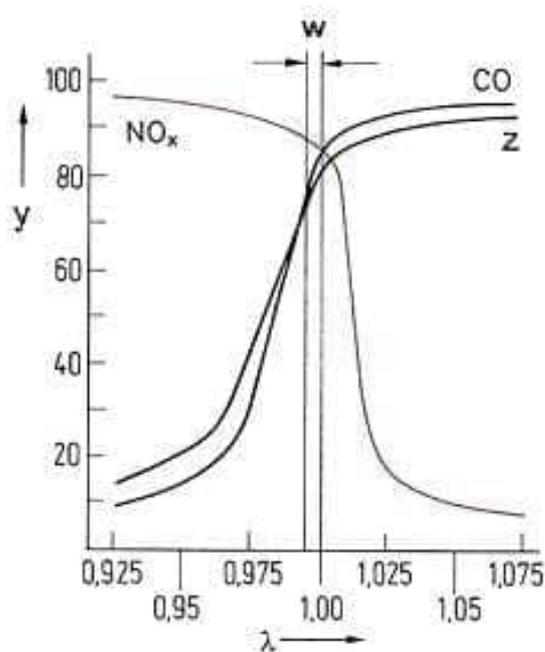
Kinetics at catalyst surfaces

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ -value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as $\lambda = \frac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}$.



w: λ -window

y: conversion efficiency (%)

z: Hydrocarbons

2.2 Decide the questions on the answer sheet concerning the λ probe.

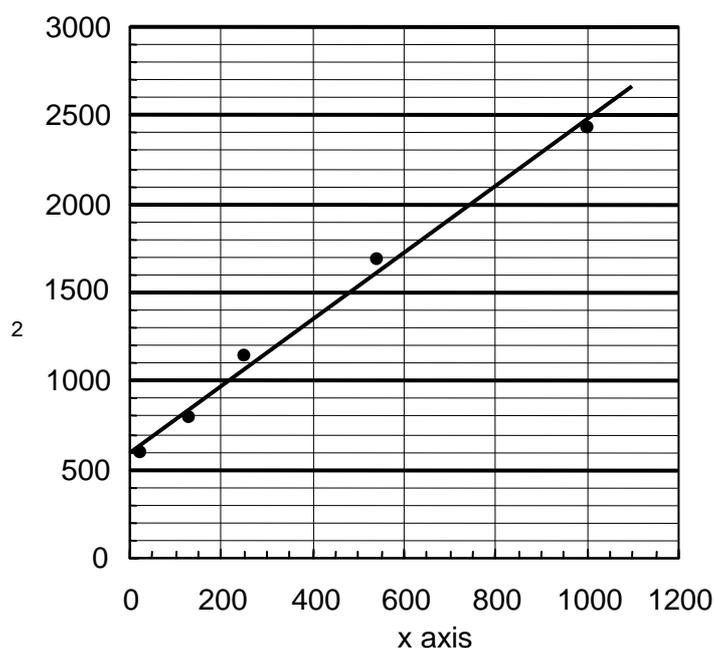
The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with $K = 0.85 \text{ kPa}^{-1}$.

- 2.3** a) Determine the surface coverage θ at a pressure of 0.65 kPa.
 b) Determine the pressure p at which 15 % of the surface is covered.
 c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k \theta$
 Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).
 d) Data for the adsorption of another gas on a metal surface (at 25 °C)



x axis: $p \cdot (\text{Pa})^{-1}$

y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

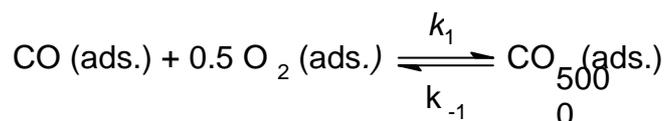
V_a is the gas volume that has been adsorbed.

If the Langmuir isotherm can be applied, determine the gas volume $V_{a,\text{max}}$ needed for a complete coverage of the metal surface and the product $K V_{a,\text{max}}$.

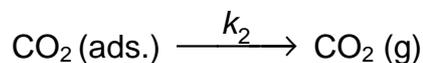
Hint: Set $\theta = V_a / V_{a,\text{max}}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,



In a slow second step, CO₂ is then desorbed from the surface:



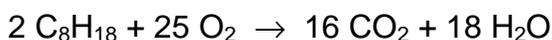
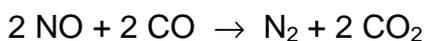
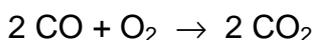
2.4 Derive the formula for the reaction rate of the CO₂(g) - formation as a function of the partial pressures of the reaction components.

Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta_i = \frac{K_i \times p_i}{1 + \sum_j K_j \times p_j} \quad \text{j: relevant gas components}$$

SOLUTION

2.1 Reaction equations:



2.2 Questions concerning the λ probe:

true false no decision

possible

If the λ -value is in the range of the λ -window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.

With $\lambda > 1$, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.

With $\lambda < 0.975$, nitrogen oxides can be reduced poorly.

2.3 a) Surface coverage:

$$\theta = \frac{0.85 \text{ kPa}^{-1} \times 0.65 \text{ kPa}}{1 + 0.85 \times 0.65}$$

$$\theta = 0.356 \text{ or } 35.6 \%$$

- b) Pressure at which 15 % of the surface is covered:

$$\theta = \frac{K \times p}{1 + K \times p} \Leftrightarrow K \times p = \theta + \theta \times K \times p \Leftrightarrow p \cdot (K - \theta \times K) = \theta \Leftrightarrow$$

$$p = \frac{\theta}{K - \theta \times K}$$

$$\theta = 0.15$$

$$p = 0.21 \text{ kPa}$$

- c) Orders of decomposition:

Order of the decomposition reaction at low gas pressures 1

Order of the decomposition reaction at high gas pressures 0

Notes:

$$r = k \times \theta = k \frac{K \times p}{1 + K \times p},$$

$$p \text{ low} \Rightarrow p \ll \frac{1}{K} \Rightarrow r = k K p \quad \text{reaction order 1.}$$

$$p \text{ high} \Rightarrow p \gg \frac{1}{K} \Rightarrow r = k \quad \text{reaction order 0.}$$

- d) Gas volume $V_{a,\max}$ and product $K \cdot V_{a,\max}$:

$$\frac{1}{\theta} = \frac{1}{K p} + 1 = \frac{V_{a,\max}}{V_a} \Rightarrow \frac{1}{K V_{a,\max}} + \frac{p}{V_{a,\max}} = \frac{p}{V_a}$$

$$\text{Slope: } \frac{1}{V_{a,\max}} = 1.9 \text{ cm}^{-3} \Rightarrow V_{a,\max} = 0.53 \text{ cm}^3$$

$$\text{Intercept: } \frac{1}{K V_{a,\max}} = 6 \times 10^2 \text{ Pa cm}^{-3} \Rightarrow K V_{a,\max} = 1.7 \times 10^{-3} \text{ Pa}^{-1} \text{ cm}^3$$

2.4 Equation for reaction rate:

The information given in the text leads directly to $r = k_2 \theta_{\text{CO}_2}$

The law of mass action for the first step of the mechanism is given by

$$\theta_{\text{CO}_2} = \frac{k_1}{k_{-1}} \cdot \theta_{\text{CO}} \theta_{\text{O}_2}^{\frac{1}{2}}, \Rightarrow r = k_2 \frac{k_1}{k_{-1}} \theta_{\text{CO}} \theta_{\text{O}_2}^{\frac{1}{2}}.$$

The Langmuir isotherm gives:

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} p_{\text{CO}}}{1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}} \quad \text{and} \quad \theta_{\text{O}_2} = \frac{K_{\text{O}_2} p_{\text{O}_2}}{1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}}$$

$$r = k_2 \frac{k_1}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} (K_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}{(1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2})^{\frac{3}{2}}}$$

PROBLEM 3

Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these “compounds” was not known but they are still of great interest to solid state chemists.

Attempts to reduce CaCl_2 to CaCl have been made with

- (a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl .

After an attempt to reduce CaCl_2 with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When CaCl_2 is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When CaCl_2 is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3 .

- 3.4** a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.
b) What compound is formed by the reaction of CaCl_2 with carbon?
(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl . One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^\circ$ for CaCl
3	Triangular	0.155 – 0.225	BN	$-663.8 \text{ kJ mol}^{-1}$
4	Tetrahedral	0.225 – 0.414	ZnS	$-704.8 \text{ kJ mol}^{-1}$
6	Octahedral	0.414 – 0.732	NaCl	$-751.9 \text{ kJ mol}^{-1}$
8	Cubic	0.732 – 1.000	CsCl	$-758.4 \text{ kJ mol}^{-1}$

$\Delta_L H^\circ(\text{CaCl})$ is defined for the reaction $\text{Ca}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{CaCl}(\text{s})$

3.5 a) What type of structure is CaCl likely to have?

$[r(\text{Ca}^+) \approx 120 \text{ pm (estimated)}, r(\text{Cl}^-) \approx 167 \text{ pm}]$

Not only the lattice energy $\Delta_L H^\circ$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^\circ$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^\circ(\text{CaCl})$ with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{\text{fusion}} H^\circ(\text{Ca})$		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1. \text{IE}} H(\text{Ca})$	$\text{Ca} \rightarrow \text{Ca}^+$	$589.7 \text{ kJ mol}^{-1}$
ionization enthalpy	$\Delta_{2. \text{IE}} H(\text{Ca})$	$\text{Ca}^+ \rightarrow \text{Ca}^{2+}$	$1145.0 \text{ kJ mol}^{-1}$
heat of vaporization	$\Delta_{\text{vap}} H^\circ(\text{Ca})$		$150.0 \text{ kJ mol}^{-1}$
dissociation energy	$\Delta_{\text{diss}} H(\text{Cl}_2)$	$\text{Cl}_2 \rightarrow 2 \text{ Cl}$	$240.0 \text{ kJ mol}^{-1}$

enthalpy of formation	$\Delta_f H^\ominus(\text{CaCl}_2)$		$-796.0 \text{ kJ mol}^{-1}$
electron affinity	$\Delta_{\text{EA}} H(\text{Cl})$	$\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$	$-349.0 \text{ kJ mol}^{-1}$

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and CaCl₂ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

SOLUTION

3.1 Chemical equations:

- (a) $\text{CaCl}_2 + \text{Ca} \rightarrow 2 \text{CaCl}$
 (b) $2 \text{CaCl}_2 + \text{H}_2 \rightarrow 2 \text{CaCl} + 2 \text{HCl}$
 (c) $4 \text{CaCl}_2 + \text{C} \rightarrow 4 \text{CaCl} + \text{CCl}_4$

3.2

Silvery metallic particles: Ca

Colourless crystals: CaCl₂

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and CaCl₂

3.3 Empirical formula:

$$100 \% - (\text{mass \% Ca} + \text{mass \% Cl}) = \text{mass \% X}$$

$$100 \% - (52.36 \% + 46.32 \%) = 1.32 \% \text{ X}$$

$$\text{mol \% of Ca} = 52.36 \text{ mass \%} / M(\text{Ca})$$

$$= 52.36 \text{ mass \%} / 40.08 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$\text{mol \% of Cl} = 46.32 \text{ mass \%} / M(\text{Cl})$$

$$= 46.32 \text{ mass \%} / 35.45 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$\text{mol \% of X} = 1.32 \% \text{ X} / M(\text{H})$$

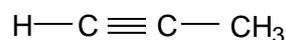
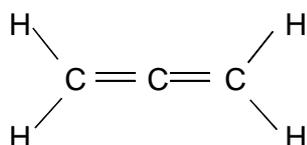
$$= 1.32 \% \text{ X} / 1.01 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$n(\text{Ca}) : n(\text{Cl}) : n(\text{H}) = 1 : 1 : 1$$

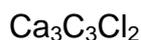
Empirical formula: CaClH

Notes: The reaction of CaCl_2 with hydrogen does not lead to CaCl . The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.

3.4 a) Structures only:



b) Empirical formula of the compound formed:



Notes: If the ratio of $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$ [or better = $3 : 2$ which can be rewritten as $\text{CaCl}_2 \cdot 2 \text{Ca}^{2+} = \text{Ca}_3\text{Cl}_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the composition $\text{Ca}_3\text{C}_3\text{Cl}_2$ will follow.

3.5 a) Structure type CaCl likely to have:

$$r(\text{Ca}^+)/r(\text{Cl}^-) = 120 \text{ pm} / 167 \text{ pm} = 0.719$$

NaCl	CsCl	ZnS	BN	no decision possible
<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

b) $\Delta_f H^\circ(\text{CaCl})$ with a Born-Haber-cycle:

PROBLEM 4**Determining atomic masses**

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2 : 1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

- 4.1** Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is $m(\text{Ag}) : m(\text{Y}) = 11.88 : 1$. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S . To convert 10.0 g of Argyrodite completely, 0.295 dm^3 of hydrogen are needed at 400 K and 100 kPa.

- 4.2** Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties. To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$ - vibrational frequency of the bond, in wavenumbers (cm^{-1})

c - speed of light

k - force constant, indicating the strength of the bond ($\text{N m}^{-1} = \text{kg s}^{-2}$)

μ - reduced mass in AB_4 , which is given by $\mu = \frac{3 m(\text{A}) m(\text{B})}{3 m(\text{A}) + 4 m(\text{B})}$

$m(\text{A}), m(\text{B})$ - the masses of the two bond atoms

The vibrational frequency of the C-H bond of methane is known to be 3030.00 cm^{-1} . The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1} . The bond enthalpy of a C-H bond in methane is $438.4 \text{ kJ mol}^{-1}$. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be $450.2 \text{ kJ mol}^{-1}$.

4.3 Determine the force constant k of a C-H bond using Hooke's law.

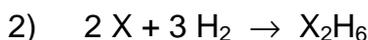
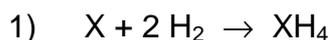
Estimate the force constant k of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

SOLUTION

4.1 Atomic mass of X, symbol of X, structures:



i) $5.0 \text{ g} = [n_1(X) + n_2(X)] \cdot M(X)$

ii) $5.628 \text{ g} =$

$$= n_1(\text{XH}_4) \times [M(X) + 4 \times 1.01 \text{ g mol}^{-1}] + n_2(\text{X}_2\text{H}_6) \times [2 M(X) + 6 \times 1.01 \text{ g mol}^{-1}]$$

iii) $n_1(\text{XH}_4) = 2 n_2(\text{X}_2\text{H}_6)$

iii,i) \rightarrow i') $2 n_1(X) \times M(X) = 5.0 \text{ g}$

iii,ii) \rightarrow ii') $n_1(X) \times [2M(X) + 7.07 \text{ g mol}^{-1}] = 5.628 \text{ g}$

i',ii') \rightarrow vi) $(5.0 \text{ g}) \times [2 M(X)]^{-1} = (5.628 \text{ g}) \times [2 M(X) + 7.07 \text{ g mol}^{-1}]^{-1}$

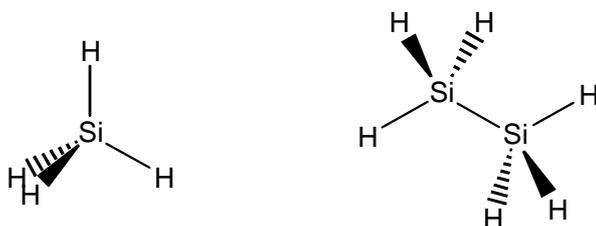
$$M(X) = 3.535 \text{ g mol}^{-1} \times (5.628 \text{ g})^{-1} \times [(5.0 \text{ g})^{-1} - (5.628 \text{ g})^{-1}]^{-1}$$

$$M(X) = 28.14 \text{ g mol}^{-1}$$

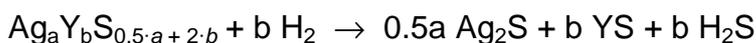
Atomic mass of X: $M(X) = 28.14 \text{ g mol}^{-1}$

Chemical symbol of X: Si

3D structures of the two products:



4.2 Atomic mass of Y and empirical formula of Argyrodite:



$$\text{i) } 10 \text{ g} = n(\text{Ag}_a\text{Y}_b\text{S}_{0.5\cdot a+2\cdot b}) \times [a \cdot 107.87 \text{ g mol}^{-1} + b M(\text{Y}) + (0.5 a + 2 b) \times 32.07 \text{ g mol}^{-1}]$$

$$\text{ii) } n(\text{H}_2) = \frac{p V(\text{H}_2)}{RT} \qquad n(\text{H}_2) = \frac{100 \text{ kPa} \times 0.295 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}$$

$$n(\text{H}_2) = 8.871 \times 10^{-3} \text{ mol} \qquad n(\text{Ag}_a\text{Y}_b\text{S}_{0.5\cdot a+2\cdot b}) = b^{-1} \times 8.871 \cdot 10^{-3} \text{ mol}$$

$$\text{iii) } 11.88 = \frac{a \times 107.87 \text{ g mol}^{-1}}{b \times M(\text{Y})} \qquad a \cdot 107.87 \text{ g mol}^{-1} = 11.88 \times b \times M(\text{Y})$$

ii,i) \rightarrow ii')

$$b \times 10 \text{ g} \times (8.871 \cdot 10^{-3} \text{ mol})^{-1} =$$

$$= a \cdot 107.87 \text{ g mol}^{-1} + b M(\text{Y}) + (0.5 a + 2 b) \times 32.07 \text{ g mol}^{-1}$$

$$b \cdot 1127 \text{ g mol}^{-1} = a \cdot 107.87 \text{ g mol}^{-1} + b M(\text{Y}) + (0.5 a + 2 b) \times 32.07 \text{ g mol}^{-1}$$

iii,ii') \rightarrow iv)

$$b \cdot 1127 \text{ g mol}^{-1} = 11.88 \cdot b \cdot M(\text{Y}) + b \cdot M(\text{Y}) + (0.5 \cdot a + 2b) \cdot 32.07 \text{ g mol}^{-1}$$

$$b \cdot 1127 \text{ g mol}^{-1} =$$

$$= 11.88 b M(\text{Y}) + b M(\text{Y}) + (0.5 \frac{11.88 \times b \times M(\text{Y})}{107.87 \text{ g mol}^{-1}} + 2 b) \times 32.07 \text{ g mol}^{-1}$$

$$M(\text{Y}) = 72.57 \text{ g mol}^{-1} \rightarrow \text{iii} \qquad a : b = 8 : 1$$

Chemical symbol of Y: Ge

Empirical formula of Argyrodite: Ag_8GeS_6

4.3 The force constants of a C-H bond:

$$k(\text{C-H}) = [2\pi c \tilde{\nu}(\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3 M(\text{C}) \times M(\text{H})}{3 M(\text{C}) + 4 M(\text{H})}$$

$$= [2\pi \times 3 \cdot 10^{10} \text{ cm s}^{-1} \times 3030 \text{ cm}^{-1}]^2 \frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{3 \times 12.01 \times 1.01}{3 \times 12.01 + 4 \times 1.01} \text{ g mol}^{-1}$$

$$k(\text{C-H}) = 491.94 \text{ N m}^{-1}$$

The force constants of a Z-H bond:

 $k(\text{Z-H})$

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(\text{Z-H})}{\Delta_b H(\text{C-H})}$$

$$= 491.94 \text{ N m}^{-1} \cdot 450.2 \text{ kJ mol}^{-1} \cdot [438.4 \text{ kJ mol}^{-1}]^{-1} = 505.18 \text{ N m}^{-1}$$

The atomic mass and symbol of Z:

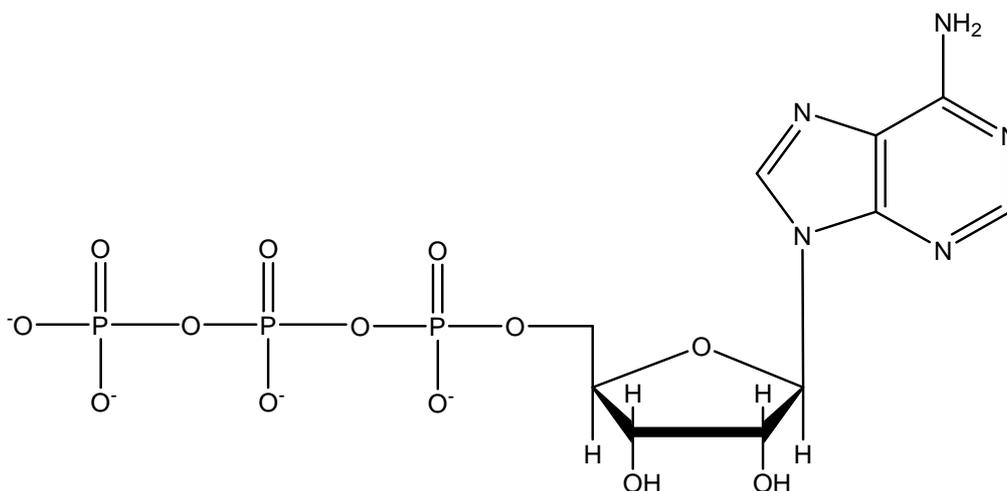
$$\frac{3 M(\text{Z}) \times M(\text{H})}{3 M(\text{Z}) + 4 M(\text{H})} = \frac{k(\text{Z-H}) \times N_A}{[2\pi c \tilde{\nu}(\text{Z-H})]^2}$$

$$M(\text{Z}) = \frac{4}{3} \left(\frac{[2\pi c \tilde{\nu}(\text{Z-H})]^2}{k(\text{Z-H}) \cdot N_A} - \frac{1}{M(\text{H})} \right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3} \left(\frac{[2\pi \times 3 \cdot 10^{10} \times 2938.45]^2}{505180 \times 6.022 \cdot 10^{23}} - \frac{1}{1.01} \right)^{-1} \text{ g mol}^{-1}$$

Atomic mass of Z: $M(\text{Z}) = 72.68 \text{ g mol}^{-1}$

Chemical symbol of Z: Ge

PROBLEM 5**Biochemistry with Thermodynamics**Structure of ATP⁴⁻

Shifting chemical equilibria with ATP:

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$$c(\text{ATP}^{4-}) = 2.25 \text{ mmol dm}^{-3}$$

$$c(\text{ADP}^{3-}) = 0.25 \text{ mmol dm}^{-3}$$

$$c(\text{HPO}_4^{2-}) = 1.65 \text{ mmol dm}^{-3}$$

Free energy stored in ATP can be released according to the following reaction:



As the pH is close to 7 in most living cells, biochemists use ΔG° instead of ΔG° . The standard state of ΔG° is defined as having a constant pH of 7. In equations with ΔG° and K for reactions at $pH = 7$ the concentration of H^+ is therefore omitted. Standard concentration is 1 mol dm^{-3} .

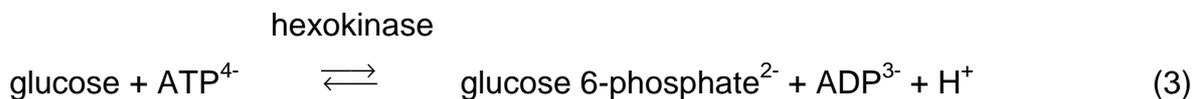
5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25 °C and $pH = 7$.

In living cells many so-called “anabolic” reactions take place, which are at first sight thermodynamically unfavourable because of a positive ΔG . The phosphorylation of glucose is an example:



5.2 Calculate first the equilibrium constant K of reaction (2) and then the ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$ in the red blood cell in chemical equilibrium at 25 °C and $pH = 7$.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:



5.3 Calculate ΔG° and K of reaction (3).

What is now the ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$ in the red blood cell in chemical equilibrium at 25 °C and $pH = 7$?

ATP synthesis:

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

- 5.4** a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of -52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.
- b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?
- c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.

In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

- 5.5 a) How many protons (H^+) are in a spherical mitochondrion with a diameter of 1 μm at $pH = 7$?
- b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.

SOLUTION

5.1 Actual $\Delta G'$ of reaction (1):

$$\begin{aligned}\Delta G' &= \Delta G^{\circ'} + R T \ln \frac{[ADP^{3-}][HPO_4^{2-}]}{[ATP^{4-}]} \\ &= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln \frac{0.00025 \times 0.00165}{0.00225} \\ &= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1} = -51.8 \text{ kJ mol}^{-1}\end{aligned}$$

5.2 Equilibrium constant K' of reaction (2), ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$:

$$\begin{aligned}\Delta G^{\circ'} &= -R T \ln K' \\ K' &= e^{-\Delta G^{\circ'}/RT} = e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 0.0038 \\ K' &= \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}][HPO_4^{2-}]} \\ \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]} &= K' \cdot [HPO_4^{2-}] \\ &= 0.0038 \cdot 0.00165 \\ &= 6.3 \cdot 10^{-6}\end{aligned}$$

5.3 ΔG° and K' of reaction (3), ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$:

$$\begin{aligned}\Delta G^{\circ}(3) &= \Delta G^{\circ}(1) + \Delta G^{\circ}(2) = -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1} = -16.7 \text{ kJ mol}^{-1} \\ \Delta G^{\circ} &= -R T \ln K' \\ K' &= e^{-\Delta G^{\circ}/RT} = e^{16700 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 843\end{aligned}$$

$$K' = \frac{c(\text{glucose 6-phosphate}) \times c(\text{ADP}^{3-})}{c(\text{glucose}) \times c(\text{ATP}^{4-})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})}$$

$$= 843 \times (2.25 \text{ mmol dm}^{-3} / 0.25 \text{ mmol dm}^{-3}) = 7587$$

5.4 a) Mass of ATP produced per day:

Energy available for ATP synthesis: $8000 \text{ kJ day}^{-1} \times 0.5 = 4000 \text{ kJ day}^{-1}$

Energy required for synthesis of ATP: 52 kJ mol^{-1}

Amount of ATP produced: $4000 \text{ kJ day}^{-1} / 52 \text{ kJ mol}^{-1} = 76.9 \text{ mol day}^{-1}$

Mass of ATP produced: $76.9 \text{ mol day}^{-1} \times 503 \text{ g mol}^{-1} = 38700 \text{ g day}^{-1}$

$$\underline{m_{\text{day-1}} = 38.7 \text{ kg day}^{-1}}$$

b) Mass of ATP in the human body:

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day

Mass of ATP in the body: $38.7 \text{ kg day}^{-1} / (1440 \text{ min day}^{-1}) \cdot 1 \text{ min} = 26.9 \text{ g}$

$$m_{\text{body}} = 26.9 \text{ g}$$

c) What happens to the rest of the free energy? Mark one correct answer:

- It is used to reduce the entropy of the body.
- It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule.
- It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP.
- It heats the body of the person.

5.5 a) How many protons are in a spherical mitochondrion with a diameter of 1 μm at $\text{pH} = 7$?

$$V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (0.5 \times 10^{-6} \text{ m})^3 = 5.2 \times 10^{-19} \text{ m}^3 = 5.2 \times 10^{-16} \text{ dm}^3$$

$$c = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

$$n = V c \cdot N_A = 5.2 \times 10^{-16} \text{ dm}^3 \times 1 \times 10^{-7} \text{ mol dm}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 31$$

b) How many protons have to enter a mitochondrium?

Number of ATP molecules:

$$n(\text{ATP}) = \frac{m(\text{ATP}) N_A}{M(\text{ATP})} = \frac{0.2 \times 10^{-15} \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{503 \text{ g mol}^{-1}} = 239400$$

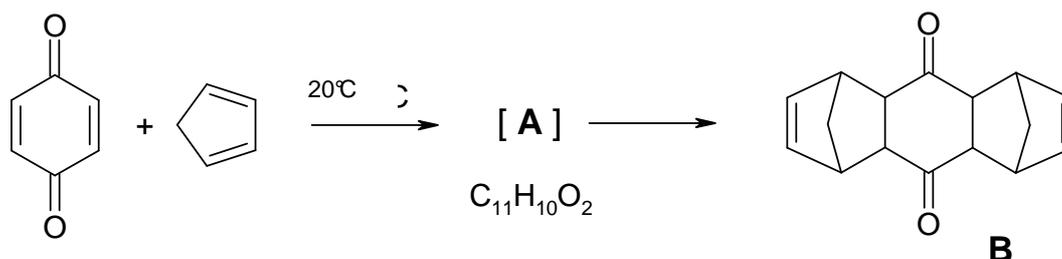
$$\text{Number of H}^+ \text{ per cell: } n(\text{H}^+_{\text{per cell}}) = n(\text{ATP}) \times 3 = 718300$$

$$\text{Number of H}^+ \text{ per mitochondrium: } n(\text{H}^+_{\text{mit}}) = n(\text{H}^+_{\text{per cell}}) / 1000 = 718$$

PROBLEM 6

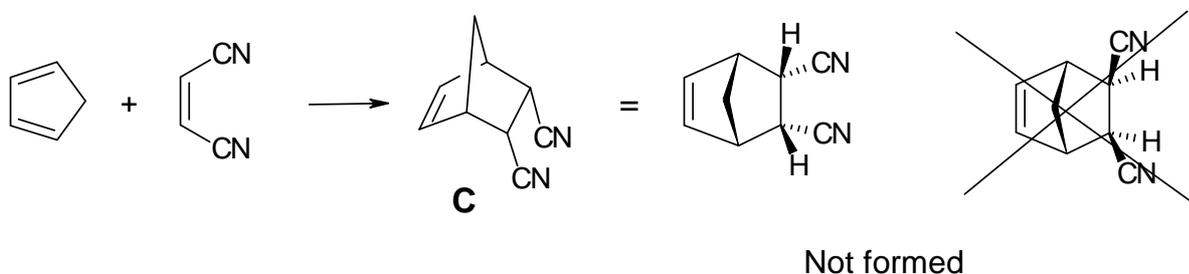
Diels-Alder Reactions

The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:



6.1 Draw the structure of **A** (without stereochemical information).

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



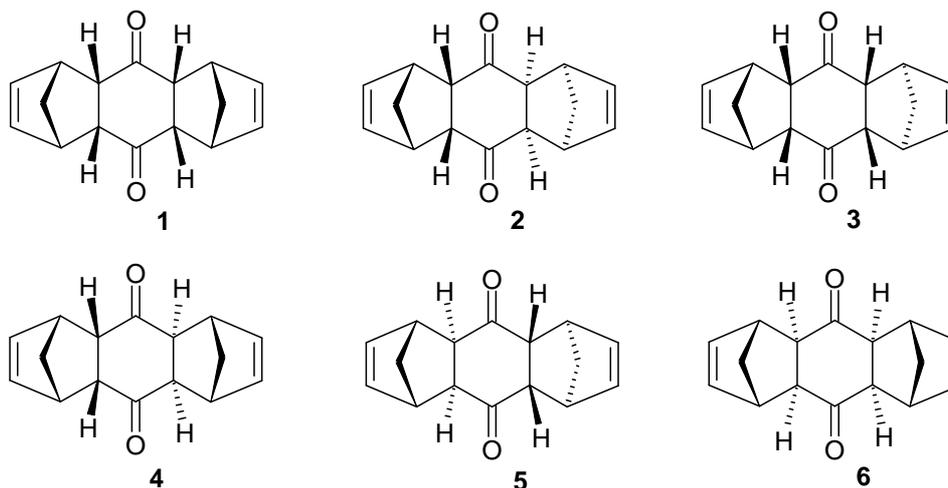
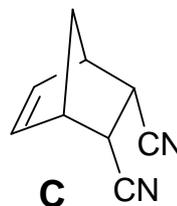
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

6.2 Give the structures of **D1** and **D2**.

Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

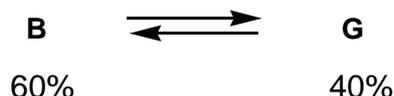
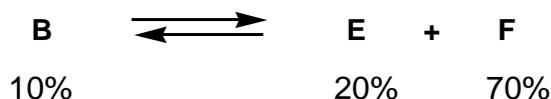
Hints:

- keep the stereospecific formation of **C** in mind and
- the sterically less hindered isomer forms.



6.3 Which single isomer of the six stereoisomers 1-6 of **B** shown above did they isolate?

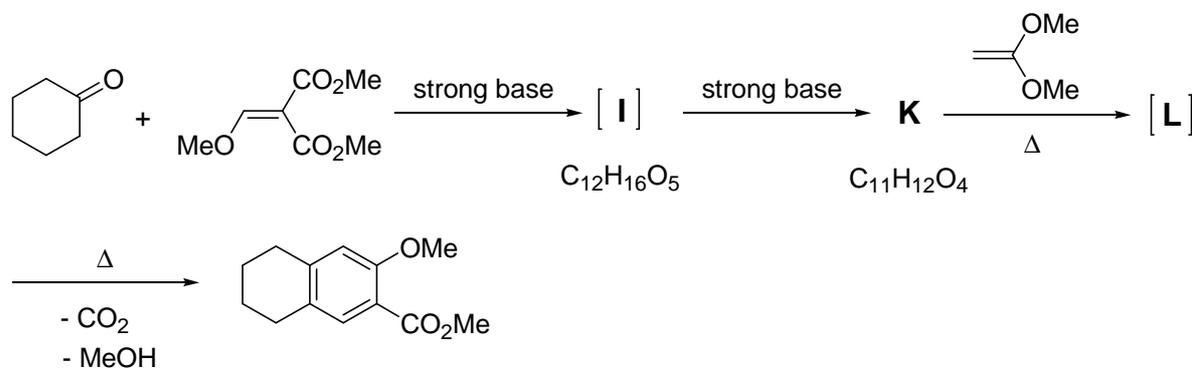
After prolonged heating (15h, 120 °C) of the originally isolated stereoisomer **B** (melting point mp: 157 °C), Diels and Alder obtained two new stereoisomers **E** (mp: 153 °C) and **F** (mp: 163 °C). Equilibration of **B** with a catalytic amount of a strong base at 25 °C gave a further stereoisomer **G** (mp: 184 °C).



6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.

Hint: You do not need to know, which of the six stereoisomers 1 – 6 (shown above) corresponds to either **E**, **F** or **G** in order to answer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.



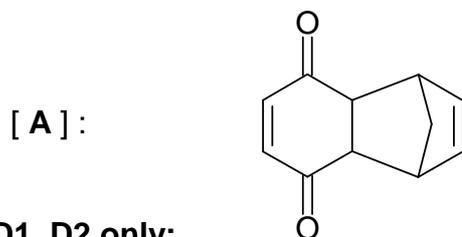
6.5 Draw the structures for I, K and L.

Hints: - K has only one methyl group.

- L is the Diels-Alder adduct of K and the alkene shown.

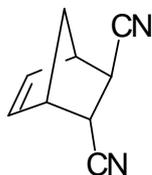
SOLUTION

6.1 Structure of A only:

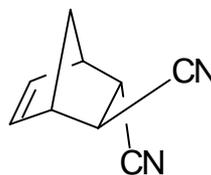


6.2 Structures of D1, D2 only:

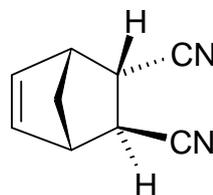
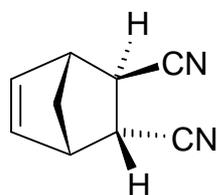
D1:



D2:



alternatively, the following structures are also correct:



Note: The two compounds are enantiomers

6.3 Correct structure of **B** (circle only one):

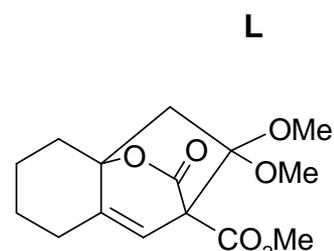
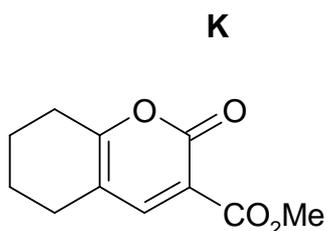
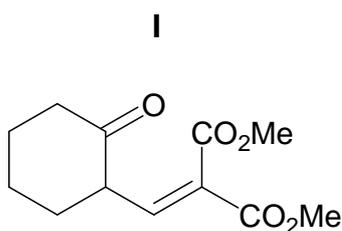
1 **2** 3 4 5 6

Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure **C**. As shown in structure **C** this endo- configuration is characterized by the two H atoms and the CH₂-bridge of the bicyclic system being on the same side of the ring. Only structures **1** and **2** of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure **1** the three rings form a U-shaped molecule which is sterically more hindered than structure **2** which has a zig-zag structure.

6.4 Decide the questions concerning the Diels-Alder reaction.

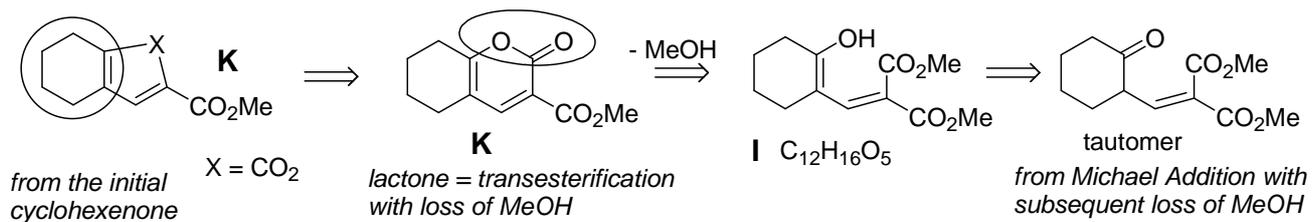
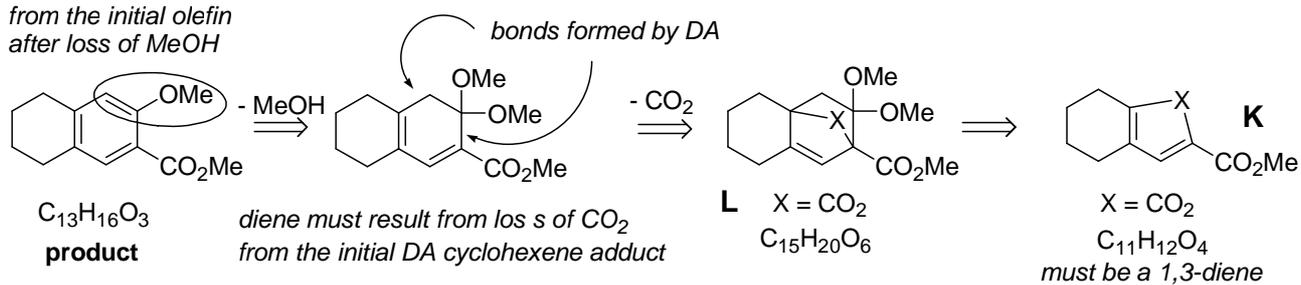
	true	false	no decision possible
• The Diels-Alder reaction is reversible	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
• The formation of B in the original reaction is thermodynamically controlled	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
• B is thermodynamically more stable than E	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
• E is thermodynamically less stable than F	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
• G is an enantiomer of B	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
• G is thermodynamically more stable than F	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>

6.5 Structures of **I**, **K**, **L** only:



Notes:

from the initial olefin
after loss of MeOH

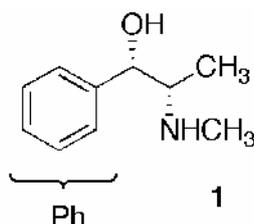


PROBLEM 7**Stereochemistry in Drugs**

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

- 7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system.

Pseudoephedrine (**1**) is a constituent in many common drugs against colds, e.g. in nasal sprays.



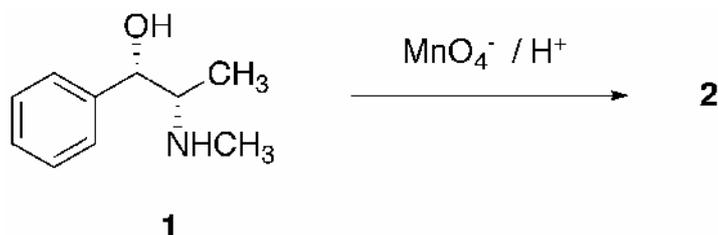
- 7.2 Mark the stereocenters in **1** with an asterisk * on the answer sheet.

Order the substituents on each stereocenter in **1** according to their priority and determine their absolute configuration (*R* or *S*).

- 7.3 Draw a Newman or a sawhorse representation of **1**.

Draw a Fischer representation of **1**.

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:



- 7.4 Draw the stereochemically correct structure of compound **2** and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on all atoms which undergo a change in their formal oxidation numbers.

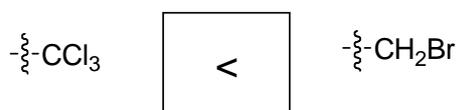
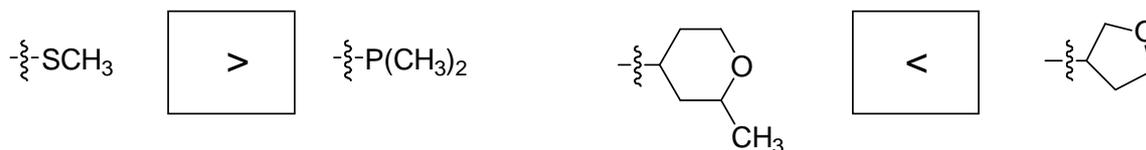
The treatment of **2** with LiAlH_4 results exclusively in compound **3**, which differs from **1** in its melting point.



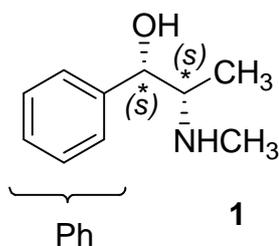
- 7.5** a) Draw the stereochemically correct structure of **3**.
 b) Decide the statements on the answer sheet concerning isomers.
 c) Draw a structural model to rationalize the exclusive formation of **3** from **2**.

SOLUTION

7.1 Fill in < or > (A < B means A has a priority lower than B) :

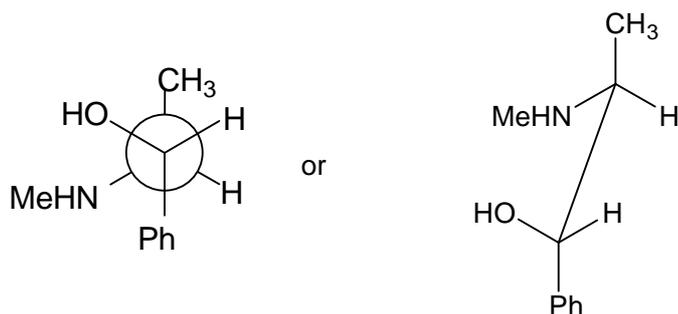


7.2



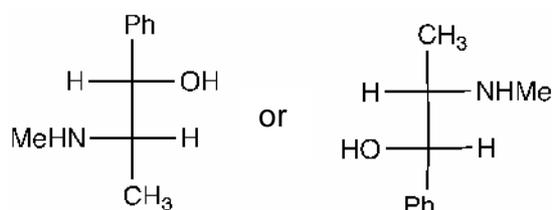
highest priority	lowest priority		
→			
OH	CH(NHCH ₃)CH ₃	Ph	H
NHCH ₃	CH(OH)Ph	CH ₃	H

7.3 Newman projection or sawhorse projection of **1**:



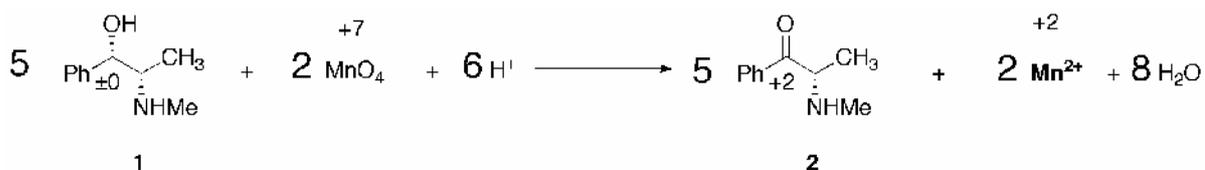
(Me = CH₃)

Fischer projection of **1**:

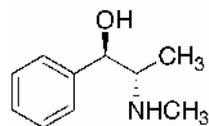


(Me = CH₃)

7.4 Equation with oxidation numbers and stereochemically correct structure of **2**:



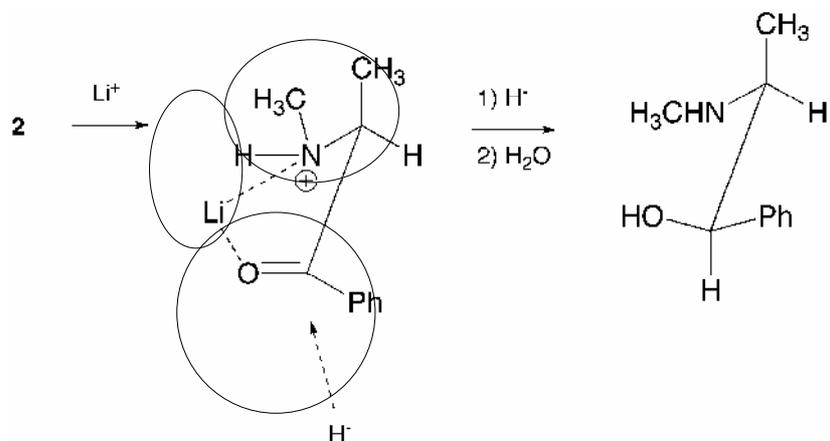
7.5 a) Structure of **3** (correct stereochemistry):



b) Statements concerning isomers:

	true	false
1 and 3 are stereo-isomers	<input checked="" type="checkbox"/>	<input type="checkbox"/>
1 and 3 are enantiomers	<input type="checkbox"/>	<input checked="" type="checkbox"/>
1 and 3 are diastereomers	<input checked="" type="checkbox"/>	<input type="checkbox"/>
1 and 3 are conformational isomers	<input type="checkbox"/>	<input checked="" type="checkbox"/>

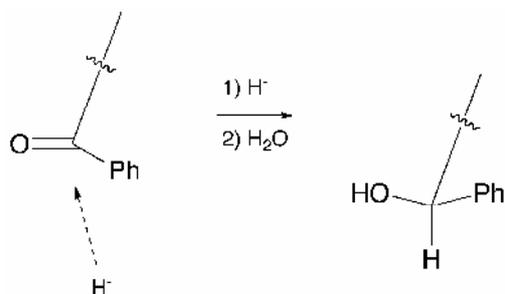
- c) Draw a structural model to rationalize the exclusive formation of **3** from **2**



Notes: Attack of hydride occurs from the sterically least hindered side.

Full points will also be given for an explanation using the formation of a hydrogen bond.

1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.



PROBLEM 8

Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

($T = 298.15$ K throughout whole problem)

Solution **A** is an aqueous solution of CaCl_2 with a concentration of 1.780 g dm^{-3} .

Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3} .

$$pK_{a1}(\text{H}_2\text{CO}_3) = 6.37$$

$$pK_{a2}(\text{HCO}_3^-) = 10.33$$

8.1 Calculate the pH of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**.

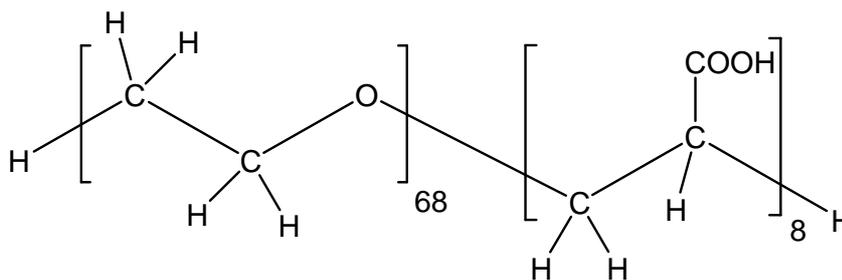
Solution **C** is adjusted to pH 10. A precipitate forms.

$$K_{sp}(\text{Ca}(\text{OH})_2) = 6.46 \times 10^{-6}$$

$$K_{sp}(\text{CaCO}_3) = 3.31 \times 10^{-9}$$

8.2 Show by calculation for each of the compounds $\text{Ca}(\text{OH})_2$ and CaCO_3 whether it can be found in the precipitate or not.

In a similar experiment 100 cm^3 of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (**A+B**) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3 Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 cm³ of an aqueous NaOH solution ($c(\text{NaOH}) = 0.19 \text{ mol dm}^{-3}$). The solution is diluted by the addition of 200 cm³ of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a pH of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8 \text{ g mol}^{-1}$
- The charge of the particles is found to be $Z = -800$ (number of unit charges). ($pK_a(\text{COOH}, \text{copolymer}) = 4.88$)

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

8.5 Calculate which modification of calcium carbonate has been formed.

Modification	density
Calcite	2.71 g cm ⁻³
Vaterite	2.54 g cm ⁻³
Aragonite	2.95 g cm ⁻³

SOLUTION

8.1 pH of solution B:

$$K_{b2} = \frac{c(\text{HCO}_3^-)/(1 \text{ mol dm}^{-3}) \times c(\text{OH}^-)/(1 \text{ mol dm}^{-3})}{c(\text{CO}_3^{2-})/(1 \text{ mol dm}^{-3})} \quad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$$K_{b2} = 2.14 \times 10^{-4}$$

$$K_{b1} = 2.34 \times 10^{-8}$$

Since $K_{b2} \gg K_{b1}$, only one protonation step of the CO_3^{2-} has to be considered.

$$c(\text{HCO}_3^-) = c(\text{OH}^-) = x \quad \text{and} \quad c(\text{CO}_3^{2-}) = c_0(\text{CO}_3^{2-}) - x$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g dm}^{-3}}{105.99 \text{ g mol}^{-1}}$$

$$c_0(\text{Na}_2\text{CO}_3) = c_0(\text{CO}_3^{2-}) = 0.016 \text{ mol dm}^{-3}$$

$$K_{b2} = \frac{x^2 / (1 \text{ mol dm}^{-3})}{(c_0(\text{CO}_3^{2-}) - x)} \quad x = c(\text{OH}^-) = 1.75 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = 11.2$$

8.2 Ca(OH)₂, CaCO₃ in the precipitate?

$$M(\text{CaCl}_2) = 110.98 \text{ g mol}^{-1} \quad pH = 10, \quad c(\text{OH}^-) = 1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g cm}^{-3}}{105.99 \text{ g mol}^{-1} \times 2} \quad c(\text{CaCl}_2) = \frac{1.780 \text{ g dm}^{-3}}{110.98 \text{ g mol}^{-1} \times 2}$$

$$c_0(\text{Na}_2\text{CO}_3) = 8.0 \times 10^{-3} \text{ mol dm}^{-3} \quad c(\text{CaCl}_2) = c_0(\text{Ca}^{2+}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Calculations for Ca(OH)₂:

$$c(\text{OH}^-)^2 \times c_0(\text{Ca}^{2+}) = 8 \times 10^{-11} < 6.46 \times 10^{-6} = K_{sp}(\text{Ca(OH)}_2) \quad \text{no precipitate}$$

Calculations for CaCO₃:

$$K_{b2} = \frac{c(\text{HCO}_3^-) \times c(\text{OH}^-)}{c(\text{CO}_3^{2-})}, \quad c(\text{HCO}_3^-) = \frac{K_{b2}}{c(\text{OH}^-)} \times c(\text{CO}_3^{2-})$$

$$c(\text{HCO}_3^-) = 2.14 \times c(\text{CO}_3^{2-}) \quad \text{and} \quad c(\text{HCO}_3^-) + c(\text{CO}_3^{2-}) = c_0(\text{Na}_2\text{CO}_3)$$

$$2.14 \times c(\text{CO}_3^{2-}) + c(\text{CO}_3^{2-}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Initial concentration of CO}_3^{2-} \text{ in solution } \mathbf{C}: \quad c(\text{CO}_3^{2-}) = 2.55 \times 10^{-3} \text{ mol dm}^{-3}$$

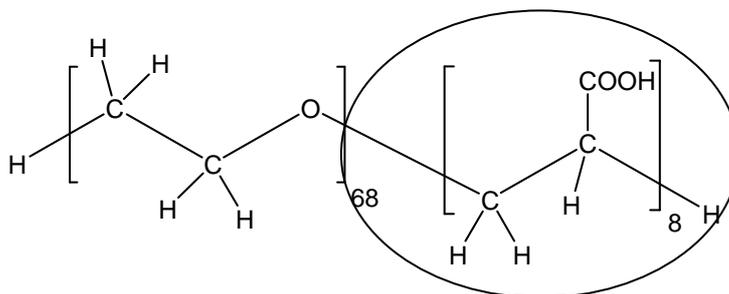
$$\text{Initial concentration of Ca}^{2+} \text{ in solution } \mathbf{C}: \quad c(\text{Ca}^{2+}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

hence $c(\text{CO}_3^{2-}) \times c(\text{Ca}^{2+}) = 2.04 \times 10^{-5} > 3.3 \times 10^{-9} = K_{sp}(\text{CaCO}_3)$ precipitate

$\text{Ca}(\text{OH})_2$ will be found in the precipitate yes no

CaCO_3 will be found in the precipitate yes no

8.3 Circle the block that attaches to the CaCO_3 crystal:



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?



pH and pK_a lead to the total concentration of COOH groups in the solution:

$$\begin{aligned} c(\text{COO}^-) &= x & c(\text{COOH}) &= c_0(\text{COOH}) - x & x &= c_0(\text{OH}^-) - c(\text{OH}^-) \\ c_0(\text{OH}^-) &= \frac{50 \text{ cm}^3}{250 \text{ cm}^3} \cdot 0.19 \text{ mol dm}^{-3} & & & c_0(\text{OH}^-) &= 0.038 \text{ mol dm}^{-3} \\ c(\text{OH}^-) &= 10^{-1.7} \text{ mol dm}^{-3} = 0.02 \text{ mol dm}^{-3} & & & x &= 0.018 \text{ mol dm}^{-3} \end{aligned}$$

$$K_b = \frac{(c_0(\text{COOH}) - x) / (1 \text{ mol dm}^{-3}) \times c(\text{OH}^-) / (1 \text{ mol dm}^{-3})}{x / (1 \text{ mol dm}^{-3})}$$

$$c_0(\text{COOH}) = \frac{K_b \cdot x \times (1 \text{ mol dm}^{-3})}{c(\text{OH}^-)} + x$$

$$c_0(\text{COOH}) = \left(\frac{0.018 \times 10^{-9.12}}{0.02} + 0.018 \right) \text{ mol dm}^{-3}$$

$$c_0(\text{COOH}) = 0.018 \text{ mol dm}^{-3}$$

$$\text{(Or as } \text{pH} \gg \text{p}K_a: \quad c_0(\text{COOH}) = \alpha(\text{COOH}) + x \approx x \text{)}$$

$$\text{Total concentration of polymer chains} \quad c(\text{polymer}) = \frac{c_0(\text{COOH})}{8}$$

$$M(\text{polymer}) = M(\text{C}_{160}\text{O}_{84}\text{H}_{306}) = 3574.66 \text{ g mol}^{-1}$$

$$m(\text{polymer}) = c(\text{polymer}) \times V \times M(\text{polymer})$$

$$m(\text{polymer}) = \frac{c_0(\text{COOH}) \times V \times M(\text{polymer})}{8} = \frac{0.018 \times 0.250 \times 3574.66}{8} \text{ g} = 2.0 \text{ g}$$

8.5 Modification of CaCO_3 :

The charge of the particles is caused by the number of protonized COOH groups per particle.

$$c(\text{COO}^-) \approx c_0(\text{COOH}), \alpha \approx 1$$

$$\text{Number of COOH groups per particle:} \quad N_{\text{COOH}} = \frac{|Z|}{\alpha} \quad N_{\text{COOH}} = 800$$

$$\text{Number of polymer chains per particle:} \quad N_{\text{polymer}} = \frac{N_{\text{COOH}}}{8} = 100$$

The number of polymers per particle indicates the mass of polymer per particle.

Thus, the mass of the calcium carbonate particle can be calculated:

$$M(\text{CaCO}_3 \text{ particle}) = M(\text{total particle}) - N_{\text{polymer}} M(\text{polymer})$$

$$M(\text{CaCO}_3 \text{ particle}) = 8.01 \times 10^8 \text{ g mol}^{-1} - 100 \times 3574.66 \text{ g mol}^{-1}$$

$$M(\text{CaCO}_3 \text{ particle}) = 8.01 \times 10^8 \text{ g mol}^{-1}$$

$$\text{Mass of one } \text{CaCO}_3 \text{ particle:} \quad m(\text{CaCO}_3 \text{ particle}) = M(\text{CaCO}_3 \text{ particle}) \cdot N_A^{-1}$$

and with the volume of the spherical particle ($V = \frac{4}{3} \pi r^3$) the density can be

calculated:

$$\begin{aligned}\rho(\text{CaCO}_3) &= \frac{m(\text{CaCO}_3 \text{ particle})}{V(\text{CaCO}_3 \text{ particle})} = \frac{3 m(\text{CaCO}_3 \text{ particle})}{4 \pi r^3} \\ &= \frac{3 (M (\text{total particle}) - N_{\text{polymer}} M(\text{polymer}))}{N_A 4 \pi r^3} \\ &= \frac{3 \times 8.01 \times 10^8 \text{ g mol}^{-1}}{N_A \cdot 4 \pi (5 \times 10^{-6} \text{ cm})^3} = 2.54 \text{ g cm}^{-3}\end{aligned}$$

The modification of calcium carbonate is Calcite Vaterite Aragonite

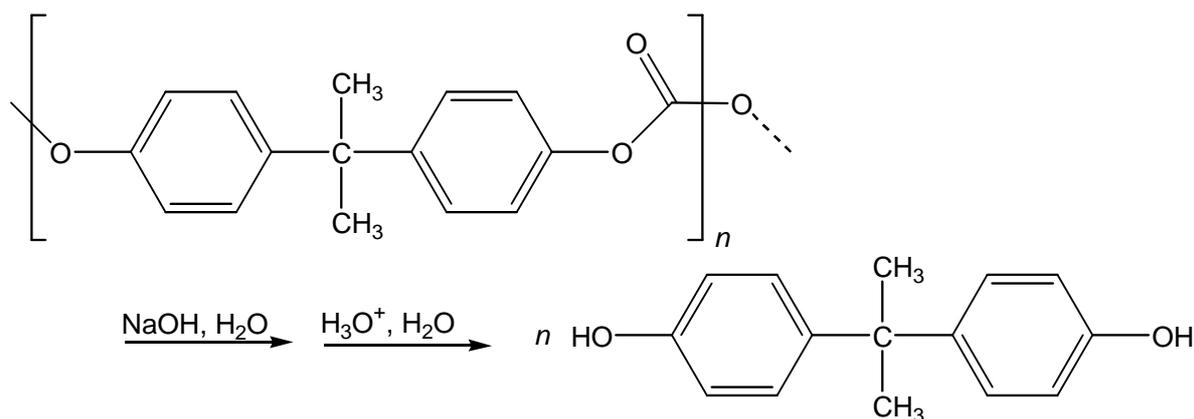
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

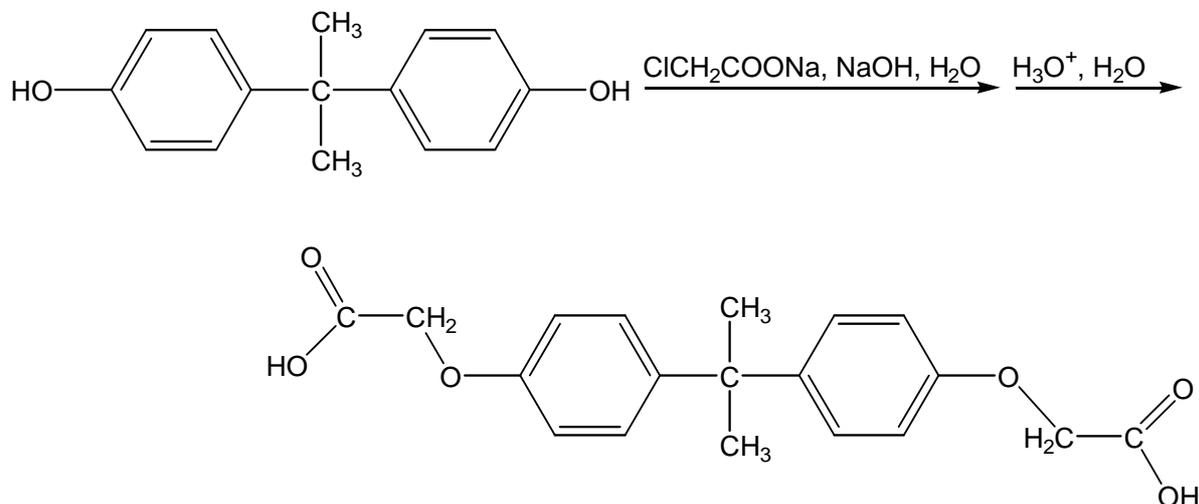
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
(Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
(Filling of the melting point tubes in step 1 will be done by the organizer.)
(The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1: Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. 1), 4.0 g of sodium hydroxide (No. 5) and 3 cm³ of demineralized water into a 100 cm³ Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 cm³ of ethanol (No. 2) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 cm³ of demineralized water and transfer the reaction mixture into a 400 cm³ beaker. Rinse the Erlenmeyer flask with 25 cm³ of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm³ with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 cm³ of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm³ portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- For drying and weighing deliver your labelled beaker A into the instructor room.
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. **28**), your starting material of the second step.
- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

**Step 2: Reaction of Bisphenol A with Chloroacetic Acid
forming 2,2-Bis(p-phenyleneoxyacetic acid)propane
(Bisphenol A bis(carboxymethyl)ether)**

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 cm³ Erlenmeyer flask with ground-glass joint.
- Add 10 cm³ of an aqueous sodium-hydroxide solution (No. **6**), 1 cm³ of demineralized water and a magnetic stirring bar.

- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. 4) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating must be stopped.
- After that, 50 cm³ of ethanol (No. 2) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 cm³ of ethanol (No. 2) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 cm³ of ethanol (No. 2). The precipitate is washed twice with 10 cm³ portions of ethanol (No. 2). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 cm³ of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 cm³ of hydrochloric acid (No. 3) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm³ portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.

- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.

SOLUTION

- 1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

$$M_1(\text{polycarbonate}) = M_1(\text{C}_{16}\text{H}_{14}\text{O}_3)_n\text{H}_2 \approx M_1(\text{C}_{16}\text{H}_{14}\text{O}_3) = 254.30 \text{ g mol}^{-1}$$

$$m_1 = 2.54 \text{ g}$$

$$M_2(\text{C}_{15}\text{H}_{16}\text{O}_2) = 228.31 \text{ g/mol}$$

$$m_2 = m_1 \times M_1^{-1} \times M_2$$

Theoretical yield of bisphenol A: 2.28 g

- 1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A.

$$M_2(\text{C}_{15}\text{H}_{16}\text{O}_2) = 228.31 \text{ g/mol}$$

$$m_2 = 2.00 \text{ g}$$

$$M_3(\text{C}_{19}\text{H}_{20}\text{O}_6) = 344.39 \text{ g/mol}$$

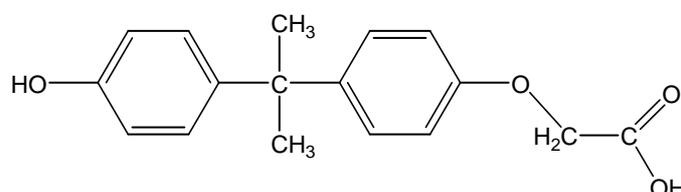
$$m_3 = m_2 \times M_2^{-1} \times M_3$$

Theoretical yield of bisphenol A bis(carboxymethyl)ether: 3.02 g

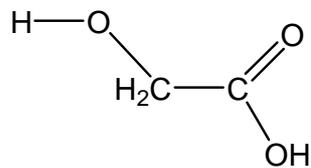
1.3

Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products.

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



2. Alkaline hydrolysis of sodium chloroacetate:



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.

Answer the additional questions and write the results with adequate accuracy.

The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 Qualitative determination of the alkaline earth metal(s)

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$; No. **14**).

At the beginning, lanthanum has to be separated as an insoluble residue.

All steps must be carried out in the hood!

Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.

Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow BaCrO_4 precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is divided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.
 1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3 . From now on this solution is called "parent solution".

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa ; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of

about 75 cm³. The *pH*-value has to be about **pH 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na₂-EDTA solution (No. 7). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 Quantitative determination of the copper content

Transfer 25.00 cm³ of your parent solution (No. 13) into the 100 cm³ volumetric flask and fill up with demineralized water to a volume of 100.0 cm³. For each titration, transfer 25.00 cm³ of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. 6), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. 12) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm³ of sodium-iodide solution (No. 9), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. 10). Add some starch solution (No. 11) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

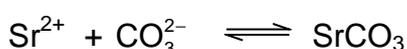
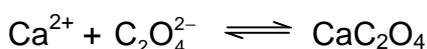
Repeat this procedure as many times as necessary.

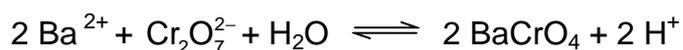
SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

- | | | | | | |
|------------------|--------------------------|-----------|--------------------------|-----------|-------------------------------------|
| Ca | <input type="checkbox"/> | Sr | <input type="checkbox"/> | Ba | <input checked="" type="checkbox"/> |
| Ca and Sr | <input type="checkbox"/> | Ca and Ba | <input type="checkbox"/> | Sr and Ba | <input type="checkbox"/> |
| Ca and Sr and Ba | <input type="checkbox"/> | | | | |

Complete the following reaction equations:





2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm⁻³ EDTA solution: $V = 11.60 \text{ cm}^3$

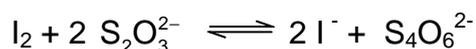
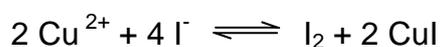
(according to 100 cm³ of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm⁻³ Na₂S₂O₃ solution: $V = 10.50 \text{ cm}^3$

(according to 100 cm³ of superconductor solution)

Complete the following reaction equations:



2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

$$[M(\text{Cu}) = 63.55 \text{ g mol}^{-1}; M(\text{La}) = 138.91 \text{ g mol}^{-1}]$$

Amount of copper:

$$10,50 \text{ cm}^3 \times 0.01 \text{ mol dm}^{-3} \times 4 \times 10 \times 63.55 \text{ g mol}^{-1} = 266.9 \text{ mg}$$

Amount of lanthanum:

$$[11.60 - (10.50 / 10 \times 4)] \text{ cm}^3 \times 0.1 \text{ mol dm}^{-3} \times 10 \times 138.91 \text{ g mol}^{-1} = 1028 \text{ mg}$$

$$\text{Mass Cu: } m(\text{Cu}) = 266.9 \text{ mg}$$

$$\text{Mass La: } m(\text{La}) = 1028 \text{ mg}$$

2.5 Assume a fictive consumption of 39.90 cm³ of 0.1000 mol dm⁻³ EDTA solution and 35.00 cm³ of 0.01000 mol dm⁻³ Na₂S₂O₃ solution. Calculate the coefficient x in the formula La_xM_(2-x)CuO₄ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = $[39.90 - (35.00/10 \times 4)] \text{ cm}^3 = 25.90 \text{ cm}^3$

Consumption for copper = $(39.90 - 25.90) \text{ cm}^3 = 14.00 \text{ cm}^3$

$n(\text{La}) : n(\text{Cu}) = 25.90 : 14.00 = 1.85 : 1$

coefficient x: 1.85

formula: $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$

37th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-SEVENTH INTERNATIONAL CHEMISTRY OLYMPIAD 16–25 JULY 2005, TAIPEI, TAIWAN

THEORETICAL PROBLEMS

PROBLEM 1

Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms N,N-dimethylformamide (DMF), which can be described as the following resonance structures.



1.1 Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide ($\text{CH}_3\text{CONHCH}_3$, compound **B**), and propionamide (compound **C**, $\text{CH}_3\text{CH}_2\text{CONH}_2$). Express your answer from high to low melting point as follows:

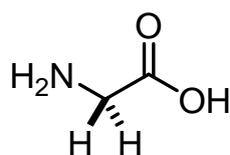
____ > ____ > ____ (Insert compound codes **A**, **B**, **C**)

1.2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.

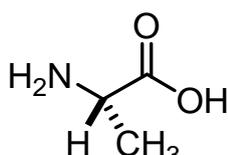
- (a) 1660 cm^{-1} because of the shorter carbonyl bond length.
- (b) 1660 cm^{-1} because of the longer carbonyl bond length.
- (c) 1740 cm^{-1} because of the shorter carbonyl bond length.
- (d) 1740 cm^{-1} because of the longer carbonyl bond length.

1.3 Glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) is an α -amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

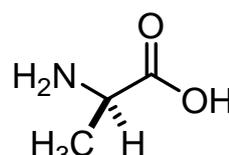
1.4 When an α -amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?



Glycine (Gly)



L-Alanine (L-Ala)



D-Alanine (D-Ala)

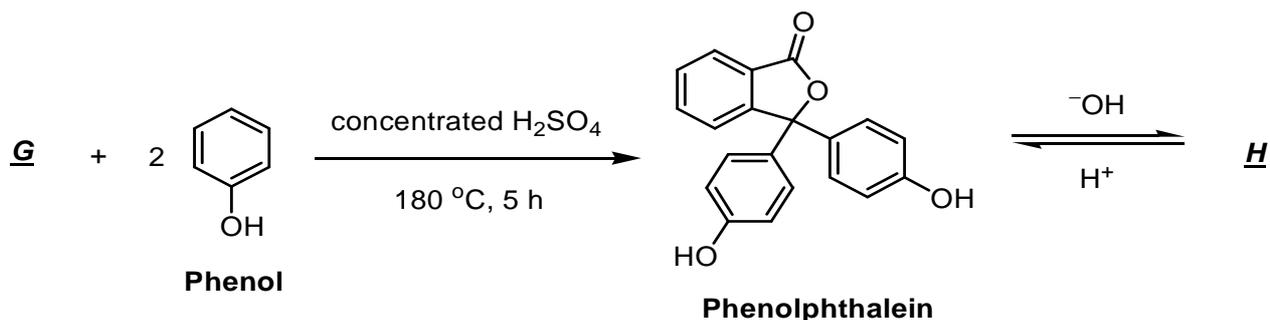
1.5 Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

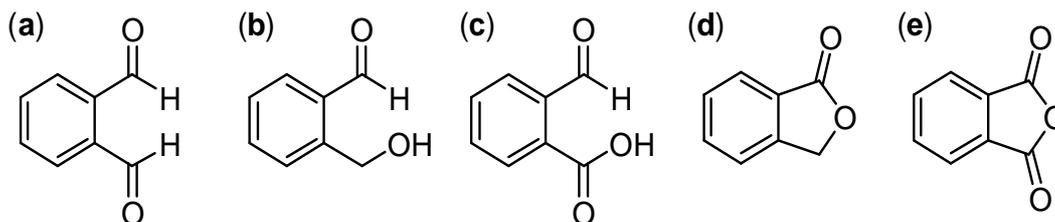
1.6 Predict the binding affinity of phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) with a polyamide gel. Express your answer from high to low binding affinity as follows:

_____ > _____ > _____. (Insert compound codes **D**, **E**, and **F**)

The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary colour. For example, phenolphthalein is a commonly used acid-base indicator, which is colourless in acidic and neutral solutions, but reddish pink in basic solutions (pH 8.3 – 10.0).



- 1.7 Draw the structural formula of **H** derived from phenolphthalein that is attributable to the reddish pink colour in aqueous NaOH solution.
- 1.8 A simple way to prepare phenolphthalein is via condensation of compound **G** with 2 equivalents of phenol. What is the most effective reagent for **G** to accomplish this transformation? Select your answer from the following compounds.



SOLUTION

- 1.1 The order of the melting points is: **C > B > A**

The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bonding, but not tertiary amide.

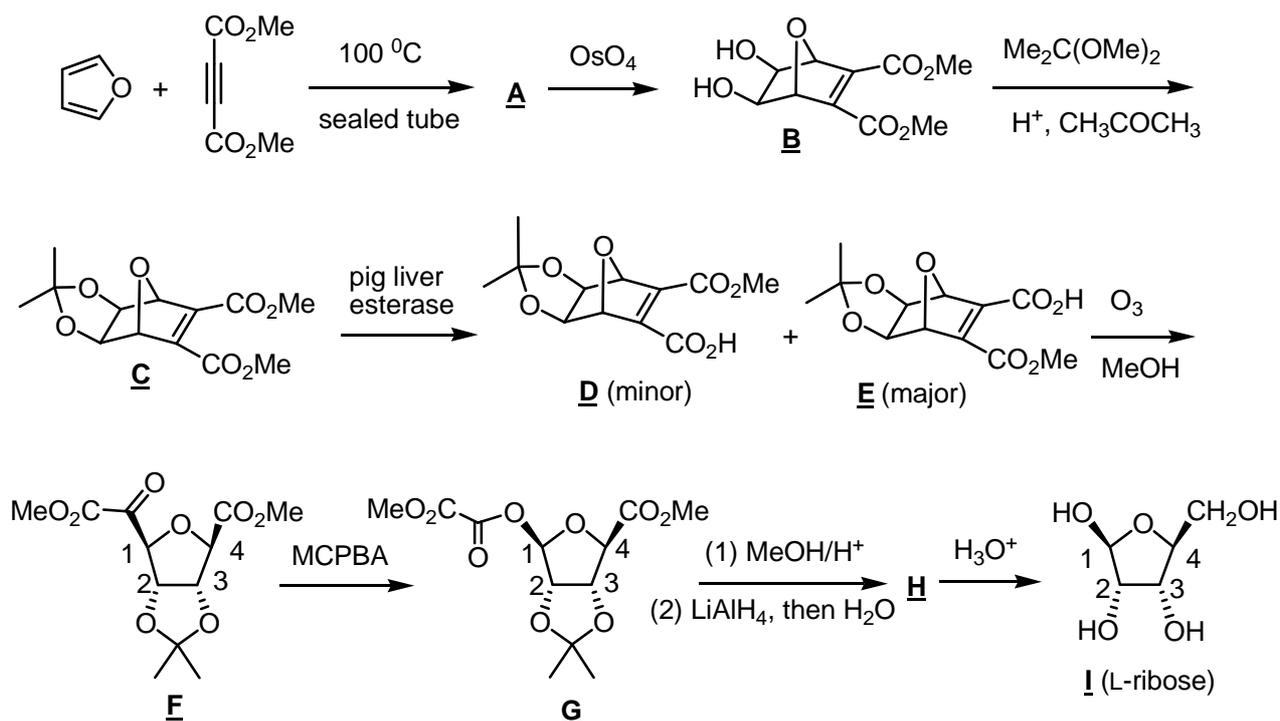
Propionamide, m.p. = 79 °C; *N*-methylacetamide, m.p. = 28 °C;

N,N-dimethylformamide, m.p. = -61 °C.

- 1.2 Correct: (b), 1660 cm⁻¹ due to a longer carbonyl bond length.

PROBLEM 2**Organic Synthesis and Stereochemistry**

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound **I**).



2.1 Compound **A** has the molecular formula of $C_{10}H_{10}O_5$. Draw the structural formula of **A**.

2.2 Given the chemistry described for reaction sequence **A** to **C**, indicate whether the following statements are true or false (Use T to represent true and F to represent false).

- ___ (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.
- ___ (b) MeOH is generated as a by-product in the reaction of **B** to **C**.
- ___ (c) Protons act as the catalyst in the transformation of **B** to **C**.
- ___ (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$.

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20} = -37.1^\circ$. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20} = -49.0^\circ$.

2.3 What is the molar ratio of **D/E** in the product mixture before the recrystallization?

Show your work.

2.4 Reaction of **F** with meta-chloroperbenzoic acid (MCPBA) afforded **G** as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

_____ (a) The reaction was to oxidize compound **F**.

_____ (b) The oxygen atom inserted originated from MCPBA.

_____ (c) The *R/S* notation of C-1 remained unchanged before and after the reaction.

The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows:

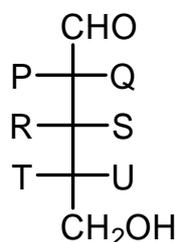
1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, $J = 6$ Hz, 1H), 4.74 (d, $J = 6$ Hz, 1H), 4.89 (s, 1H).

2.5 Draw the configurational formula of **H**.

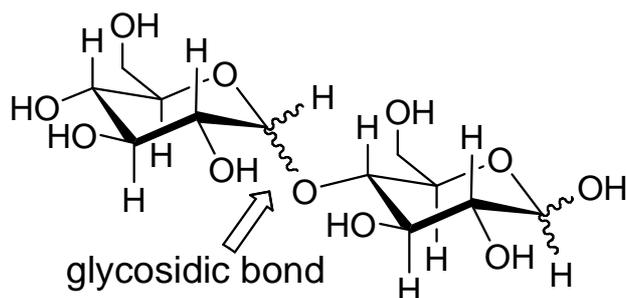
2.6 Assign *R/S* notations for compound **I** at C-1, C-2, C-3 and C-4. Give your answers as follows:

C-1: _____; C-2: _____; C-3: _____; C-4: _____.

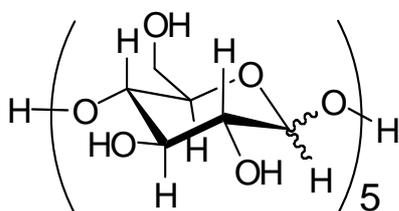
2.7 What are the identities of P, Q, R, S, T and U in the Fischer projection of compound **I** (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



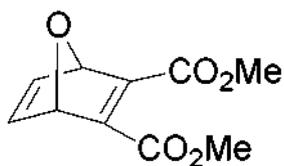
2.8 How many diastereoisomers would be obtained for pentasaccharide **J**, if it is derived from five units of D-glucose?



pentasaccharide **J** derived from D-glucose

SOLUTION

2.1



2.2

T or F

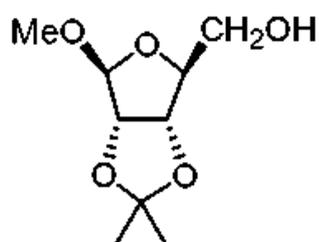
- (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.
- (b) MeOH is generated as a by-product in the reaction of **B** to **C**.
- (c) Protons act as the catalyst in the transformation of **B** to **C**.
- (d) **C** will still be formed albeit in lower yields in the absence of $\text{Me}_2\text{C}(\text{OMe})_2$

2.3 12.1 : 87.9 or 12.2 : 87.8

2.4 T or F

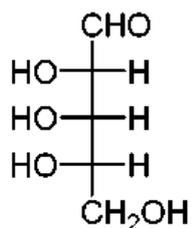
- I (a) The reaction was to oxidize compound **F**.
I (b) The oxygen atom inserted originated from MCPBA.
E (c) The *R/S* notation of C-1 remained unchanged before and after the reaction

2.5



2.6 C-1: S; C-2: S; C-3: R; C-4: S.

2.7



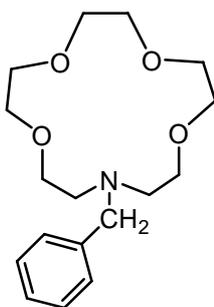
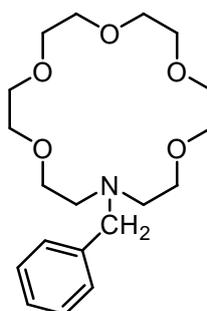
OH group for P, R, and T and H atom for Q, S, and U.

2.8 The number of stereoisomers = 2^5

PROBLEM 3

Organic Photochemistry and Photophysics

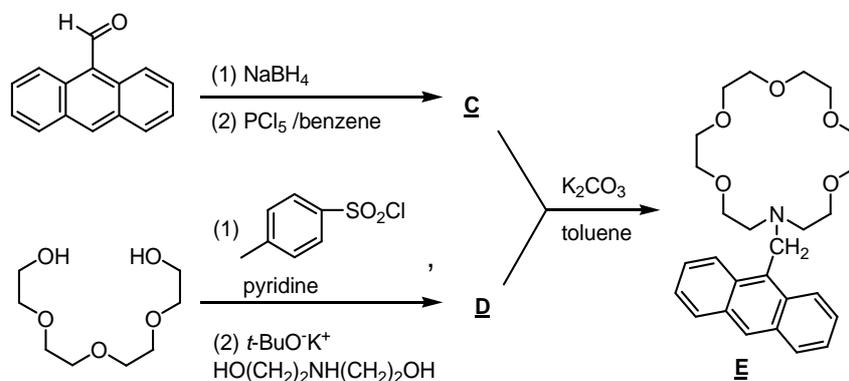
Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns **A** and **B** exhibit different binding constants for Na^+ , K^+ , and Cs^+ .

**A****B**

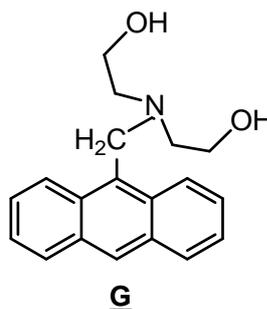
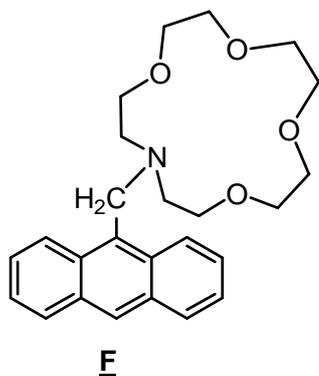
Metal ion	Radius (pm)	Binding constant ($\log_{10} K$)	
		Compound A	Compound B
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

3.1 Provide the structural formula of **C** and **D** in the following synthesis.

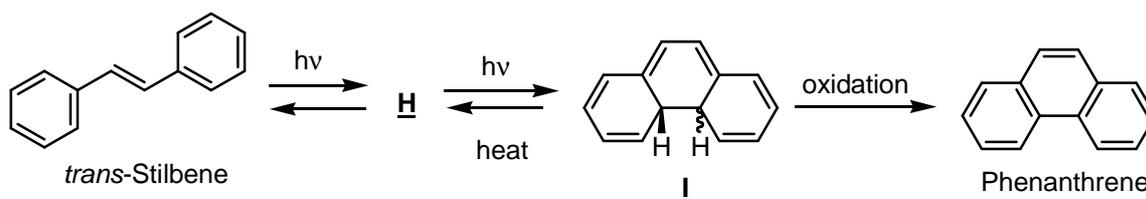


For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E**, **F**, and **G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



- 3.2** Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.
- (a) none of them (b) **E** and **F** only (c) **G** only (d) all of them
- 3.3** By adding one equivalent of potassium acetate into a dilute solution (1×10^{-5} M) of **E**, **F**, and **G** in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.
- (a) **E** (b) **F** (c) **G**
- 3.4** Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.
- (a) sodium acetate (b) potassium acetate (c) cesium acetate (d) doesn't make any difference

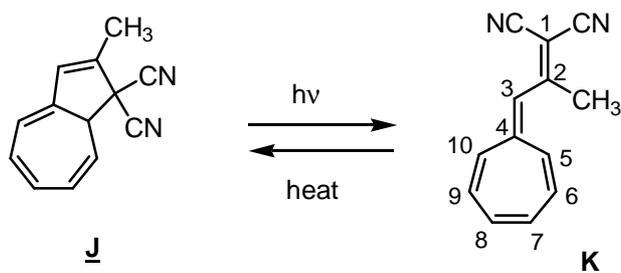
Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of **I** gives phenanthrene.



3.5 Draw the structural formula of compound **H**?

3.6 What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound **I**?

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



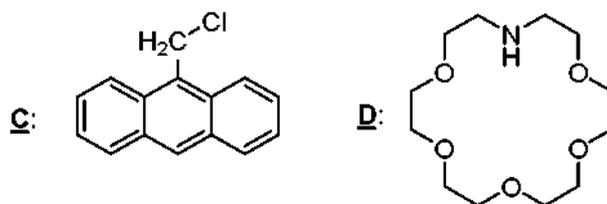
3.7 Which compound will absorb light with longer wavelength? Select your answer from the following choices: (a) **J** (b) **K**

3.8 Compound **K** can react with one equivalent of $\text{CF}_3\text{CO}_2\text{H}$ to generate a stable aromatic salt. Which position of **K** is most likely protonated? Select your answer from the following choices.

- (a) C-2 (b) C-3 (c) C-4 (d) C-5

SOLUTION

3.1

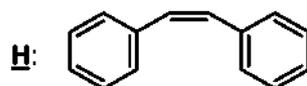


3.2 Correct is (d): All of them

3.3 Correct is (a): **E**

3.4 Correct is (a): sodium acetate

3.5



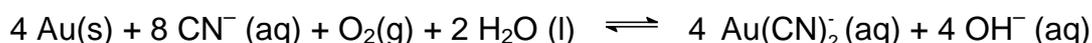
3.6 Trans

3.7 Correct is (b): **K**

3.8 Correct is (b): C-3

PROBLEM 4**A**Gold Capital of Asia

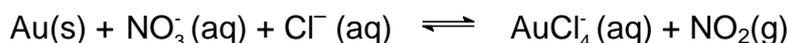
Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines in Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN⁻) solutions in the presence of air to form Au(CN)₂⁻, which is stable in aqueous solution.



4.A-1 Draw a structure for Au(CN)₂⁻ showing the spatial arrangements of the atoms.

4.A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to “dissolve” gold. The process is actually a redox reaction with the following simplified chemical equation:



4.A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4.A-4 What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion AuCl₄⁻ forms. Consider the following half-reactions:



An electrochemical cell can be formed from these two redox couples.

4.A-5 Calculate the formation constant for AuCl₄⁻ at 25 °C:

$$K = \frac{[\text{AuCl}_4^{-}]}{[\text{Au}^{3+}][\text{Cl}^{-}]^4}$$

4.A-6 The function of HCl is to provide Cl^- . What is the purpose of the Cl^- for the above reaction. Select your answer from the following choices.

- (a) Cl^- is an oxidizing agent
 - (b) Cl^- is a reducing agent
 - (c) Cl^- is a complexing agent
 - (d) Cl^- is a catalyst
-

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of HAuCl_4 is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of NaBH_4 . Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4.B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

- (a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
- (b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

4.B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry AlCl_4^- from an aqueous phase to an organic phase. Which

property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

- (a) one side of the molecule is electropositive, the other side is electronegative.
- (b) one side of the molecule is hydrophilic, the other side is hydrophobic.
- (c) one side of the molecule is acidic, the other side is basic.

4.B-3 What is the function of NaBH_4 in this preparation? Select your answer from the following choices.

- (a) reducing agent
- (b) oxidizing agent
- (c) neutralization agent
- (d) complexing agent

4.B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

- (a) 10^2
- (b) 10^3
- (c) 10^4
- (d) 10^5

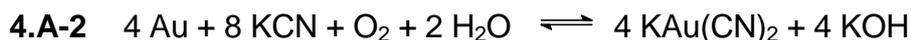
4.B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

- (a) 20 – 30 %
- (b) 40 – 50 %
- (c) 60 – 70 %
- (d) 80 – 90 %

SOLUTION

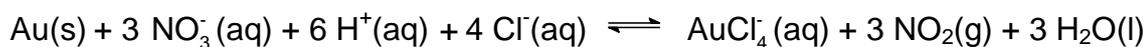
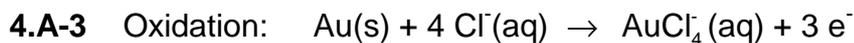


The structure of $\text{Au}(\text{CN})_2^-$ is linear.



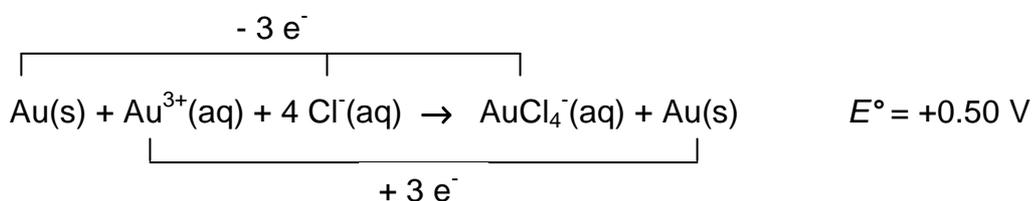
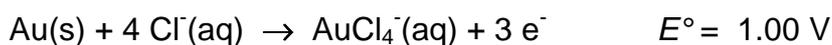
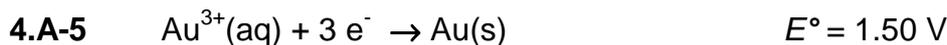
$$20 \text{ g} \div 197 \text{ g mol}^{-1} \approx 0.10 \text{ mol (Au)}$$

$$0.10 \text{ mol} \times (8/4) \times 65.12 \text{ g mol}^{-1} = 13.024 \text{ g KCN}$$



4.A-4 Oxidizing agent: HNO_3 or nitric acid

Reducing agent: Au



$$E = E^\circ - (0.059 / n) \log Q$$

At equilibrium, $Q = K$, $E = 0$, $K = [\text{AuCl}_4^-] / [\text{Au}^{3+}] [\text{Cl}^-]^4$

$$E = (0.059 / n) \log K, \quad 0.50 = (0.059 / 3) \log K, \quad K = 10^{25.42} = 2.6 \times 10^{25}$$

$$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$$

$$(-n F E_1^0) + (-n F E_2^0) = -RT \ln K$$

$$E^\circ = (RT / nF) \ln K = (0.059 / n) \log K,$$

$$0.50 = (0.059 / 3) \log K,$$

$$K = 10^{25.42} = 2.6 \times 10^{25}$$

4.A-6 Answer for multiple choice question: (c)

4.B-1 Answer for multiple choice question: (b)

4.B-2 Answer for multiple choice question: (b)

4.B-3 Answer for multiple choice question: (a)

4.B-4 Answer for multiple choice question: (b)

Calculation:

$$V_{\text{AuNPs}} = \frac{4}{3} \pi r_{\text{AuNPs}}^3$$

$$V_{\text{Au}} = \frac{4}{3} \pi r_{\text{Au}}^3$$

$$N_{\text{Au}} = \frac{V_{\text{AuNPs}}}{V_{\text{Au}}} = \frac{\frac{4}{3} \pi r_{\text{AuNPs}}^3}{\frac{4}{3} \pi r_{\text{Au}}^3} = \left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}} \right)^3 = \left(\frac{15 \text{ \AA}}{1,44 \text{ \AA}} \right)^3 \approx 1000$$

4B-5 Calculation:

Method 1:

$$4/3 \times \pi \times r_{\text{AuNPs}}^3 = 4/3 \times \pi \times r_{\text{Au}}^3 \times N_{\text{Au}}$$

$$r_{\text{AuNPs}}^3 = r_{\text{Au}}^3 \times N_{\text{Au}}$$

Surface area of a gold nanoparticle: $S_{\text{AuNPs}} = 4 \pi r_{\text{AuNPs}}^2$

$$S_{\text{AuNPs}} = 4 \pi r_{\text{Au}}^2 N_{\text{Au}}^{2/3}$$

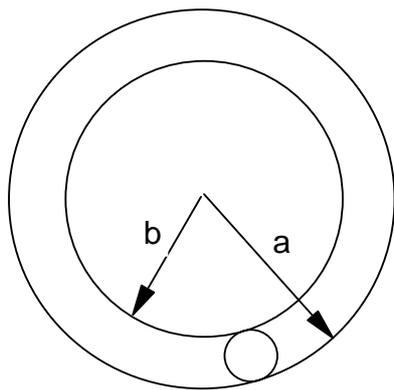
$$N_{\text{S}} \approx S_{\text{AuNPs}} / \pi r_{\text{Au}}^2 = 4 N_{\text{Au}}^{2/3}$$

$$P \approx N_{\text{S}} / N_{\text{Au}} = 4 / N_{\text{Au}}^{1/3}$$

$$N_{\text{Au}} \approx 1000$$

$$P \approx 40 \%$$

or Method 2:



$$a = r_{\text{AuNPs}}$$

$$b = r'_{\text{AuNPs}} = r_{\text{AuNPs}} + 2 r_{\text{Au}}$$

$$P \% = \frac{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}} - \frac{V'_{\text{AuNPs}}}{V_{\text{Au}}}}{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}}} \times 100 \% = \frac{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3 - \left(\frac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3}{\left(\frac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3} \times 100 \% =$$

$$= \frac{(15 \text{ \AA})^3 - (12.12 \text{ \AA})^3}{(15 \text{ \AA})^3} \times 100 \% = 47 \%$$

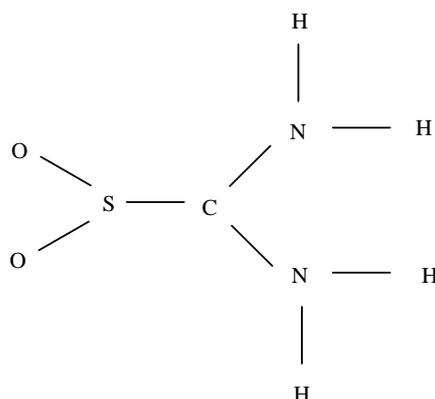
PROBLEM 5**Lewis Structure**

5.1 Draw one Lewis structure for each of the following molecules.

- a) N₂
- b) NH₃
- c) O₃
- d) SO₃

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, O₂SC(NH₂)₂, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

5.4a What is the geometry around the sulfur atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

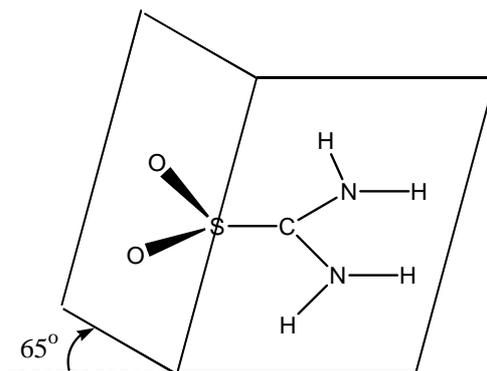
5.4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

5.4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:

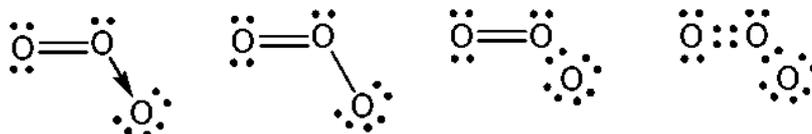
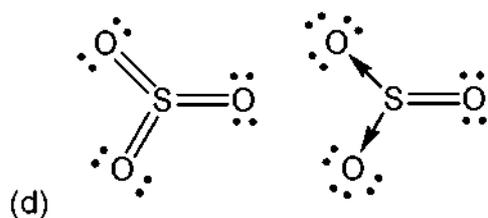
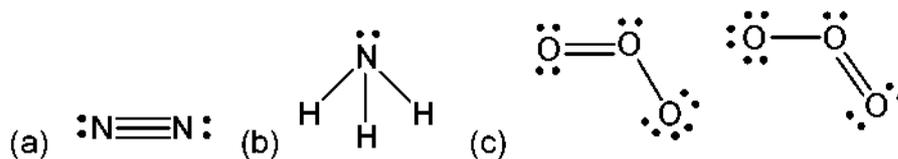


All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the SC(NH₂)₂ plane is 65°.

5.5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

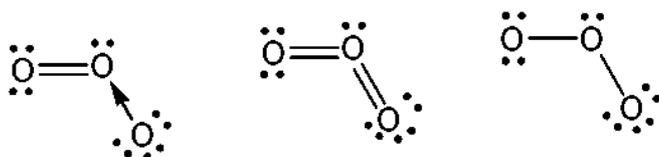
SOLUTION

5.1

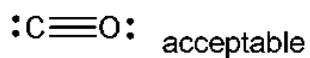


are all correct answers

But



are incorrect answers

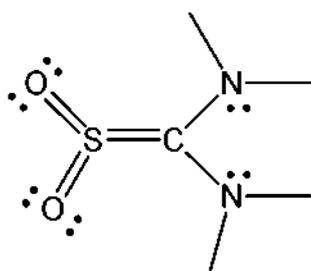


5.2

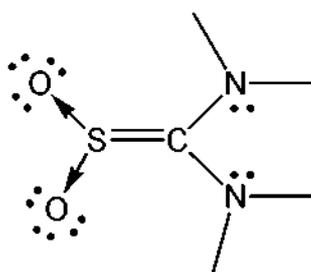
Formal charge C^{-1} ; O^{+1}

Oxidation state C^{2+} ; O^{2-}

5.3



The structure is correct.



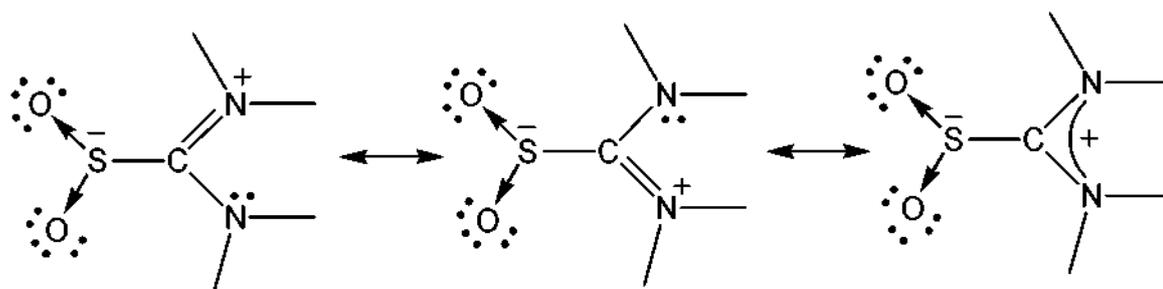
The structure would have a formal charge and is incorrect.

5.4 Sulphur: (b) trigonal planar

Carbon: (b) trigonal planar

Nitrogen: (a) trigonal pyramidal

5.5

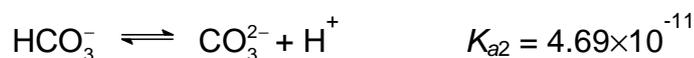
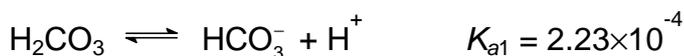
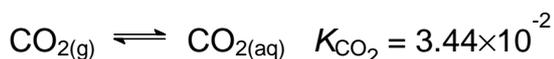


PROBLEM 6**Alkalinity of Water and Solubility of CO₂**

The capacity of water to accept H⁺ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO₃⁻, CO₃²⁻, and OH⁻. At *pH* values below 7, H⁺ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO₃⁻, CO₃²⁻, and OH⁻ are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The contributions made by different species to alkalinity depend upon *pH*. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:



Note: Calculations must be shown.

6.1 Natural waters (river or lake water) generally contain dissolved CO₂. The ratio of [H₂CO₃] : [HCO₃⁻] : [CO₃²⁻] in a water at [H⁺] = 1.00 × 10⁻⁷ M will be:

(a) : 1.00 : (b). Calculate (a) and (b).

6.2 Gaseous CO₂ in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of CO_{2(aq)} (mol dm⁻³) in pure water that is in equilibrium with the unpolluted air at 1.01 × 10⁵ Pa and 298 K containing 0.0360 % (molar ratio) CO₂. (assuming standard pressure = 1.01 × 10⁵ Pa).

If you are unable to solve this problem, assume that concentration of $\text{CO}_2(\text{aq})$ is equal to 1.11×10^{-5} M for further calculations.

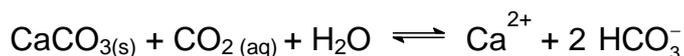
The solubility (S) of CO_2 in water can be defined as

$$S = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01×10^5 Pa will vary with alkalinity.

- 6-3** Find the solubility of atmospheric CO_2 in pure water (mol dm^{-3}). Neglect dissociation of water.
- 6.4** Find the solubility of atmospheric CO_2 (mol dm^{-3}) in a 1.00×10^{-3} mol dm^{-3} NaOH solution.

At 298 K, 1.01×10^5 Pa unpolluted air is in equilibrium with natural water saturated with CaCO_3 . The following main equilibrium may exist:



- 6.5** Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant $K_{\text{eq}} = 5.00 \times 10^{-5}$ for further calculations.

- 6.6** Calculate the concentration of Ca^{2+} (mg dm^{-3}) in CaCO_3 -saturated natural water that is in equilibrium with atmospheric CO_2 .

If you are unable to solve this problem, assume that concentration of $\text{Ca}^{2+}_{(\text{aq})} = 40.1$ mg dm^{-3} for further calculations.

- 6.7** Find the alkalinity (mol/L) of the above solution.
- 6.8** In an underground lake saturated with CaCO_3 , the water has a high content of CO_2 . The concentration of Ca^{2+} in this lake was found to be as high as 100 mg dm^{-3} . Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

SOLUTION

6.1 $[H^+] = 1.00 \times 10^{-7}$

$$K_{a1} = [HCO_3^-][H^+] / [H_2CO_3] = 2.23 \times 10^{-4},$$

$$[HCO_3^-] / [H_2CO_3] = 2.23 \times 10^3$$

$$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69 \times 10^{-11},$$

$$[CO_3^{2-}] / [HCO_3^-] = 4.69 \times 10^{-4}$$

$$[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = 4.48 \times 10^{-4} : 1.00 : 4.69 \times 10^{-4}$$

6.2 $p(\text{CO}_2(\text{aq})) = 1.01 \times 10^5 \text{ Pa} \times 3.60 \times 10^{-4} = 36.36 \text{ Pa}$

$$[\text{CO}_2(\text{aq})] = K_{\text{CO}_2} \times p(\text{CO}_2) = 0.0344 \times (36.36 \text{ Pa} / 1.01 \times 10^5 \text{ Pa}) = 1.24 \times 10^{-5}$$

(If you are unable to solve this problem, for further calculations assume that $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$.)

6.3

(a) Solubility = $[\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-]$

$$([\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] \times K_{\text{H}_2\text{CO}_3} = 2.48 \times 10^{-8}$$

$$\text{and } [\text{CO}_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69 \times 10^{-11}$$

both can be neglected.)

$$[H^+][HCO_3^-] / [\text{CO}_2(\text{aq})] = K_{a1} K_{\text{H}_2\text{CO}_3} = (2.23 \times 10^{-4}) (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

From 6-2: $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$,

$$[H^+] = [HCO_3^-] = 2.35 \times 10^{-6}$$

$$\text{Solubility} = [\text{CO}_2(\text{aq})] + [HCO_3^-] = 1.24 \times 10^{-5} + 2.35 \times 10^{-6} = 1.48 \times 10^{-5} \text{ mol dm}^{-3}$$

(b) (Using $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$ for calculation)

$$\text{Solubility} = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [HCO_3^-]$$

$$([\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] \times K_{\text{H}_2\text{CO}_3} = 2.22 \times 10^{-8} \text{ and } [\text{CO}_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) =$$

$K_{a2} = 4.69 \times 10^{-11}$ both can be neglected.)

$$[H^+][HCO_3^-] / [\text{CO}_2(\text{aq})] = K_{a1} K_{\text{H}_2\text{CO}_3} = (2.23 \times 10^{-4}) (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

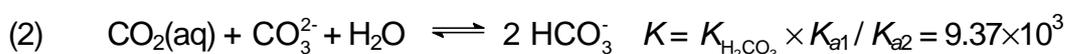
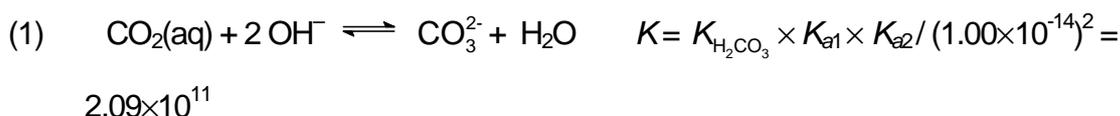
From 6.2: $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{H}^+] = [\text{HCO}_3^-] = 2.225 \times 10^{-6}$

Solubility = $[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] = 1.11 \times 10^{-5} + 2.225 \times 10^{-6} = 1.34 \times 10^{-5}$

6.4 (Using $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$ for calculation)

In $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ NaOH solution the solubility of CO_2 will be much higher because of the following reactions:



Combining (1) and (2): $\text{CO}_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \quad K = 4.43 \times 10^7$

With such a large K value all OH^- will finally be converted to HCO_3^- .

$[\text{HCO}_3^-] = 1.00 \times 10^{-3}$

$[\text{OH}^-] = 1.82 \times 10^{-6}$

$[\text{H}^+] = 5.49 \times 10^{-9} \quad [\text{CO}_3^{2-}] = 8.54 \times 10^{-6}$

Solubility = $[\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.24 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} = 1.02 \times 10^{-3} \text{ mol dm}^{-3}$

$$6.5 \quad K_{\text{eq}} = K_{\text{sp}} \times K_{\text{H}_2\text{CO}_3} \times K_{\text{a1}} / K_{\text{a2}} = (4.50 \times 10^{-9}) \times (2.00 \times 10^{-3}) \times (2.23 \times 10^{-4}) / (4.69 \times 10^{-11}) = 4.28 \times 10^{-5}$$

(If you are unable to solve this problem, assume that $K_{\text{eq}} = 5.00 \times 10^{-5}$ for further calculations.)

6.6

(a) (Using $K_{\text{eq}} = 4.28 \times 10^{-5}$ and $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$ for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From 6.5: $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-] / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From 6.2: $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$

$[\text{Ca}^{2+}] = 0.510 \times 10^{-3} = 20.5 \text{ mg dm}^{-3}$

- (b) (Using
- $K_{\text{eq}} = 5.00 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$
- for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**: $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**: $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.5177 \times 10^{-3} = 20.75 \text{ mg dm}^{-3}$

- (c) (Using
- $K_{\text{eq}} = 5.00 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$
- for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**: $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**: $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.5372 \times 10^{-3} = 21.53 \text{ mg dm}^{-3}$

- (d) (Using
- $K_{\text{eq}} = 4.28 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$
- for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**: $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**: $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.4916 \times 10^{-3} = 19.70 \text{ mg dm}^{-3}$

(If you are unable to solve this problem, assume that $[\text{Ca}^{2+}]_{(\text{aq})} = 40.1$ for further calculations.)

6.7 HCO_3^- is the major species in solution.

The pH of the solution can be estimated as $pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33) / 2 = 6.99 \approx 7.00$,

where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3 .

At pH 7.00, both $[\text{OH}^-]$ and $[\text{H}^+]$ can be neglected. Besides, $[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-]$

(from **6.1**)

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \approx [\text{HCO}_3^-]$$

From 6-6, mass balance, $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

- (a) 1.02×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6.6 (a))
- (b) 1.035×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6.6 (b))
- (c) 1.0744×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6-6 (c))
- (d) 0.9831×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6-6 (d))
- (e) 2.00×10^{-3} (assuming $[\text{Ca}^{2+}]_{(\text{aq})} = 40.1$)

Alkalinity = (a) or (b) or (c) or (d) or (e)

6.8

- (a) (Using $K_{\text{eq}} = 4.28 \times 10^{-5}$ for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

$[\text{Ca}^{2+}] = 100 \text{ mg dm}^{-3} = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$

Inserting into $K_{\text{eq}} = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = 4 [\text{Ca}^{2+}]^3 / [\text{CO}_2(\text{aq})]$

$[\text{CO}_2(\text{aq})] = 1.46 \times 10^{-3}$

$p_{\text{CO}_2} = ([\text{CO}_2(\text{aq})] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 4.28 \times 10^3 \text{ Pa}$

- (b) (Using $K_{\text{eq}} = 5.00 \times 10^{-5}$ for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

$[\text{Ca}^{2+}] = 100 \text{ mg dm}^{-3} = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$

Inserting into $K_{\text{eq}} = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = 4 [\text{Ca}^{2+}]^3 / [\text{CO}_2(\text{aq})]$

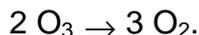
$[\text{CO}_2(\text{aq})] = 1.25 \times 10^{-3}$

$p_{\text{CO}_2} = ([\text{CO}_2(\text{aq})] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 3.67 \times 10^3 \text{ Pa}$

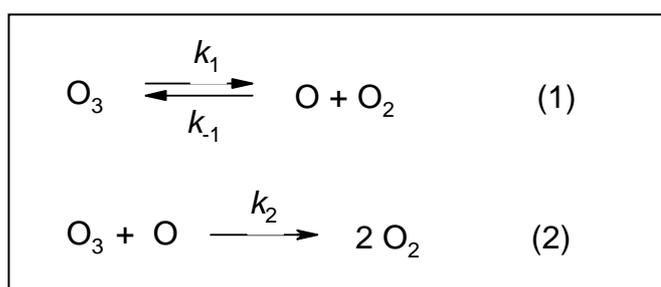
PROBLEM 7**Kinetic Behaviour of Ozone**

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,



One of the proposed mechanisms is expressed as



where k_1 , k_{-1} , and k_2 are the rate constants.

7.1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3 , O_2 , and O at time t , assuming step 2 is irreversible.

7.2 Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.

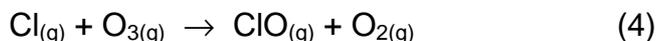
7.3 Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is $d[O]/dt = 0$, show that the rate equation is:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \rightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:



7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:



Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ mol^{-1} , while the activation energy for the reaction without the presence of catalyst is 14.0 kJ mol^{-1} . Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C . Assume the frequency factor is the same for each reaction.

SOLUTION

$$\begin{aligned} 7.1 \quad -\frac{d[\text{O}_3]}{dt} &= k_1 [\text{O}_3] - k_{-1} [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] \\ -\frac{d[\text{O}_2]}{dt} &= -k_1 [\text{O}_3] + k_{-1} [\text{O}][\text{O}_2] - 2k_2 [\text{O}_3][\text{O}] \\ -\frac{d[\text{O}]}{dt} &= -k_1 [\text{O}_3] + k_{-1} [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] \end{aligned}$$

7.2 Equilibrium constant K is expressed as

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]} = \frac{k_1}{k_{-1}}$$

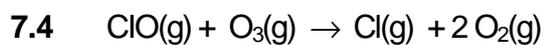
$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

$$-\frac{d[\text{O}_3]}{dt} = k_2[\text{O}_3][\text{O}] = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}$$

$$7.3 \quad -\frac{d[\text{O}]}{dt} = 0$$

$$-k_1 [\text{O}_3] + k_1 [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] = 0$$

$$\text{Thus } -\frac{d[\text{O}_3]}{dt} = 2k_2 [\text{O}_3][\text{O}] = \frac{2k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}$$



7.5 According to equation $k = A \exp(-E_a/RT)$,
the ratio of rate constants yields

$$\text{Ratio} = \exp[(14.0 - 2.1) \times 1000 / (8.314 \times 298)] = 122.$$

PROBLEM 8

Protein Folding

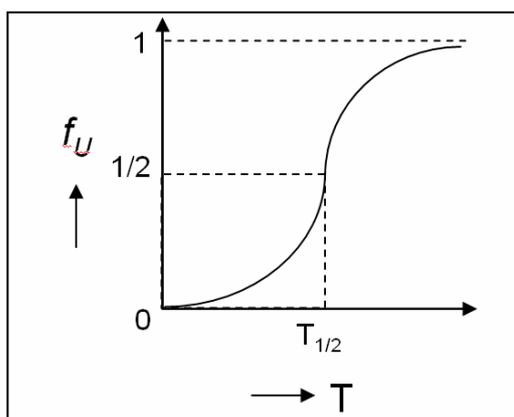
Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:



where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. $K(T)$ is the equilibrium constant for the process at absolute temperature T .

- 8.1** What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?
- 8.2** What is the standard free energy change of the process ($\Delta G^\circ(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.
- 8.3** If $(C_N)_{\text{eq}}$ and $(C_U)_{\text{eq}}$ denote the equilibrium concentrations of N and U in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{\text{eq}}/C$. Deduce an expression for f_U in terms of the equilibrium constant K . Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by $f_U = \frac{1}{2}$ and $T = T_{1/2}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{1/2}$, f_U increases above $\frac{1}{2}$, but at temperatures lower than $T_{1/2}$, f_U decreases below $\frac{1}{2}$.

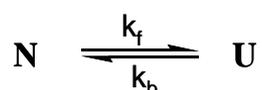
8.4 What is the sign of $\Delta G^\circ(T)$ at temperatures below and above $T_{1/2}$? Select your answer from the following choices.

- Negative both below and above $T_{1/2}$.
- Positive both below and above $T_{1/2}$.
- Positive below $T_{1/2}$, but negative above $T_{1/2}$.
- Negative below $T_{1/2}$, but positive above $T_{1/2}$.

8.5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{1/2}$ and (ii) decreases below $T_{1/2}$? Select your answer from the following choices.

- Decrease in both cases.
- Increase in both cases.
- Increases above $T_{1/2}$, but decreases below $T_{1/2}$.
- Decreases above $T_{1/2}$, but increases below $T_{1/2}$.

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:



where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8.6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b ?

8.7 Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{\text{eq}}$.

SOLUTION

8.1 Answer: 1

8.2 Answer: 0 kJ mol⁻¹

$$8.3 \quad f_U = \frac{C_U^{\text{eq}}}{C_N^{\text{eq}} + C_U^{\text{eq}}} = \frac{\frac{C_U^{\text{eq}}}{C_N^{\text{eq}}}}{1 + \frac{C_U^{\text{eq}}}{C_N^{\text{eq}}}} = \frac{K}{1 + K}$$

8.4 Correct answer is (c). Positive below $T_{1/2}$, but negative above $T_{1/2}$ 8.5 Correct answer is (d). Decreases above $T_{1/2}$, but increases below $T_{1/2}$.8.6 Answer: $K = k_f / k_b$

$$8.7 \quad \begin{aligned} dC_U/dt &= k_f C_N - k_b C_U \\ &= k_f (C - C_U) - k_b C_U = k_f C - k_f C_U - k_b C_U = k_f C - (k_f + k_b) C_U \end{aligned} \quad (1)$$

$$K = k_f / k_b = (C_U)_{\text{eq}} / (C_N)_{\text{eq}}$$

$$1 / K = k_b / k_f = (C_N)_{\text{eq}} / (C_U)_{\text{eq}}$$

$$\Rightarrow k_b / k_f + 1 = (C_N)_{\text{eq}} / (C_U)_{\text{eq}} + 1$$

$$\Rightarrow (k_b + k_f) / k_f = [(C_N)_{\text{eq}} + (C_U)_{\text{eq}}] / (C_U)_{\text{eq}}$$

$$\Rightarrow (k_b + k_f) / k_f = C / (C_U)_{\text{eq}}$$

$$C = [(k_b + k_f) (C_U)_{\text{eq}}] / k_f \quad (2)$$

Now substitute C obtained from eq (2) to eq (1).

$$\text{We get } k_f \{ [(k_b + k_f) (C_U)_{\text{eq}}] / k_f \} - (k_f + k_b) C_U$$

$$\Rightarrow [(k_b + k_f) (C_U)_{\text{eq}}] - (k_f + k_b) C_U$$

$$\Rightarrow - (k_f + k_b) [C_U - (C_U)_{\text{eq}}]$$

So we get

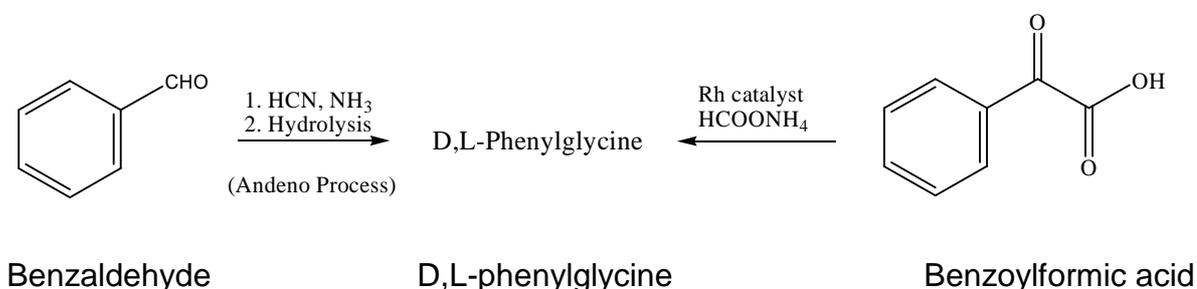
$$dC_U/dt = - (k_f + k_b) [C_U - (C_U)_{\text{eq}}]$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β -lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH₃ following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as *R*- and *S*-isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H₂O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H₂O at 25 °C. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

- To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighted (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass

on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (NOTE: irritant, do not contact with skin), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and 22 cm^3 of the pre-mixed solvents at ambient temperature.

- Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (NOTE: the solvent is air cooled, so there is no tap water running through the condenser.) The temperature of the water bath needs to be maintained in the range of 68 to 72 °C by adjusting the thermostat of the hot plate/stirrer.
- The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.
- Add 15 cm^3 of deionized water to the resulting mixture and stir for 10 minutes.
- Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 cm^3 each). For each washing, **break the aspirator pressure**, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.
- For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 °C for 1.5 hour.

During the drying period you can start working on Experiment 2 (analytical experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

- Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by ^1H NMR spectrum

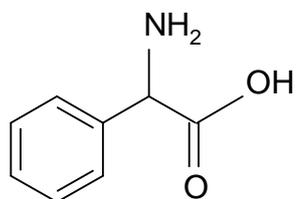
analysis. Turn in the product in a vial (**blue label** with ^1H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

Step 2. Enantiomeric Resolution of D,L-phenylglycine by (+)-Camphorsulfonic Acid [(+)-CSA]

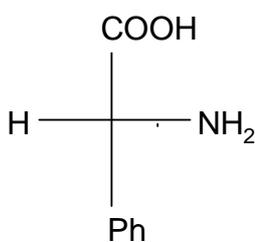
1. To a 25 cm³ round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 cm³) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.
2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.
3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 cm³ each).
4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).
5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (pink label labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant. The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

SOLUTION

1.4 Structural formula (A) and stereochemical formula (B) of the isolated phenylglycine:
(Task appeared in the answer sheet only.)



A



B

PROBLEM 2 (Practical)**Identification of Unknown Inorganic Samples**

Note

- (1) This practical exercise is a kind of "spot test". You can do it on the pallet or on a sheet of black film (for white precipitate).
- (2) Please check all items written in the equipment and reagent list.
- (3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.
- (4) The volume of each unknown solution is about 1.5 cm^3 (about 30 drops). No more reagents or samples will be provided.
- (5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.
- (6) Make sure the switch on the battery box is closed.
- (7) You will get 8 points for each correct identification.

Introduction

There are 12 unknown samples in your plastic bag □ 9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the List of Unknown Inorganic Samples carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 cm^3 solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol dm^{-3}).

The unknown samples are as follows:

HCl	H_2O_2	H_2SO_4	ZnCl_2	NH_4SCN
NaOH	Na_2CO_3	Na_2SO_3	BaCl_2	$\text{K}_4\text{Fe}(\text{CN})$

6

Note

- 1) Two unknown samples are duplicates.

2) The crystal water (. H₂O) is omitted in the formulas listed above.

2.1 Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

2.2 In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is ZnCl₂.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).

SOLUTION

2.2A $\text{Zn}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq}) \rightarrow \text{Cl}_2(\text{g})$ (anode) + Zn(s) (deposit on cathode)

2.2B $\text{Zn}(\text{s}) + 2 \text{H}^{+}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Zn}^{2+}(\text{aq})$

or

$\text{Zn}(\text{s}) + 2 \text{OH}^{-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + [\text{Zn}(\text{OH})_4]^{2-}(\text{aq})$

38th



International Chemistry Olympiad

**11 theoretical problems
3 practical problems**

THE THIRTY-EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD 2–11 JULY 2006, GYEONGSAN, KOREA

THEORETICAL PROBLEMS

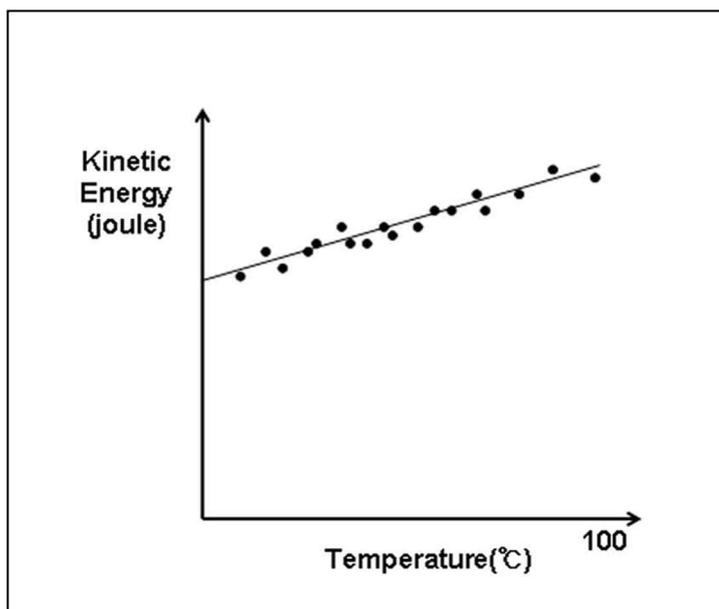
PROBLEM 1

Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27 °C, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm s⁻¹ at 27 °C. The density of a water droplet is 1.0 g cm⁻³.

- 1.1 Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27 °C. The volume of a sphere is given by $(4/3) \pi r^3$ where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0 °C and 100 °C as a function of temperature is found to be linear. Assume that it remains linear below 0 °C.



At thermal equilibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).

The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is $0.31 \text{ J g}^{-1} \text{ K}^{-1}$.

1.2. Calculate Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

SOLUTION

1.1 The mass of a water droplet:

$$m = V \rho = \left[\frac{4}{3} \pi r^3 \right] \rho = \frac{4}{3} \pi (0.5 \times 10^{-6} \text{ m})^3 (1.0 \text{ g cm}^{-3}) = 5.2 \times 10^{-16} \text{ kg}$$

Average kinetic energy at 27°C :

$$E_k = \frac{m v^2}{2} = \frac{(5.2 \times 10^{-16} \text{ kg}) \times (0.51 \times 10^{-2} \text{ m/s})^2}{2} = 6.9 \times 10^{-21} \text{ kg m}^2/\text{s}^2 = \underline{6.9 \times 10^{-21} \text{ J}}$$

1.2 The average kinetic energy of an argon atom is the same as that of a water droplet.

E_k becomes zero at -273°C .

From the linear relationship in the figure, $E_k = a T$ (absolute temperature) where a is the increase in kinetic energy of an argon atom per degree.

$$a = \frac{E_k}{T} = \frac{6.9 \times 10^{-21} \text{ J}}{(27 + 273) \text{ K}} = 2.3 \times 10^{-23} \text{ J K}^{-1}$$

S: specific heat of argon N: number of atoms in 1g of argon

$$S = 0.31 \text{ J g}^{-1} \text{ K}^{-1} = a \times N$$

$$N = \frac{S}{a} = \frac{0.31 \text{ J g}^{-1} \text{ K}^{-1}}{2.3 \times 10^{-23} \text{ J K}^{-1}} = 1.4 \times 10^{22} \text{ g}^{-1}$$

Avogadro's number (N_A): Number of argon atoms in 40 g of argon

$$N_A = 40 \text{ g mol}^{-1} \times 1.4 \times 10^{22} \text{ g}^{-1} = \underline{5.6 \times 10^{23} \text{ mol}^{-1}}$$

PROBLEM 2

Detection of hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

- 2.1** There are about 1×10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g cm^{-3} ; 3/4 hydrogen and 1/4 helium by mass). Estimate the number of stellar protons in the universe to one significant figure.

In the 1920s Cecilia Payne discovered by spectral analysis of starlight that hydrogen is the most abundant element in most stars.

- 2.2** The electronic transition of a hydrogen atom is governed by $\Delta E(n_i \rightarrow n_f) = -C(1/n_f^2 - 1/n_i^2)$, where n is principle quantum number, and C is a constant. For detection of the $\Delta E(3 \rightarrow 2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the $n = 2$ state. Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1 \rightarrow 2)$ transition.
- 2.3** According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $\lambda T = 2.9 \times 10^{-3} \text{ m K}$. Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the $n = 1 \rightarrow n = 2$ excitation of hydrogen.

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

- 2.4** Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7 K, can cause the hyperfine transition. Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.
- 2.5** Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different

gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the "proton". Fill in the blank.

SOLUTION

$$2.1 \quad \text{Mass of a typical star} = (4/3) \times (3.1) \times (7 \times 10^8 \text{ m})^3 \times (1.4 \times 10^6 \text{ g m}^{-3}) = 2 \times 10^{33} \text{ g}$$

$$\text{Mass of protons of a typical star} = (2 \times 10^{33} \text{ g}) \times (3/4 + 1/8) = 1.8 \times 10^{33} \text{ g}$$

$$\text{Number of protons of a typical star} = (1.8 \times 10^{33} \text{ g}) \times (6 \times 10^{23} \text{ g}^{-1}) = 1 \times 10^{57}$$

$$\text{Number of stellar protons in the universe} = (1 \times 10^{57}) \times (10^{23}) = \underline{1 \times 10^{80}}$$

$$2.2 \quad \Delta E(2 \rightarrow 3) = C(1/4 - 1/9) = 0.1389 C \quad \lambda(2 \rightarrow 3) = 656.3 \text{ nm}$$

$$\Delta E(1 \rightarrow 2) = C(1/1 - 1/4) = 0.75 C$$

$$\lambda(1 \rightarrow 2) = (656.3) \times (0.1389 / 0.75) = 121.5 \text{ nm}$$

$$2.3 \quad T = 2.9 \times 10^{-3} \text{ m K} / 1.215 \times 10^{-7} \text{ m} = 2.4 \times 10^4 \text{ K}$$

$$2.4 \quad \lambda = 3 \times 10^8 \text{ m} / 1.42 \times 10^9 = 0.21 \text{ m}$$

$$T = 2.9 \times 10^{-3} \text{ m K} / 0.21 \text{ m} = 0.014 \text{ K}$$



PROBLEM 3**Interstellar chemistry**

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either be desorbed from the surface or further react through surface migration with adsorbed H atoms to form CH₂, CH₃, etc.

Depending on how energetically a molecule “jumps” from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

- 3.1** Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1 \times 10^{12} \text{ s}^{-1}$ and $E_{\text{des}} = 12 \text{ kJ mol}^{-1}$.
- 3.2** Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1} , and the IIG is a sphere with a $0.1 \text{ }\mu\text{m}$ radius. Each migratory jump laterally advances the molecule by 0.3 nm . Show work and choose your answer from (a) – (e) below.
- (a) $t \leq 1 \text{ day}$ (b) $10 \text{ days} \leq t \leq 10^2 \text{ yr}$ (c) $10^3 \text{ yr} \leq t \leq 10^6 \text{ yr}$
 (d) $10^7 \text{ yr} \leq t \leq 10^{10} \text{ yr}$ (e) $t \geq 10^{11} \text{ yr}$
- 3.3** Consider the reaction of CO with H₂ to form H₂CO. The activation energy on a metal catalyst is 20 kJ mol^{-1} that is produced by formaldehyde at a rate of 1 molecule/s per site at 300 K . Estimate the rate of formaldehyde formation per site if the reaction takes place at 20 K .
- 3.4** Which is a set of all true statements? Circle one.

- (a) Most CH species are desorbed from the IIG surface before encountering other reactants by surface migration.

- (b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.
- (c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

(a) (b) (c) (a, b) (a, c) (b, c) (a, b, c)

SOLUTION

3.1 $k_{\text{des}} = A \exp(-E_{\text{des}}/RT) = (1 \times 10^{12} \text{ s}^{-1}) \times (5 \times 10^{-32}) = 5 \times 10^{-20} \text{ s}^{-1}$ at $T = 20 \text{ K}$
 surface residence time, $T_{\text{residence}} = 1 / k_{\text{des}} = 2 \times 10^{19} \text{ s} = \underline{6 \times 10^{11} \text{ yr}}$
 (full credit for $T_{\text{half-life}} = \ln 2 / k_{\text{des}} = 1 \times 10^{19} \text{ s} = 4 \times 10^{11} \text{ yr}$)
 residence time = $2 \times 10^{19} \text{ s}$

3.2 The distance to be traveled by a molecule: $x = \pi r = 300 \text{ nm}$.

$$k_{\text{mig}} = A \exp(-E_{\text{mig}}/RT) = (1 \times 10^{12} \text{ s}^{-1}) \times (2 \times 10^{-16}) = 2 \times 10^{-4} \text{ s}^{-1} \text{ at } T = 20 \text{ K}$$

Average time between migratory jumps, $T = 1 / k_{\text{mig}} = 5 \times 10^3 \text{ s}$

Time needed to move 300 nm = $(300 \text{ nm} / 0.3 \text{ nm}) \text{ jumps} \times (5 \times 10^3 \text{ s/jump}) =$
 $= 5 \times 10^6 \text{ s} = \underline{50 \text{ days}}$

The correct answer is (b).

(Full credit for the calculation using a random-walk model. In this case:

$$t = T(x/d)^2 = 5 \times 10^9 \text{ s} = 160 \text{ yr. The answer is still (b).)$$

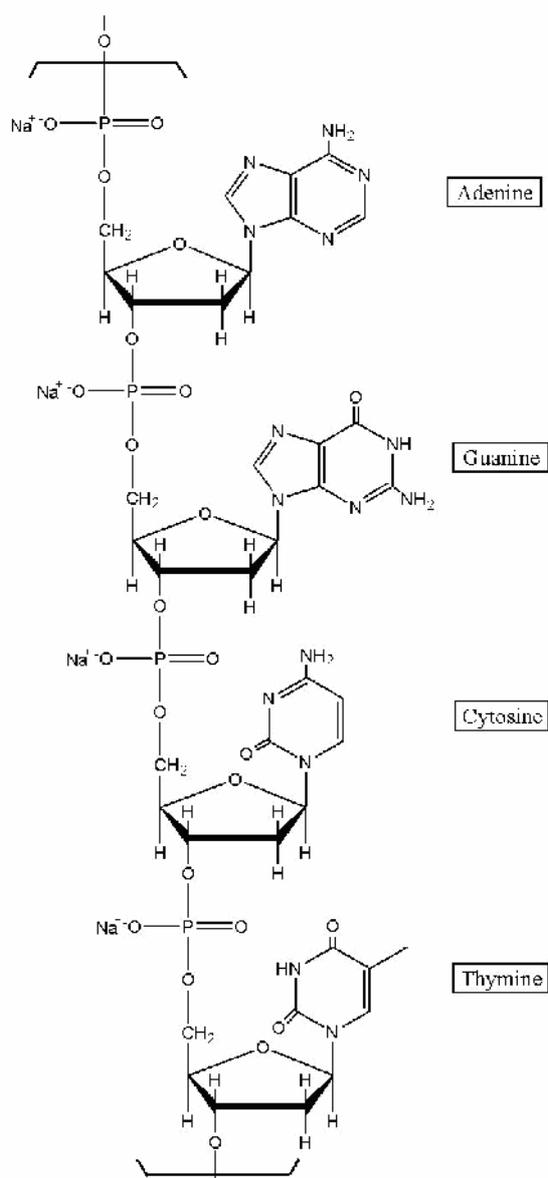
3.3 $k(20 \text{ K}) / k(300 \text{ K}) = \exp[(E/R)(1/T_1 - 1/T_2)] = e^{-112} = \sim 1 \times 10^{-49}$ for the given reaction
 The rate of formaldehyde production at 20 K = $\sim 1 \times 10^{-49}$ molecule/site/s =
 $= \sim 1 \times 10^{-42}$ molecule/site/yr

(The reaction will not occur at all during the age of the universe (1×10^{10} yr).)

3.4 The correct answer is (b, c).

PROBLEM 4**The Chemistry of DNA**

4.1 In 1944 Oswald Avery isolated a genetic material and showed by elemental analysis that it was a sodium salt of deoxyribonucleic acid. A segment of DNA with formula mass of 1323.72 is shown.



Assuming that equimolar amounts of the four bases are present in DNA, write the number of H atoms per P atom. Calculate (to 3 significant figures) the theoretical weight percentage of H expected upon elemental analysis of DNA.

4.2 Chargaff extracted the separated bases and determined their concentrations by measuring UV absorbance. The Beer-Lambert law was used to obtain the molar concentration. Chargaff discovered the following molar ratio for bases in DNA:

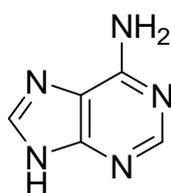
$$\begin{array}{ll} \text{adenine to guanine} = 1.43 & \text{thymine to cytosine} = 1.43 \\ \text{adenine to thymine} = 1.02 & \text{guanine to cytosine} = 1.02 \end{array}$$

Chargaff's discovery suggested that the bases might exist as pairs in DNA. Watson and Crick mentioned in their celebrated 1953 paper in *Nature*: "It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material."

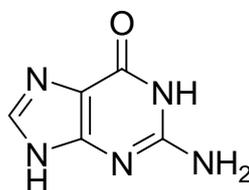
Draw structures of the specific pairing found in DNA. Indicate hydrogen bonds. Omit the sugar-phosphate backbone.

4.3 Mutation can occur through base pairings different from the above. Draw structures of any three alternative base pairs.

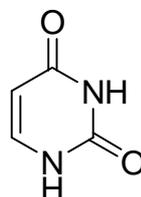
4.4 The plausibility of the formation of purine and pyrimidine bases in the prebiotic atmosphere of the Earth from HCN, NH₃, and H₂O has been demonstrated in the laboratory. Write the minimum number of HCN and H₂O molecules required for formation of the following compounds.



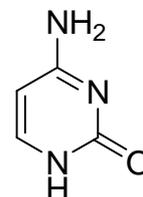
adenine



guanine



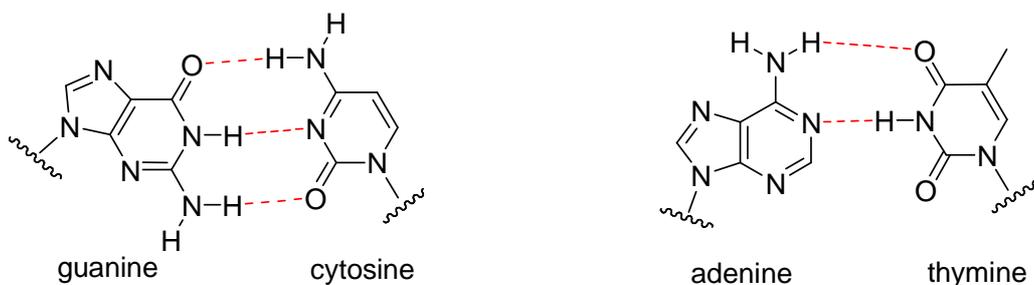
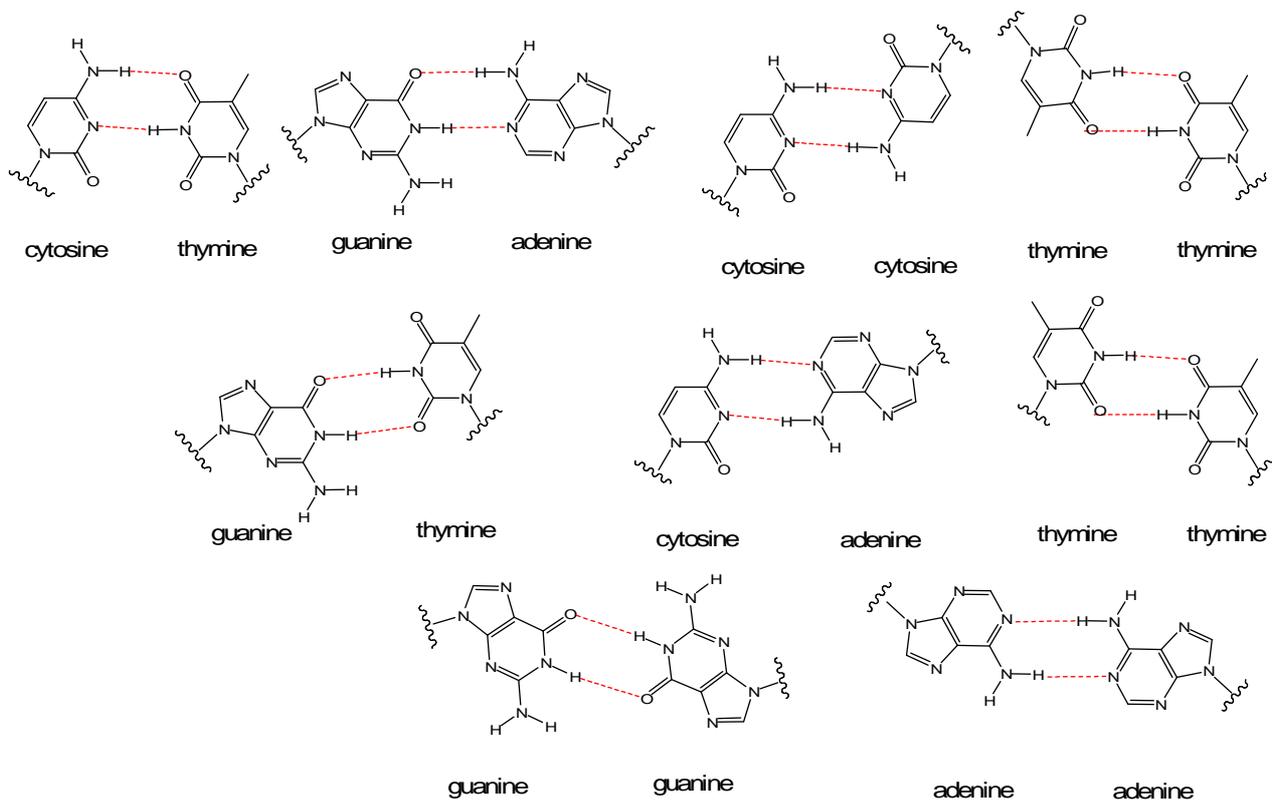
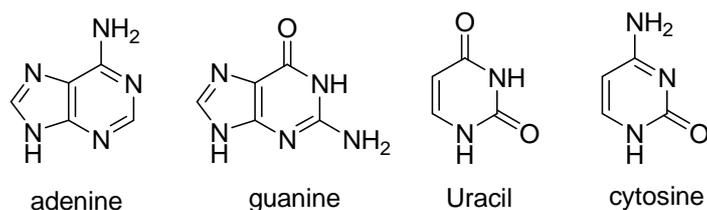
Uracil



cytosine

SOLUTION

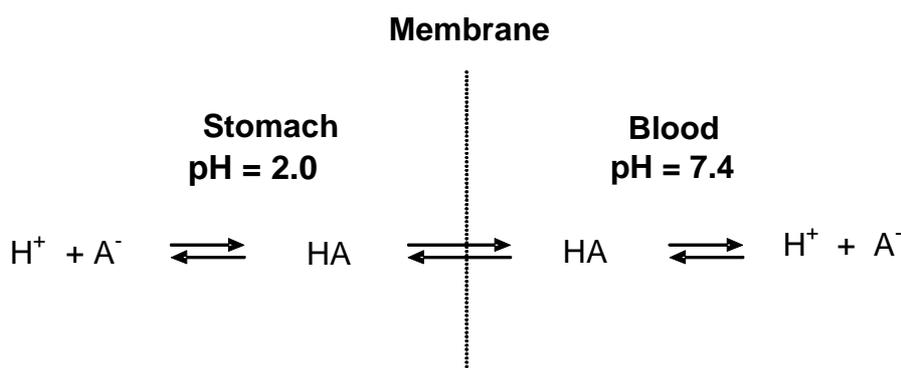
4.1	H	P
Number of atoms:	11.3	1
theoretical wt %:	3.43	

4.2

4.3

4.4


HCN	(5)	(5)	(4)	(4)
H ₂ O	(0)	(1)	(2)	(1)

PROBLEM 5**Acid-Base Chemistry**

- 5.1 Calculate $[H^+]$, $[OH^-]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in a 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0 \times 10^{-14}$, $K_2 = 1.2 \times 10^{-2}$ at 25 °C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.
- 5.2 Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm³ aqueous solution containing 3.48 cm³ of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm³, $M_r = 98.00$) ($pK_1 = 2.15$, $pK_2 = 7.20$, $pK_3 = 12.44$).
- 5.3 The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ($[HA] + [A^-]$) of aspirin (acetylsalicylic acid, $pK = 3.52$) in the blood to that in the stomach.

SOLUTION

- 5.1 1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$$[H_2SO_4] = 0$$

$$\text{2nd ionization: } [\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^-] = K_2 = 1.2 \times 10^{-2} \quad (1)$$

$$\text{Mass balance: } [\text{H}_2\text{SO}_4] + [\text{HSO}_4^-] + [\text{SO}_4^{2-}] = 1.0 \times 10^{-7} \quad (2)$$

$$\text{Charge balance: } [\text{H}^+] = [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-] \quad (3)$$

Degree of ionization is increased upon dilution.

$$[\text{H}_2\text{SO}_4] = 0$$

$$\text{Assume } [\text{H}^+]_{\text{H}_2\text{SO}_4} = 2 \times 10^{-7}$$

$$\text{From (1): } [\text{SO}_4^{2-}] / [\text{HSO}_4^-] = 6 \times 10^4 \quad (\text{2nd ionization is almost complete})$$

$$[\text{HSO}_4^-] = 0$$

$$\text{From (2): } [\text{SO}_4^{2-}] = 1.0 \times 10^{-7}$$

$$\text{From (3): } [\text{H}^+] = (2 \times 10^{-7}) + 10^{-14} / [\text{H}^+]$$

$$[\text{H}^+] = 2.4 \times 10^{-7} \quad (\text{pH} = 6.6)$$

$$[\text{OH}^-] = 1 \times 10^{-14} / (2.4 \times 10^{-7}) = 4.1 \times 10^{-8}$$

From (1):

$$[\text{HSO}_4^-] = [\text{H}^+] [\text{SO}_4^{2-}] / K_2 = (2.4 \times 10^{-7}) \times (1.0 \times 10^{-7}) / (1.2 \times 10^{-2}) = 2.0 \times 10^{-12}$$

Check charge balance:

$$2.4 \times 10^{-7} \approx (2.0 \times 10^{-12}) + 2(1.0 \times 10^{-7}) + (4.1 \times 10^{-8})$$

Check mass balance:

$$0 + 2.0 \times 10^{-12} + 1.0 \times 10^{-7} \approx 1.0 \times 10^{-7}$$

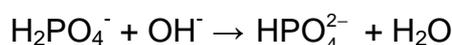
$$\mathbf{5.2} \quad n(\text{H}_3\text{PO}_4) = 0.85 \times 3.48 \text{ cm}^3 \times 1.69 \text{ g cm}^{-3} \times 1 \text{ mol} / 98.00 \text{ g} \times 1000 = 51.0 \text{ mmol}$$

The desired pH is above $\text{p}K_2$.

A 1:1 mixture of H_2PO_4^- and HPO_4^{2-} would have $\text{pH} = \text{p}K_2 = 7.20$.

If the pH is to be 7.40, there must be more HPO_4^{2-} than H_2PO_4^- .

We need to add NaOH to convert H_3PO_4 to H_2PO_4^- and to convert to the right amount of H_2PO_4^- to HPO_4^{2-} .



The volume of 0.80 NaOH needed to react with to convert H_3PO_4 to H_2PO_4^- is:
 $51.0 \text{ mmol} / 0.80 \text{ mol dm}^{-3} = 63.75 \text{ cm}^3$

To get pH of 7.40 we need:



Initial mmol	51.0	x	0
Final mmol	$51.0 - x$	0	x

$$pH = pK_2 + \log [\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$$

$$7.40 = 7.20 + \log \{x / (51.0 - x)\}; \quad x = 31.27 \text{ mmol}$$

The volume of NaOH needed to convert 31.27 mmol is:

$$31.27 \text{ mmol} / 0.80 \text{ mol dm}^{-3} = 39.09 \text{ cm}^3$$

$$\text{The total volume of NaOH} = 63.75 + 39.09 = 102.84 \text{ cm}^3 \approx 103 \text{ cm}^3$$

5.3 $pK = 3.52$

$$pH = pK_a + \log ([A^-] / [HA])$$

$$[A^-] / [HA] = 10^{(pH - pK_a)}$$

$$\text{In blood, } pH = 7.40, \quad [A^-] / [HA] = 10^{(7.40 - 3.52)} = 7586$$

$$\text{Total ASA} = 7586 + 1 = 7587$$

$$\text{In stomach, } pH = 2.00, \quad [A^-] / [HA] = 10^{(2.00 - 3.52)} = 3.02 \times 10^{-2}$$

$$\text{Total ASA} = 1 + 3.02 \times 10^{-2} = 1.03$$

$$\text{Ratio of total aspirin in blood to that in stomach} = 7587 / 1.03 = 7400$$

PROBLEM 6**Electrochemistry**

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

- 6.1** Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic. Write a balanced half-reaction for the reduction of water.
- 6.2** Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write a balanced half-reaction for the oxidation of water.
- 6.3** When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis. Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

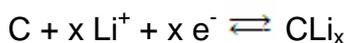
- 6.4** Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+ 0.340
Reduction of oxygen	– 2.710
Reduction of water	– 0.830
Reduction of sodium ion (Na^+)	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $\text{Cu}(\text{OH})_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25 °C. Note that $K_w = 1.00 \times 10^{-14}$ at 25 °C.

- 6.5 Precipitation of $\text{Cu}(\text{OH})_2$ begins at $\text{pH} = 4.84$. Determine the solubility product of $\text{Cu}(\text{OH})_2$.
- 6.6 Calculate the standard reduction potential for $\text{Cu}(\text{OH})_2(\text{s}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s}) + 2 \text{OH}^-$.
- 6.7 Calculate the electrode potential at $\text{pH} = 1.00$.

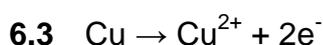
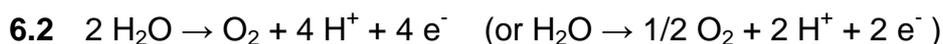
Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge/recharge cycles, the following reversible half-reactions occur.



The total amount of energy a battery can store, is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

- 6.8 Graphite has lithium intercalation sites between its layers. Assuming a maximum 6 : 1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.

SOLUTION



- 6.4 Reduction of sodium ion seldom takes place.

It has a highly negative reduction potential of -2.710 V .

Reduction potential for water to hydrogen is negative (water is very stable).

But, it is not as negative as that for sodium ion. It is -0.830 V.

Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.

In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.

Reduction potential for hydrogen ion is defined as 0.000 V.

Reduction of oxygen	_____	-2.710
Reduction of water	_____	-0.830
Reduction of sodium ion (Na^+)	_____	0.000
Reduction of hydrogen ion	_____	+1.230

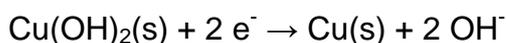
6.5 $pOH = 14.00 - 4.84 = 9.16$

$$[OH^-] = 6.92 \times 10^{-10}$$

$$K_{sp} = [Cu^{2+}] [OH^-]^2 = 0.100 \times (6.92 \times 10^{-10})^2 = 4.79 \times 10^{-20}$$

6.6 $E = E^\circ(Cu^{2+}/Cu) + (0.0592/2) \log [Cu^{2+}] = +0.340 + (0.0592/2) \log [Cu^{2+}] =$
 $= +0.340 + (0.0592/2) \log (K_{sp} / [OH^-]^2)$
 $= +0.340 + (0.0592/2) \log K_{sp} - (0.0592/2) \log [OH^-]^2$
 $= +0.340 + (0.0592/2) \log K_{sp} - 0.0592 \log [OH^-],$

By definition, the standard potential for



is the potential where $[OH^-] = 1.00$.

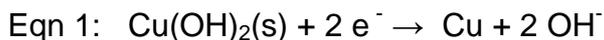
$$E = E^\circ(Cu(OH)_2/Cu) = +0.340 + (0.0592/2) \log K_{sp}$$

$$= +0.340 + (0.0592/2) \log (4.79 \times 10^{-20})$$

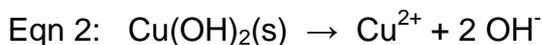
$$= +0.340 - 0.572$$

$$= -0.232 \text{ V}$$

One may solve this problem as follows.



$$E_+^{\circ} = E^{\circ}(\text{Cu(OH)}_2 / \text{Cu}) = ?$$



$$E^{\circ} = (0.05916 / n) \log K_{\text{sp}} = (0.05916 / 2) \log(4.79 \times 10^{-20}) = -0.5715 \text{ V}$$



$$E_-^{\circ} = E_+^{\circ} - E^{\circ} = E^{\circ}(\text{Cu}^{2+} / \text{Cu}) = 0.34 \text{ V}$$

$$\text{Therefore, } E_+^{\circ} = E_-^{\circ} + E^{\circ} = +0.34 + (-0.5715) = -0.232 \text{ V}$$

6.7 Below $pH = 4.84$, there is no effect of Cu(OH)_2 because of no precipitation.

Therefore,

$$\begin{aligned} E = E(\text{Cu}^{2+} / \text{Cu}) &= +0.340 + (0.0592 / 2) \log [\text{Cu}^{2+}] = \\ &= +0.340 + (0.0592 / 2) \log 0.100 = +0.340 - 0.0296 = +0.310 \text{ V} \end{aligned}$$

6.8 1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge $96487 \times 0.0139 = 1340$ coulombs.

$$1340 \text{ coulombs} / \text{g} = 1340 \text{ A sec} / \text{g} = 1340 \times 1000 \text{ mA} \times (1 / 3600) \text{ h} =$$

$$= 372 \text{ mAh} / \text{g}$$

PROBLEM 7**Hydrogen Economy**

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7.1 Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, estimate the density of hydrogen in the cylinder in kg m⁻³.

7.2 Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. $\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] = -286 \text{ kJ/mol}$, $\Delta H_f^\circ [\text{CO}_2(\text{g})] = -394 \text{ kJ/mol}$.

7.3 Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by $[1 - T_{\text{cold}}/T_{\text{hot}}]$.

$$S_{298}^\circ[\text{H}_2(\text{g})] = 131 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{298}^\circ[\text{O}_2(\text{g})] = 205 \text{ J mol}^{-1} \text{ K}^{-1}$$

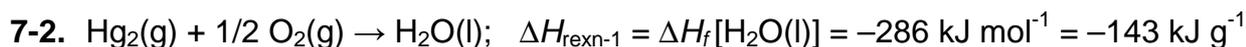
$$S_{298}^\circ[\text{H}_2\text{O}(\text{l})] = 70 \text{ J mol}^{-1} \text{ K}^{-1}$$

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

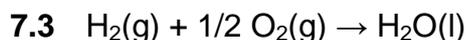
SOLUTION

$$7.1 \quad \frac{n}{V} = \frac{p}{RT} = \frac{80 \times 10^6 \text{ Pa}}{8,314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 32 \text{ kmol m}^{-3}$$

$$\rho = \frac{m}{V} = 32 \text{ kmol m}^{-3} \times 2 \text{ kg kmol}^{-1} = 64 \text{ kg m}^{-3}$$



$$\frac{(-\Delta H_{\text{rexn-1}})}{(-\Delta H_{\text{rexn-2}})} = 4.3 \quad \text{or} \quad \frac{(-\Delta H_{\text{rexn-2}})}{(-\Delta H_{\text{rexn-1}})} = 0.23$$



$$\Delta H_c = -286 \text{ kJ mol}^{-1} = -143 \text{ kJ g}^{-1} = -143 \times 10^3 \text{ kJ kg}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_c = 70 - 131 - 205/2 = -163.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_c = -286 \text{ kJ mol}^{-1} + 298 \text{ K} \times 163.5 \text{ J mol}^{-1} \text{ K}^{-1} = -237 \text{ kJ mol}^{-1} = -1.2 \times 10^5 \text{ kJ kg}^{-1}$$

(a) electric motor: $W_{\text{max}} = \Delta G_c \times 1 \text{ kg} = -1.2 \times 10^5 \text{ kJ}$

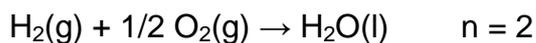
(b) heat engine: $W_{\text{max}} = \text{efficiency} \times \Delta H_c$
 $= (1 - 298 / 573) \times (-143 \times 10^3 \text{ kJ}) = -6.9 \times 10^4 \text{ kJ}$

$$119 \times 10^3 \text{ kJ} = 1 \text{ W} \times t(\text{sec})$$

$$t = 1.2 \times 10^8 \text{ s} = 3.3 \times 10^4 \text{ h} = 1.4 \times 10^3 \text{ days} = 46 \text{ month} = 3.8 \text{ yr}$$

$$\Delta G = -nFE \quad n = \text{number of electrons involved in the reaction}$$

$$F = 96.5 \text{ kC mol}^{-1}$$



$$E = \frac{-\Delta G}{nF} = \frac{237 \text{ kJ mol}^{-1}}{2 \times 96.5 \text{ kC mol}^{-1}} = 1.23 \text{ V}$$

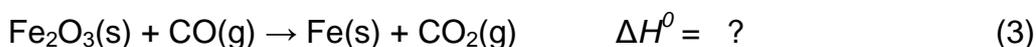
$$I = \frac{W}{E} = 0.81 \text{ A}$$

PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

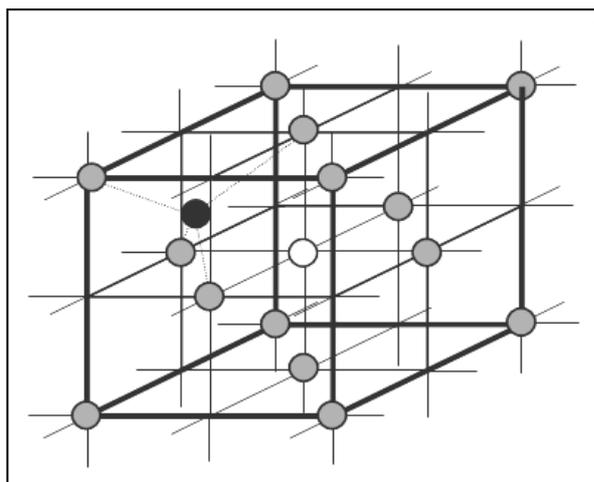


8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(\text{Fe}_2\text{O}_3\text{(s)}) = -824.2 \text{ kJ mol}^{-1}$,
 $S^\circ(\text{J mol}^{-1} \text{ K}^{-1})$: Fe(s) = 27.28, Fe₂O₃(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO₂(g) = 213.74

In the manufacture of celadon pottery, Fe₂O₃ is partially reduced in a charcoal kiln to mixed oxides of Fe₃O₄ and FeO. The amount of the different oxides seems to be related to the “mystic” color of celadon ceramics. Fe₃O₄ (magnetite) itself is a mixed oxide containing Fe²⁺ and Fe³⁺ ions and belongs to a group of compounds with a general formula of AB₂O₄. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.





- 8.3** How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

- 8.4** What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4 ?
- 8.5** Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

- 8.1** (1): C (2): C (3): CO

8.2 Balanced equation (3): $Fe_2O_3(s) + 3 CO(g) \rightarrow 2 Fe(s) + 3 CO_2(g)$



From (1) and (2):

$$\Delta H_f^{\circ}(CO(g)) = (1/2) \{172.46 + (-393.51)\} = -110.525 \text{ kJ}$$

$$\Delta H_f^0(\text{Fe}_2\text{O}_3) = -824.2 \text{ kJ}$$

$$\begin{aligned}\Delta H_{(3)}^0 &= 3 \times \Delta H_f^0(\text{CO}_2(\text{g})) - \Delta H_f^0(\text{Fe}_2\text{O}_3) - 3 \times \Delta H_f^0(\text{CO}(\text{g})) \\ &= [3 \times (-393.51)] - (-824.2) - [3 \times (-110.525)] = -24.8 \text{ kJ}\end{aligned}$$

$$\Delta S_{(3)}^0 = (2 \times 27.28) + (3 \times 213.74) - 87.4 - (3 \times 197.674) = 15.36 \text{ J K}^{-1}$$

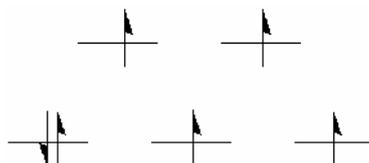
$$\begin{aligned}\Delta G_{(3)}^0 &= \Delta H^0 - T\Delta S^0 = -24.8 \text{ kJ} - (15.36 \text{ J K}^{-1} \times 1 \text{ kJ} / 1000 \text{ J} \times 1473.15 \text{ K}) = \\ &= -47.43 \text{ kJ}\end{aligned}$$

$$K = e^{(-\Delta G^0/RT)} = e^{(47430 \text{ J} / (8.314 \text{ J K}^{-1} \times 1473.15 \text{ K}))} = 48$$

8.3 One AB_2O_4 unit has available 4 ($= 1 + (1/4 \times 12)$) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives $(1/8) \times 100 \% = 12.5 \%$ occupancy in available tetrahedral sites.

8.5

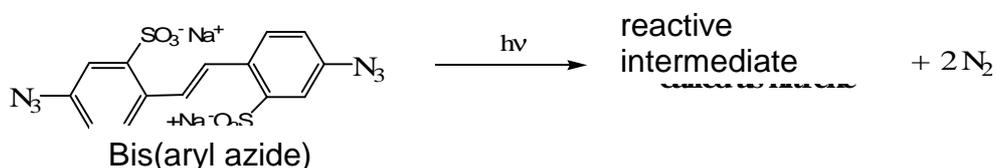


PROBLEM 9

Photolithographic process

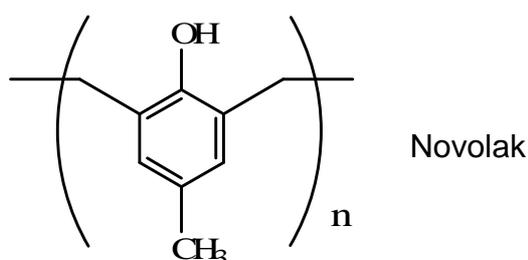
Photolithography is a process used in semiconductor device fabrication to transfer a pattern from a photomask to the surface of a substrate. In a typical photolithography process, light is projected, through a mask that defines a particular circuitry, onto a silicon wafer coated with a thin layer of photoresist.

The earliest photoresists were based on the photochemistry that generates a reactive intermediates from bis(aryl azide). Patterning becomes possible through the cross-linking reaction of the nitrenes generated from the azides.

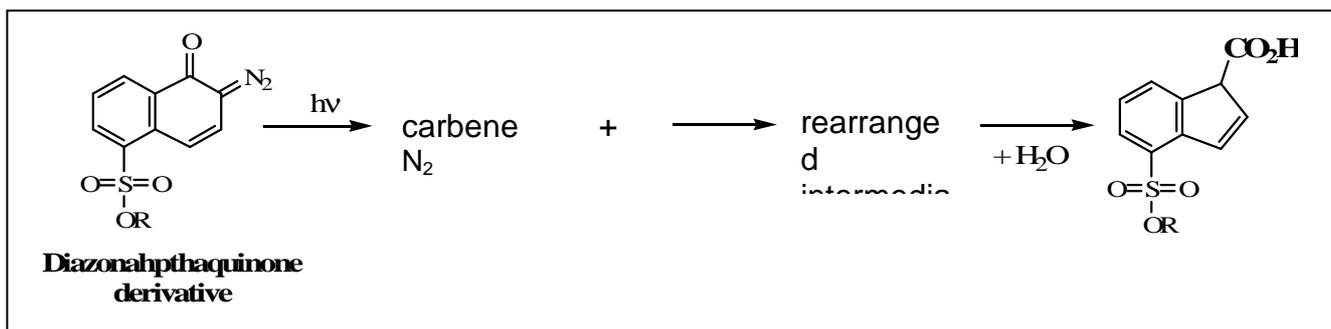


- 9.1** Draw two possible Lewis structures of $\text{CH}_3\text{-N}_3$, the simplest compound having the same active functional group of bis(aryl azide). Assign formal charges.
- 9.2** Draw the Lewis structure of nitrene expected from $\text{CH}_3\text{-N}$.
- 9.3** Draw the structures for two possible products, when this nitrene from $\text{CH}_3\text{-N}_3$ reacts with ethylene gas (CH_2CH_2).

Photoresists consisting of Novolak polymers, utilizes acid to change their solubility. The acid component can be produced photochemically from diazonaphthaquinone. In fact, “Novolaks” have been the representative “positive” photoresists of the modern microelectronic revolution.

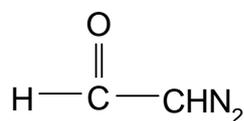


When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.



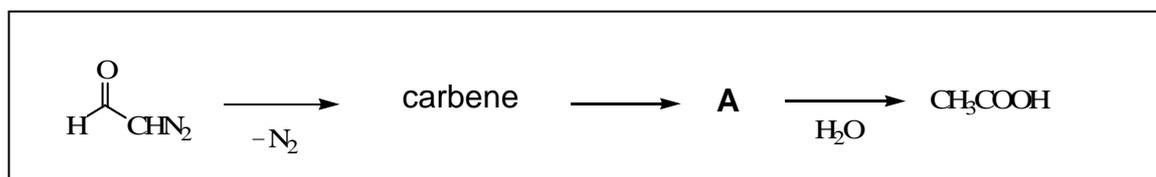
9.4 Draw three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.

Diazonaphthaquinone derivative

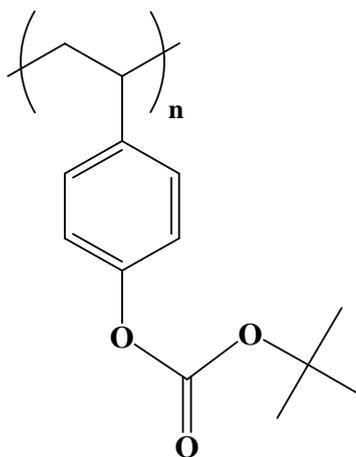


diazoacetaldehyde

9.5 Draw a Lewis structure of the rearranged intermediate, A (see below), generated from diazoacetaldehyde after losing N₂. A satisfies Lewis' octet rule and reacts with water to form acetic acid, CH₃COOH.

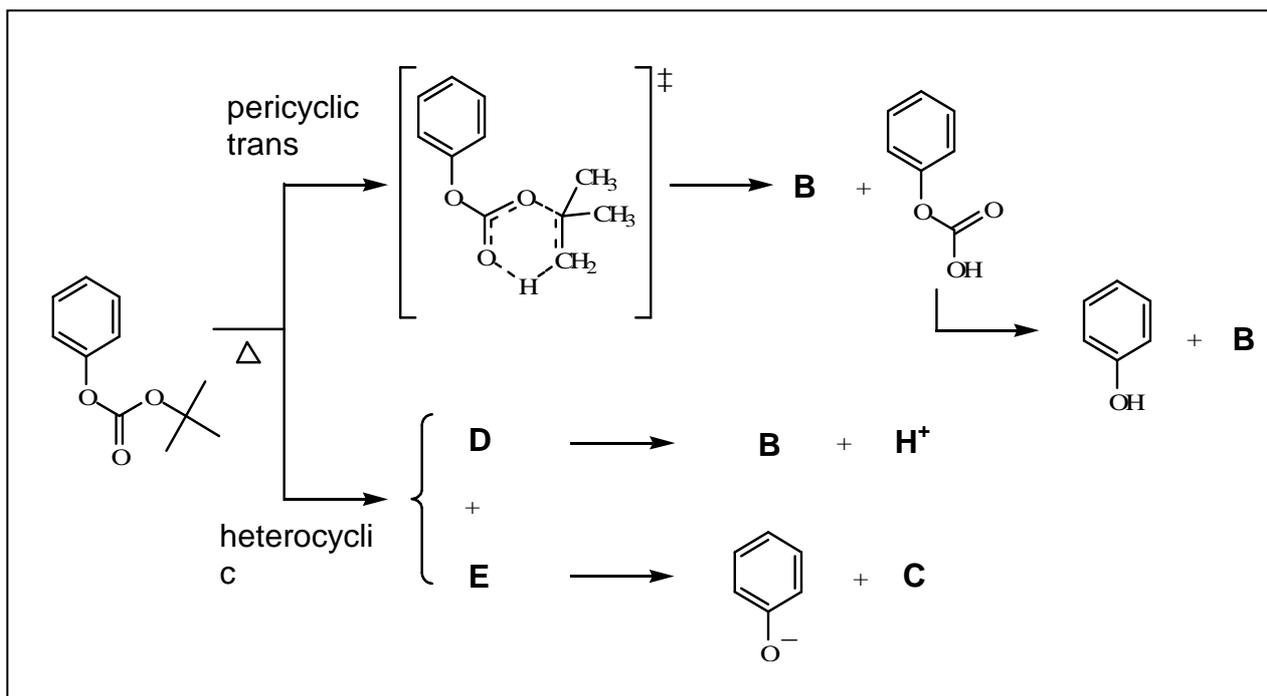


Advanced photoresists were invented in 1982 based on chemical amplification. The most popular chemical amplification for positive-tone involves the acid catalyzed deprotection of poly(*p*-hydroxystyrene) resin protected by various acid-sensitive protecting groups such as *t*-butyloxycarbonyl (*t*-BOC).

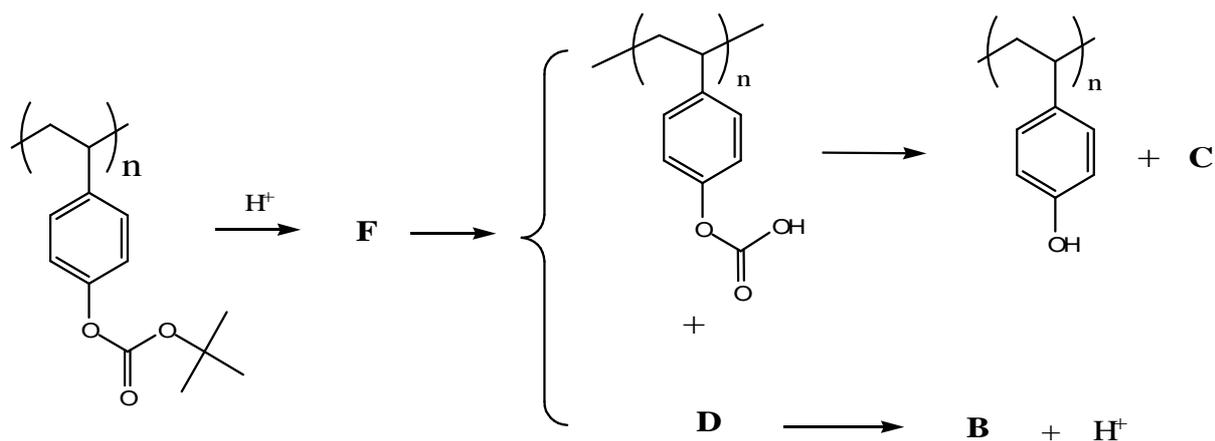


The thermal decomposition of carbonate ester itself normally occurs well above 150 °C.

9.6 Two plausible mechanisms have been suggested for this decomposition reaction having relatively high activation energy. Draw expected intermediates and products from this reaction.



9.7 In the presence of a trace amount of acid, the reaction temperature can be reduced to below 100 °C. Draw expected intermediate **F** from the following chemical amplification process based on using *t*-BOC.

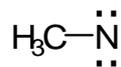


SOLUTION

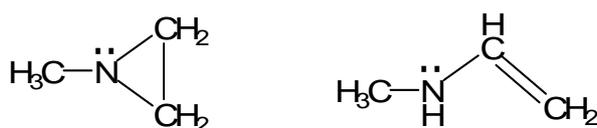
9.1



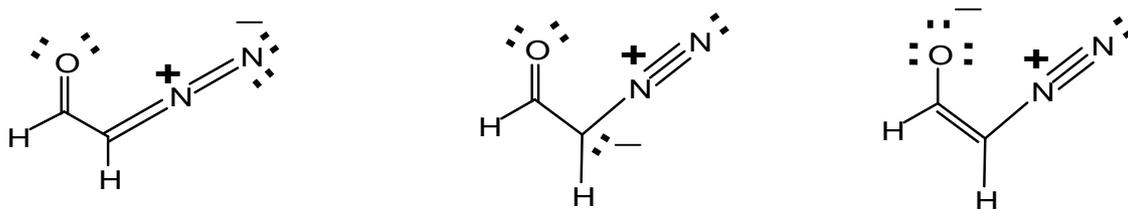
9.2



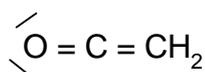
9.3



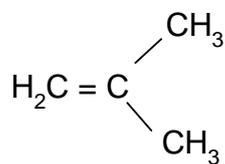
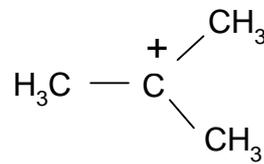
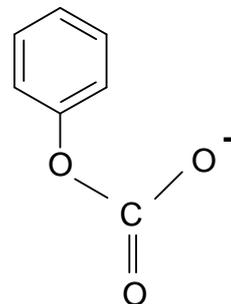
9.4



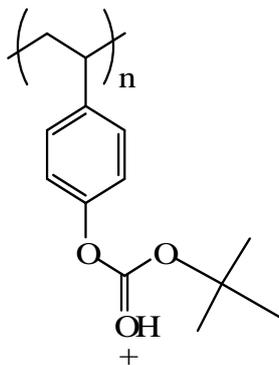
9.5

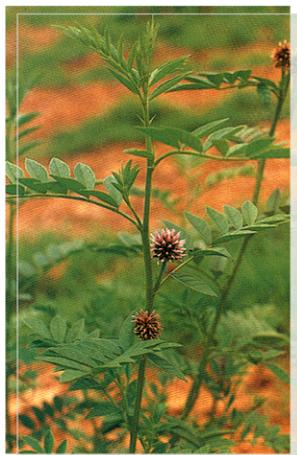


9.6

**B****C****D****E**

9.7

**F**

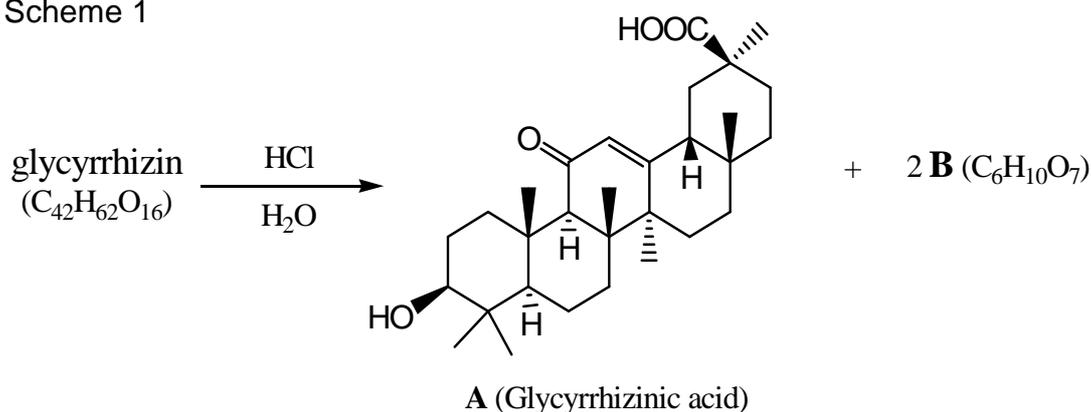
PROBLEM 10**Natural Products – Structural Analysis**Licorice (*Glycyrrhiza. Uralensis*)

Licorice Root

The flavour extracted from the licorice root is 50 – 150 times sweeter than table sugar. The most important and abundant compound responsible for the sweetness and medicinal effects of licorice is *glycyrrhizin* ($C_{42}H_{62}O_{16}$).

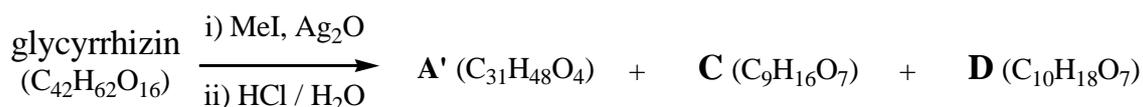
Glycyrrhizin requires three equivalents of NaOH to effect neutralization. When *glycyrrhizin* was subjected to acid hydrolysis, *Glycyrrhizinic acid* (**A** ($C_{30}H_{46}O_4$)) and **B** ($C_6H_{10}O_7$) were obtained in a 1:2 molar ratio (Scheme 1).

Scheme 1



When *glycyrrhizin* was methylated with methyl iodide (MeI) at every possible site before hydrolysis, hydrolysis produced **A'** (methyl glycyrrhizinate), **C** and **D** (Scheme 2). **B**, **C** and **D** exist as mixtures of anomers.

Scheme 2



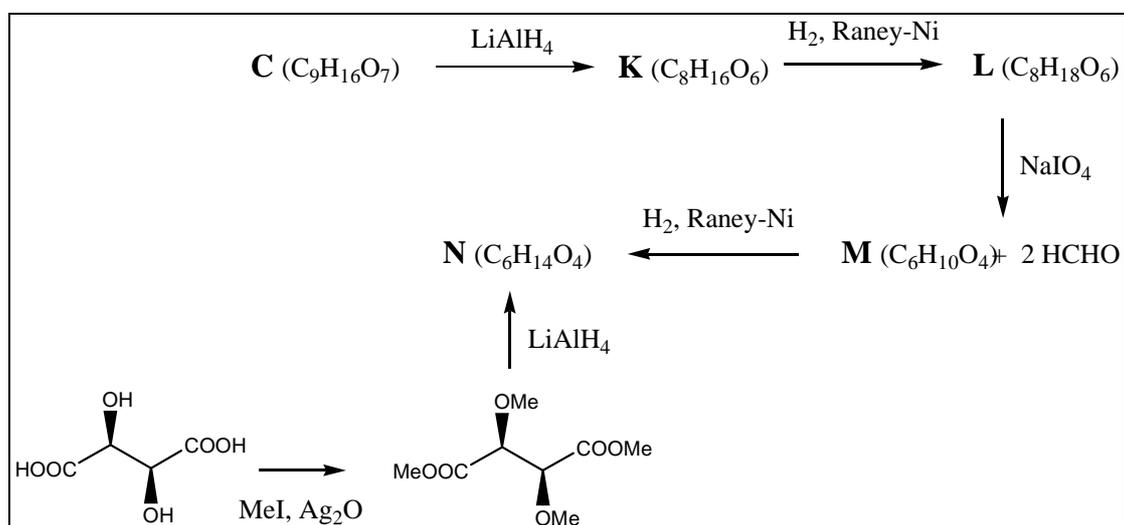
Methylation of **C** and **D** with MeI produced the same isomeric mixture of compounds, **J** (Scheme 3).

Scheme 3



C was reduced with LiAlH₄ to give **K**, and **L** was produced by the reduction of **K**. Oxidative cleavage of vicinal diol of **L** with NaIO₄ produced **M** and two equivalents of formaldehyde. Reduction of **M** produced **N**. The structure and stereochemistry of **N** was confirmed by the synthesis of **N** from D-(-)-tartaric acid through methylation followed by reduction (Scheme 4). A ¹H-NMR spectrum of **L** showed two distinct peaks for methyl groups. (There is no symmetry in **L**)

Scheme 4

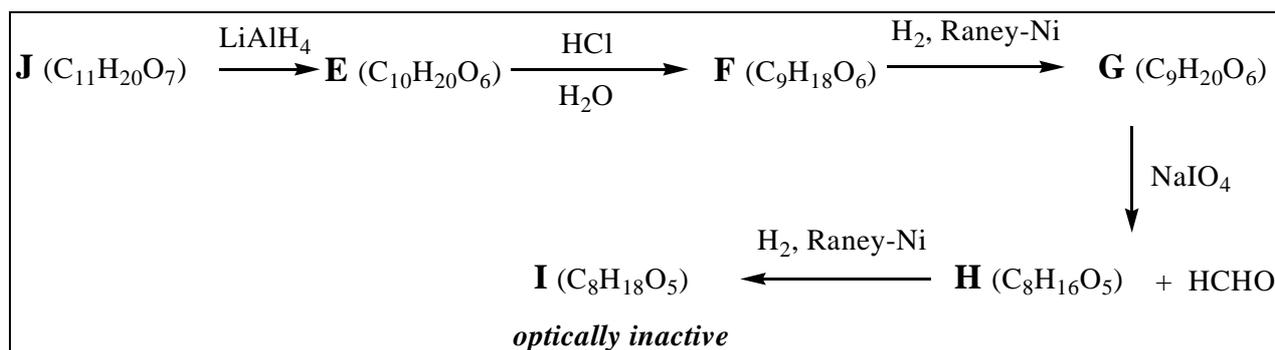


10.1 Complete structures for **L**, **M**, and **N** in the answer sheet.

10.2 How many structures for **C** are possible? Complete possible structures for **C**.

To determine the correct structure of **C**, following set of reactions were performed. **J** was reduced to **E**, and acid hydrolysis of **E** produced **F**. Reduction of **F** generated **G**, and **G** was oxidized with NaIO_4 to **H** with formation of one equivalent of formaldehyde. **I** was obtained from **H** through reduction. Among all compounds from **A** to **I**, only **I** was optically inactive (Scheme 5).

Scheme 5



10.3 Complete structures for **G** and **I**.

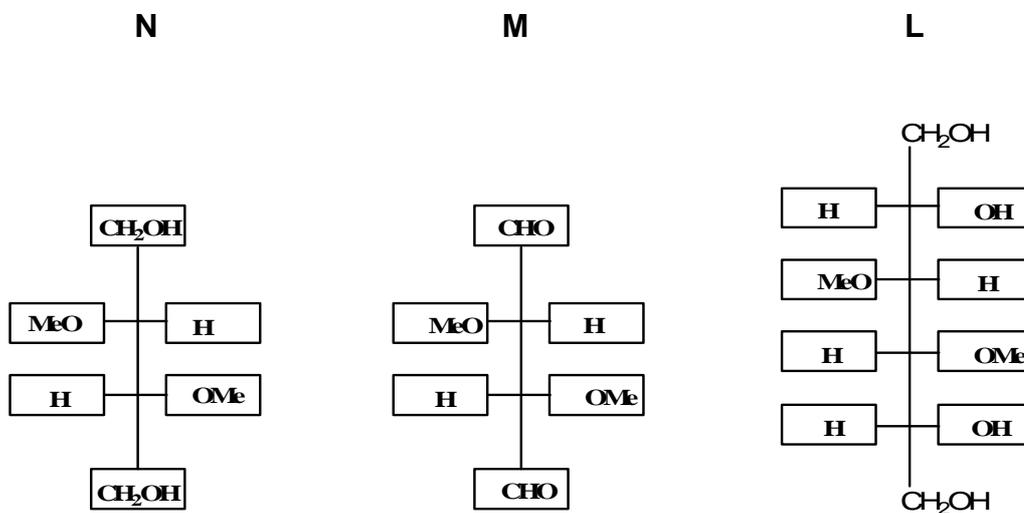
10.4 Which one is the correct structure for **C** among ones you have drawn in 10-2?

10.5 Complete structures for **B**, **D**, and **J**.

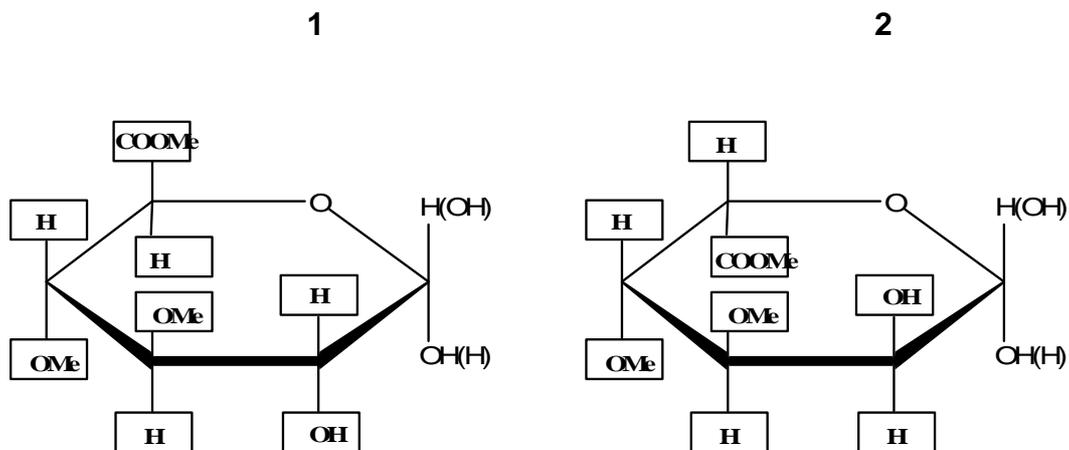
10.6 Complete the structure for Glycyrrhizin.

SOLUTION

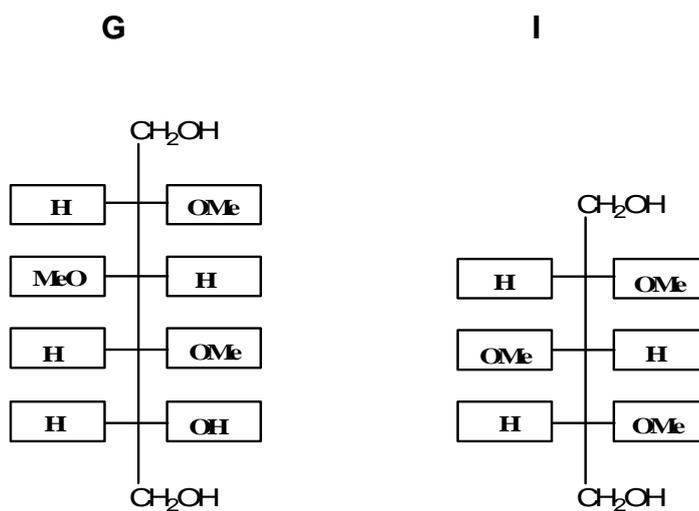
10.1



10.2 Number of possible structures 2



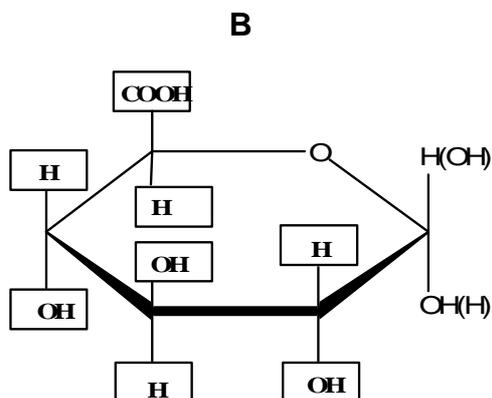
10.3



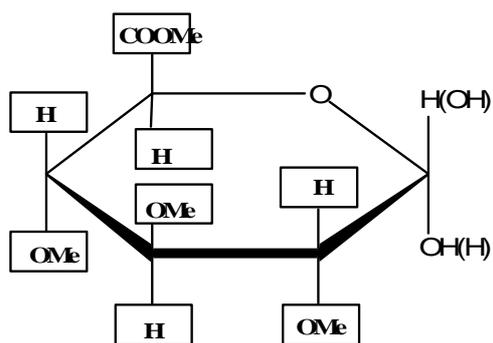
10.4

The correct structure for **C** from 10-2 is No. 1

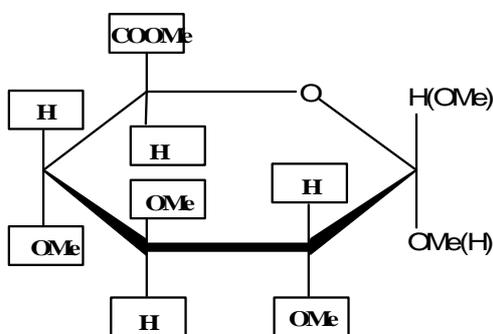
10.5



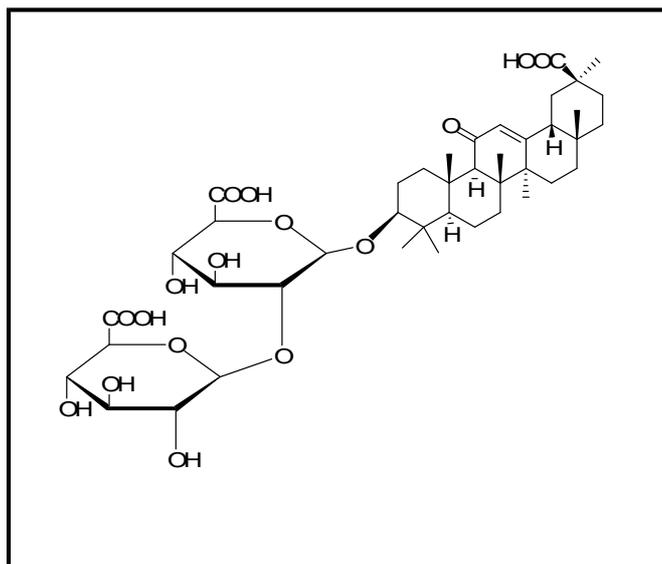
D



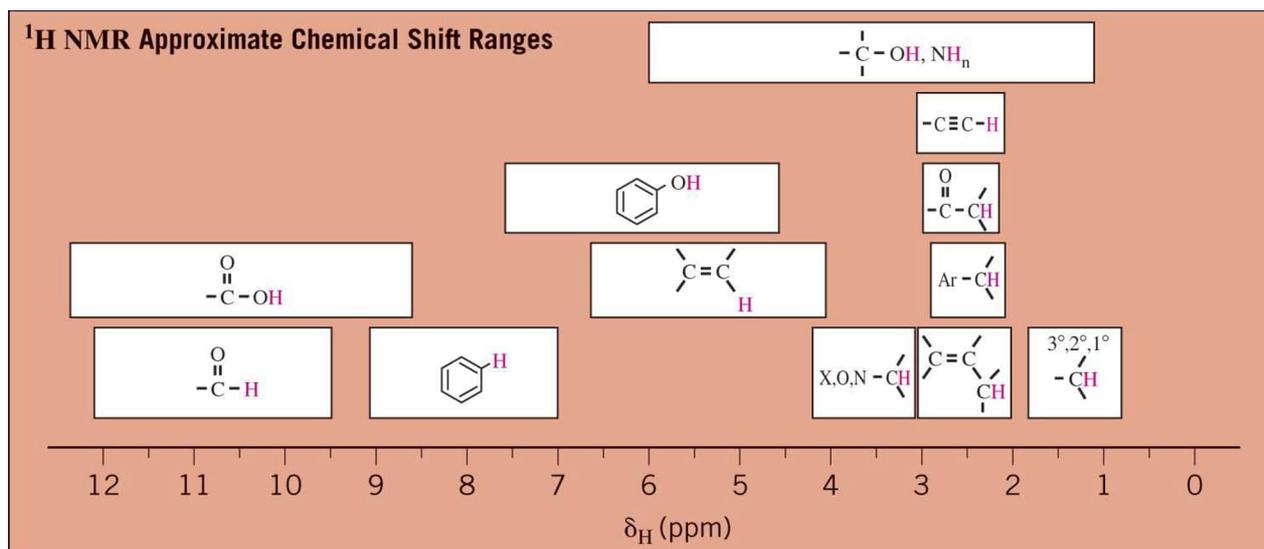
J



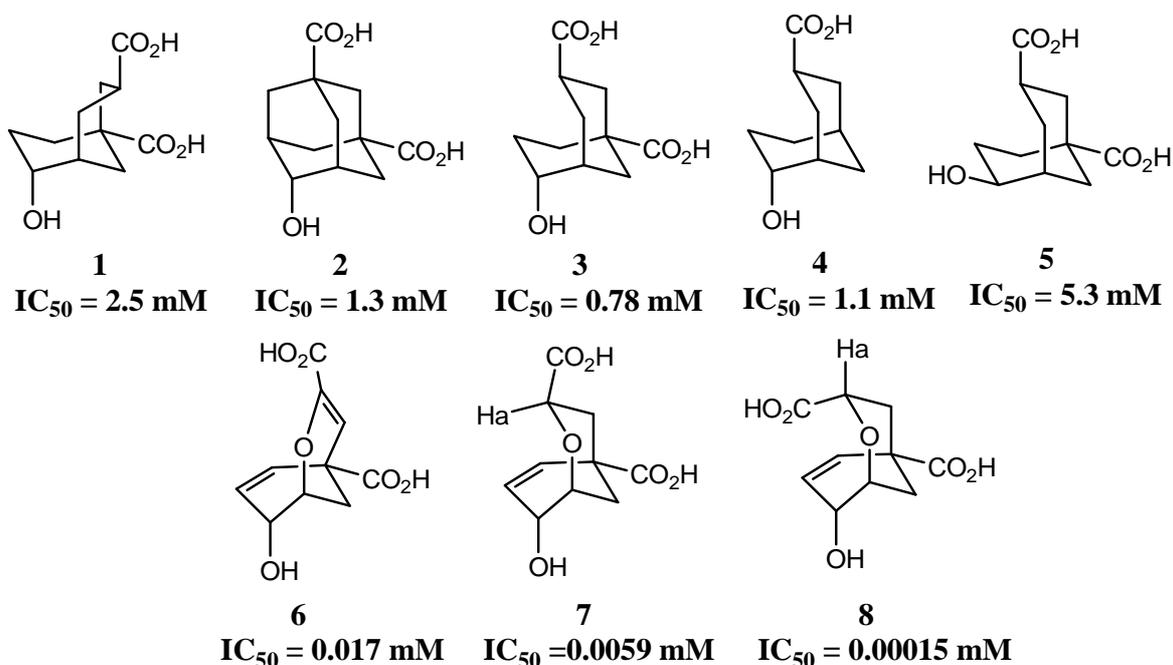
10.6



δ , chemical shift; H, integrals; d, doublet; dd, doublet of doublet; J, coupling constant; t, triplet; s, singlet



Chorismate mutase is believed to stabilize the transition state of Claisen rearrangement. Thus it is an interesting target for inhibitor design. Inhibitors, called transition state analog (TSA)s that resemble the transition state (TS, e.g., the species in brackets “[]” above) of the reaction are designed to occupy the active site. Several inhibitors were designed and synthesized, and among them eight turned out to be potent inhibitors of the enzyme. The lower is the IC_{50} (inhibitor concentration of 50 % of the enzymatic activity) value, the better is the inhibitor.



11.3 Choose all correct statements based on the structures and IC_{50} values of above inhibitors. Increase of factor 5 is considered to be important.

- (a) Configuration of the hydroxyl group plays an important role in the TS and inhibitor design.
- (b) The presence of both carboxylic groups is important in the TS and inhibitor design.
- (c) Transition state of the reaction contains two six-membered rings with one chair and one twist-boat conformation.
- (d) **7** and **8** can be distinguished on the basis of the $^1\text{H-NMR}$ of H_a .

11.4 Draw the transition state of the transformation of chorismic acid to prephenic acid based on the TSA structures and their IC_{50} values.

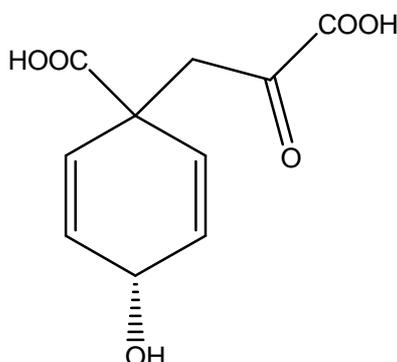
11.5 Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid 1.0×10^6 fold at $25\text{ }^\circ\text{C}$ by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at $25\text{ }^\circ\text{C}$.

$\Delta H^\ddagger_{\text{uncat}}$ is $86,900\text{ J mol}^{-1}$ for the thermal conversion of chorismic acid to prephenic acid. At what temperature will the rate of the *uncatalyzed* thermal conversion be the same as that of the *enzyme-catalyzed* conversion at $25\text{ }^\circ\text{C}$, assuming that $E_a = \Delta H^\ddagger$.

SOLUTION

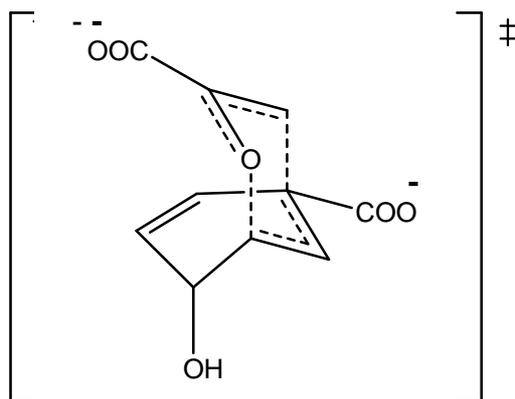
11.1 Hydroxyl group No. 3

11.2



11.3 Correct statements: (a), (c), (d).

11.4



Transition state

11.5 For the enzyme-catalyzed reaction, Arrhenius equation could be applied.

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A \exp(-E_{a, \text{cat}} / RT)}{A \exp(-E_{a, \text{uncat}} / RT)} = \exp[-\Delta E_{a, \text{cat-uncat}} / RT] =$$

$$= \frac{\exp(-\Delta E_{a, \text{cat-uncat}} (\text{J mol}^{-1}))}{2,480 \text{ J mol}^{-1}} = 1 \times 10^6$$

Therefore, $-\Delta E_{a, \text{cat-uncat}} = 34,300 \text{ J mol}^{-1}$

$$\frac{k_{\text{uncat}, T}}{k_{\text{uncat}, 298}} = \frac{A \exp(-\Delta H^{\ddagger}_{\text{uncat}} / RT)}{A \exp(-\Delta H^{\ddagger}_{\text{uncat}} / 298 R)} = \exp\left[\left(\frac{-\Delta H^{\ddagger}_{\text{uncat}}}{R}\right) \left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$\frac{k_{\text{uncat}, T}}{k_{\text{uncat}, 298}} = 13.8 = \exp\left[\left(\frac{-86900}{8.32}\right) \left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

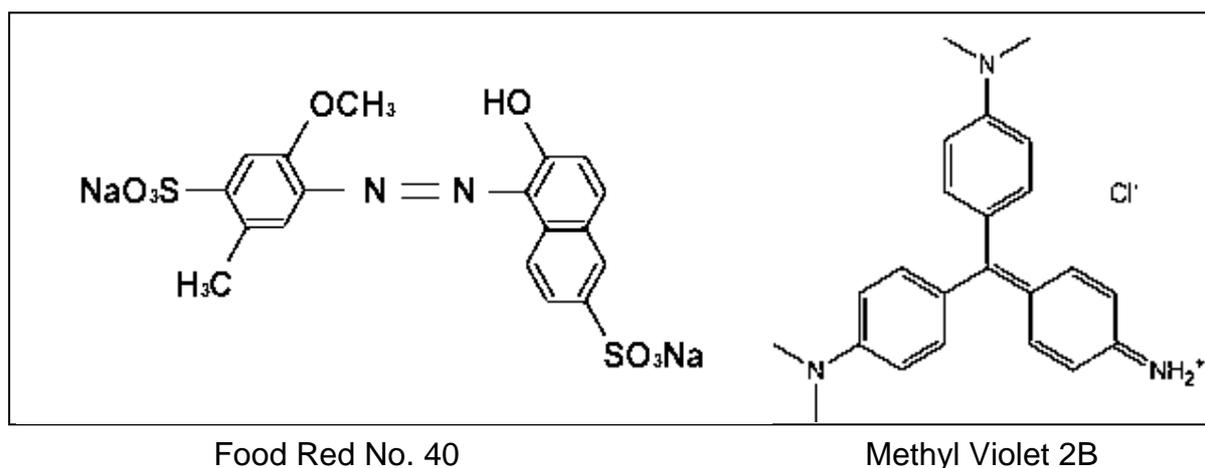
Therefore, $T = 491 \text{ K}$, or $218 \text{ }^{\circ}\text{C}$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Reverse-phase Chromatography: Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the non-polar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



1.1 Spectrophotometric Analysis of R and B in a Mixed Solution

- a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1.1).
- b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1.1.

- c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1.2 Chromatographic Separation Followed by Spectrophotometric Analysis

- a) Elute the cartridge with about 10 cm³ of Solution E using 10 cm³ syringe (Fig. C).
- b) Load 1.00 cm³ of solution MD onto the cartridge (Fig. D).
- c) Using 1 cm³ syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 cm³ volumetric flask. Repeat until the red compound is completely eluted and collected.
- d) Fill the flask to the 10 cm³ mark with Solution E and mix. Call this Solution F.
- e) Obtain the absorption spectrum of solution F as in Experiment 1.1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1.1 in red ink.
- f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1.2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.
- g) Report the concentration of R in the original Solution MD.
- h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.
-
-

PROBLEM 2 (Practical)**Reverse-phase Chromatography:****Acid-Base Titration of Acetic Acid and Salicylic Acid**

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

- a) Titrate 10 cm³ of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 cm³ of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.
- b) Standardize NaOH solution with 2.00 cm³ of the standard KHP (potassium hydrogen phthalate) solution (1.00 × 10⁻² M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.
- c) Withdraw 1.00 cm³ of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 cm³ of Solution MA.

2-2. Reverse-phase Separation and Titration

- a) Elute a new C-18 cartridge with about 10 cm³ of distilled water using 10 cm³ syringe.
- b) Load 1.00 cm³ of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).
- c) Elute with 1 cm³ of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 cm³ liquid in each tube.

- d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.
- e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.
- f) Calculate the mole percent of AA in solution MA.
-
-

PROBLEM 3 (Practical)

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

Procedure

Helpful Comments

- The weight of a spatula tip-full of a solid is about 15~20 mg.
- Wipe spatula cleanly with Kimwipe between uses.
- After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.
- To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 cm³ of CH₃CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 cm³ of 95 % EtOH. (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 cm³ of water.) Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulphuric acid and 95% ethanol (labelled as 2,4-DNPH).

Test 3: CAN test

Mix 3 cm³ of the cerium(IV) ammonium nitrate solution in dilute HNO₃ (labelled as CAN) with 3 cm³ of CH₃CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 cm³ of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm³ of water first, and then add 1 cm³ of CAN.) If there is a colour change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Bayer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm³ of CH₃CN. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 cm³ of water.) To the solution, slowly add five drops of the 0.5 % KMnO₄ solution, drop by drop while shaking.

Test 5: pH test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm³ of 95 % EtOH. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm³ of water). Measure the pH of the solution with pH paper.

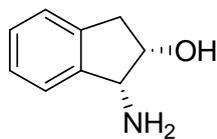
Test 6: Iron(III) chloride test

Take the solution from Test 5 and add five drops of a 2.5 % FeCl₃ solution.

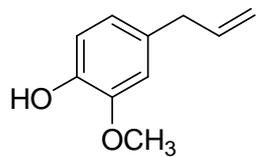
Results

1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.
2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

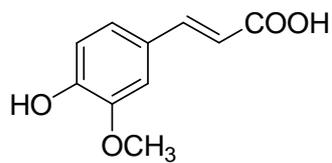
Possible Unknown Compounds (next page):



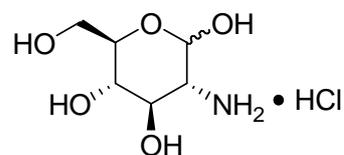
(A)



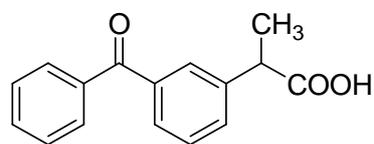
(E)



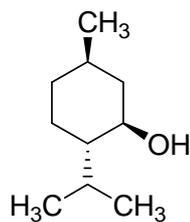
(F)



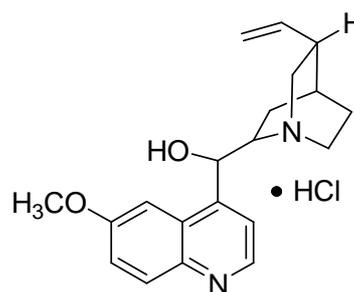
(G)



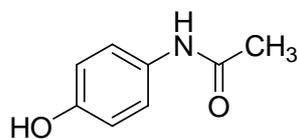
(K)



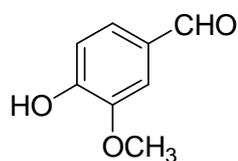
(M)



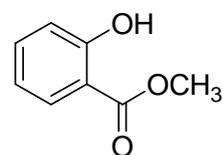
(Q)



(T)



(V)



(W)

39th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-NINTH INTERNATIONAL CHEMISTRY OLYMPIAD 15–24 JULY 2007, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

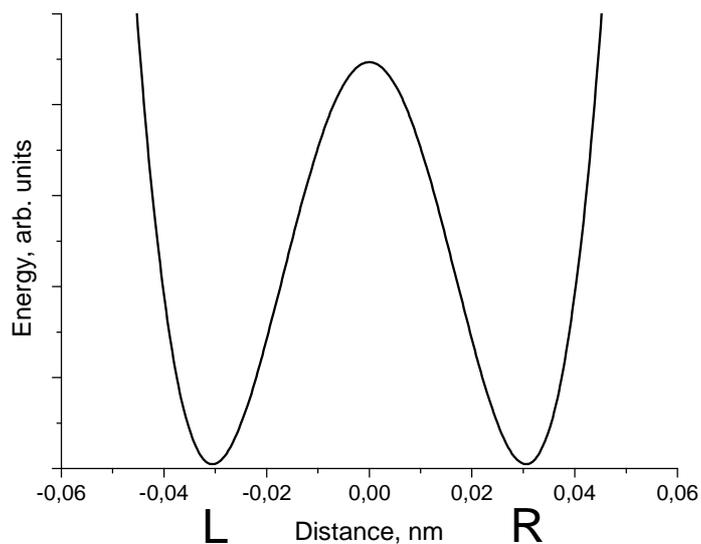
PROBLEM 1

Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

- 1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.
- 1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

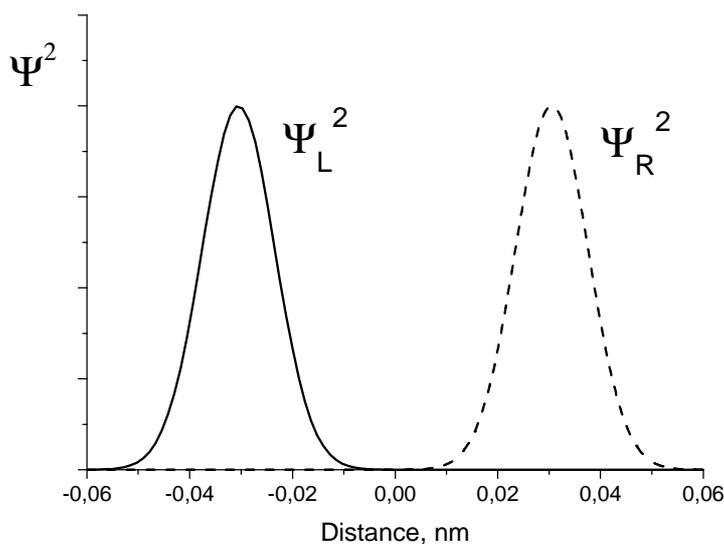


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48 \times 10^{11} \text{ s}^{-1}$. Probability density for a proton depends on time as follows:

$$\Psi^2(x, t) = \frac{1}{2} \left[\Psi_L^2(x) + \Psi_R^2(x) + (\Psi_L^2(x) - \Psi_R^2(x)) \cos(\omega t) \right],$$

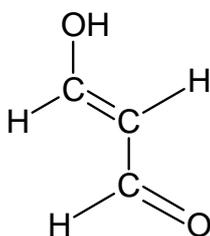
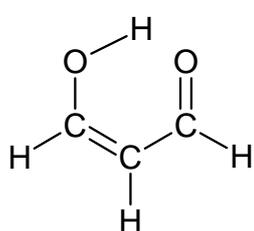
wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



- 1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.
- 1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$
- 1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?
- 1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in 1.6 and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

SOLUTION

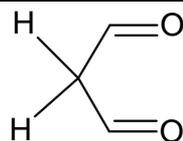
- 1.1 The structures of propanedial and two of its isomers:



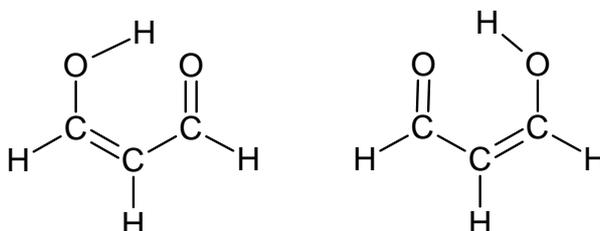
- 1.2 Acidic hydrogen atom is in CH_2 (in enol forms acidic hydrogen is in OH).
The stability of propanedial is caused by (one of the following answers had to be chosen):
- the stability of carbanion due to conjugation with two carbonyl groups,
 - weakness of C – H bond in a carbonyl group,
 - hydrogen bonds between two propanedial molecules.

The first answer is correct.

- 1.3 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



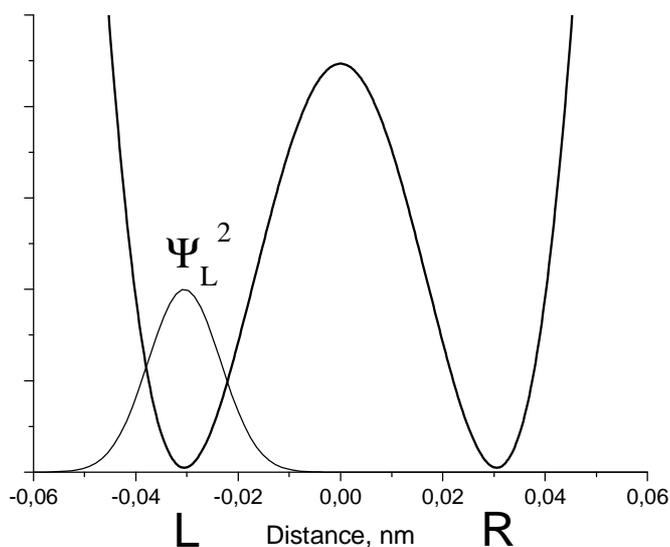
such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1.4 Expressions and plots of probability density

$$(a) \quad \Psi^2(x, 0) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x) + \Psi_L^2(x) - \Psi_R^2(x)] = \Psi_L^2(x)$$

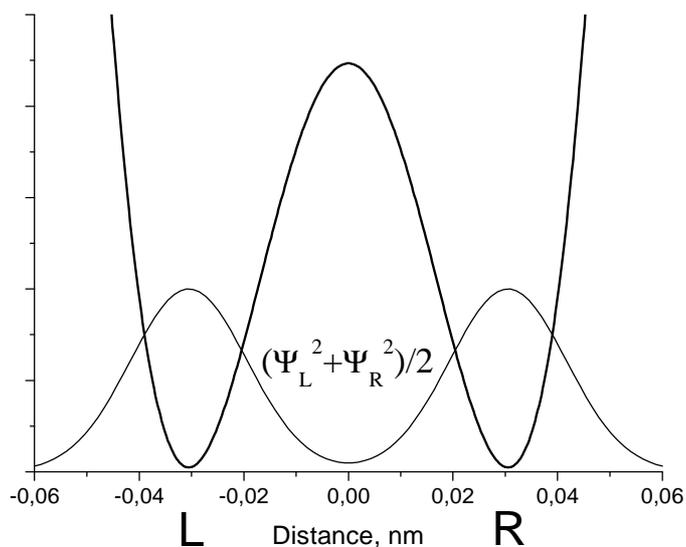
The probability density is concentrated in the left well:



(b) In the middle of the time interval

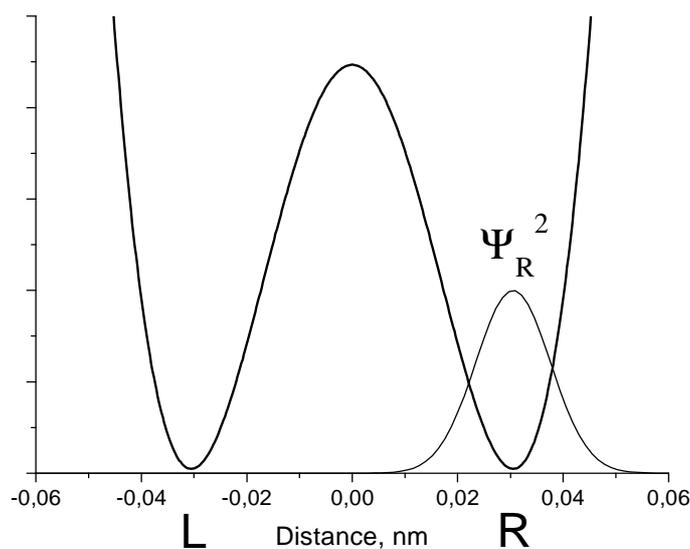
$$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x)]$$

The probability density has a symmetric form, a proton is delocalized between two wells:



$$(c) \quad \Psi^2\left(x, \frac{\pi}{\omega}\right) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x) - \Psi_L^2(x) + \Psi_R^2(x)] = \Psi_R^2(x)$$

The probability density is concentrated in the right well:



1.5 The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.6 The time of transfer from one well to another is $t = \pi / \omega$.

$$t = \frac{3.14}{6.48 \times 10^{11}} = 4.85 \times 10^{-12} \text{ s.}$$

The proton velocity:

$$v = \frac{0.06 \times 10^{-9}}{4.85 \times 10^{-12}} = 12 \text{ m s}^{-1}.$$

- 1.7** The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (0.06 nm will be also accepted).

The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta v = \frac{h}{2 m \Delta x} = \frac{1.055 \times 10^{-34}}{2 \times \frac{0.001}{6.02 \times 10^{23}} \times 0.03 \times 10^{-9}} \approx 1000 \text{ m s}^{-1}.$$

Comparing this uncertainty with the velocity 12 m s^{-1} we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

PROBLEM 2**Nanochemistry**

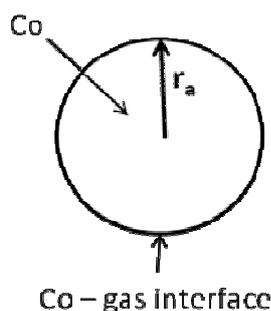
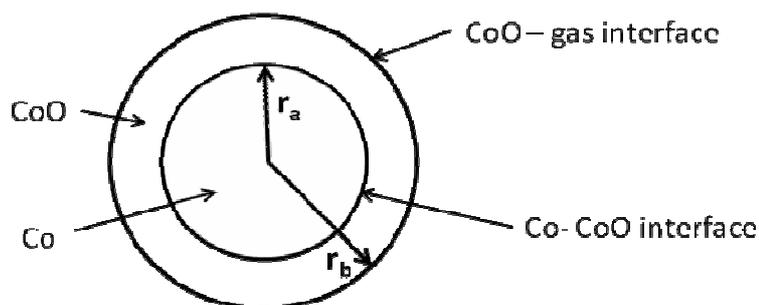
Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)



Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:



Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

**Fig. 1****Fig. 2**

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^{\circ}(r) = G^{\circ}(\text{bulk}) + \frac{2\sigma}{r} V$$

- 2.1** Calculate the standard Gibbs energy $\Delta_r G^{\circ}(1)$ and the equilibrium constant for the reaction (1) at $T = 500 \text{ K}$.
- 2.2** Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

- (a) 10^{-8} m ,
 (b) 10^{-9} m .

The surface tension at the Co-gas interface is 0.16 J m^{-2} . CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO , CH_4 , H_2 , H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is $p = 1$ bar, temperature is $T = 500$ K. The mole fraction of hydrogen (%) in the mixture is 0.15 %.

2.3 At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of

- (a) a bulk phase
- (b) spherical nanoparticles with $r_a = 1$ nm (Fig. 1).

2.4 What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:

- (a) to increase r_a ;
- (b) to decrease r_a ;
- (c) change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a , r_b , molar volumes as $V(\text{Co})$; $V(\text{CoO})$.

2.5 Write down the expression for the standard molar Gibbs function of CoO .

2.6 Write down the expression for the standard molar Gibbs function of Co .

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{in} - P_{ex} = \Delta P = \Delta P_1 + \Delta P_2 = 2 \frac{\sigma_1}{r_1} + 2 \frac{\sigma_2}{r_2}$$

r_i , σ_i are radius and surface tension at the spherical interface i , respectively.

2.7 Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1, r_a, r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a , r_b , $V(\text{Co})$; $V(\text{CoO})$ and $\Delta_r G^0(1)$.

2.8 When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, $r_a = r_b = r_0$, and $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. Assume that

$\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1, r_0)$ on r_0 ?

- 2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:
- increase r_0
 - decrease r_0
 - change of r_0 has no effect.

Reference data:

Substance	ρ , g cm ⁻³	$\Delta_f G_{500}^0$, kJ mol ⁻¹
Co (s)	8.90	
CoO (s)	5.68	-198.4
H ₂ O (gas)		-219.1

SOLUTION

- 2.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G_{500}^0(1) = \Delta G_{f,500}^0(\text{CoO}, \text{s}) - \Delta G_{f,500}^0(\text{H}_2\text{O}, \text{g}) = -198.4 + 219.1 = 20.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta_r G_{500}^0(1)}{RT}} = e^{-\frac{20700}{8.314 \times 500}} = 6.88 \times 10^{-3}$$

- 2.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\begin{aligned} \Delta_r G_{500}^0(1, r_a) &= G_{\text{bulk},500}^0(\text{CoO}, \text{s}) + G_{500}^0(\text{H}_2, \text{g}) - G_{500}^0(\text{H}_2\text{O}, \text{g}) - G_{\text{sph}}^0(\text{Co}) = \\ &= G_{500}^0(\text{CoO}, \text{s}) + G_{500}^0(\text{H}_2, \text{g}) - G_{500}^0(\text{H}_2\text{O}, \text{gas}) - \left(G_{500}^0(\text{Co}, \text{s}) + \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} \right) = \\ &= \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a}; \end{aligned}$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{1 \times 10^{-6} \times 59.0}{8.90} = 6.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$$\frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J mol}^{-1}$$

$\Delta_r G_{500}^0(1, r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ mol^{-1} , respectively.

The equilibrium constant is calculated from the equation

$$K(1, r_a) = \exp\left(-\frac{\Delta_r G_{500}^0(1, r_a)}{RT}\right)$$

$$K(1, r_a) = 7.22 \times 10^{-3}; \quad r_a = 10^{-8} \text{ m} \quad K(1, r_a) = 11.4 \times 10^{-3}; \quad r_a = 10^{-9} \text{ m}$$

2.3 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G_{500}^0(1, r_a) = \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co})$$

$\Delta_r G_{500}^0(1)$ is 20.7 kJ mol^{-1} . For spherical cobalt particles with $r_a = 1 \text{ nm}$ $\Delta_r G_{500}^0(1, r_a)$ is 18.6 kJ mol^{-1} .

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G_{500}^0(1) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G_{500}^0(1) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \leq 0$$

and for spherical cobalt nanoparticles with $r_a = 1 \text{ nm}$:

$$\begin{aligned} \Delta_r G(1, r_a) &= \Delta_r G_{500}^0(1, r_a) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \\ &= \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \leq 0 \end{aligned}$$

$\Delta_r G_{500}^0(1)$ is equal to 20.7 kJ mol^{-1} . For spherical cobalt particles with $r_a = 1 \text{ nm}$ equals to 18.6 kJ mol^{-1}

2.4 For the spontaneous oxidation

$$\Delta_r G(1, r_a) = \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln \left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)} \right) \leq 0$$

and

$$\Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \leq RT \ln \left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)} \right)$$

The left hand side of the last inequality becomes more positive with the increase of r_a . At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a . The answer (a) is correct.

2.5 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G_{\text{sph}}^0(\text{CoO}, r_b) = G_{\text{bulk}}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^0(\text{CoO}, \text{s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

2.6 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$\begin{aligned} G_{\text{sph}}^0(\text{Co}, r_a, r_b) &= G_{\text{bulk}}(\text{Co}) + V(\text{Co}) \left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a} \right) = \\ &= G^0(\text{Co}, \text{s}) + V(\text{Co}) \left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a} \right) \end{aligned}$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

2.7 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\begin{aligned} \Delta_r G^0(1, r_a, r_b) &= G_{\text{sph}}^0(\text{CoO}, r_b) + G^0(\text{H}_2, \text{gas}) - G^0(\text{H}_2\text{O}, \text{gas}) - G_{\text{sph}}^0(\text{Co}, r_a, r_b) = \\ &= G^0(\text{CoO}, \text{s}) + G^0(\text{H}_2, \text{gas}) - G^0(\text{H}_2\text{O}, \text{gas}) - G^0(\text{Co}, \text{s}) + \\ &\quad + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) - 2V(\text{Co}) \left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a} \right) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} (V(\text{CoO}) - V(\text{Co})) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) \end{aligned}$$

2.8 Under the assumptions made

$$\begin{aligned}\Delta_r G^0(1, r_a, r_b) &= \Delta_r G^0(1, r_0) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} (V(\text{CoO}) - V(\text{Co})) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0} \left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right)\end{aligned}$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right) = 6.56 \times 10^{-6} \text{ m}^3$$

$\Delta_r G^0(1, r_0)$ is directly proportional to $\left(\frac{1}{r_0} \right)$. The plot (a) is correct.

2.9 The spontaneous forward reaction (1) is possible, when $\Delta_r G(1, r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0} \left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right) \leq RT \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0 . At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0 .

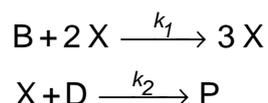
The answer (b) is correct.

PROBLEM 3

Unstable chemical reactions

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:



(B and D are reagents, X is an intermediate and P is a product).

- 3.1** Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.
- 3.2** Deduce a rate equation using steady-state approximation. Find the orders:
- a partial reaction order with respect to B;
 - a partial reaction order with respect to D;
 - the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: $[\text{B}] = [\text{D}] = \text{const}$.

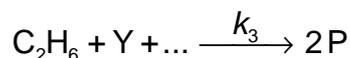
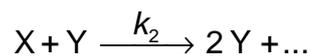
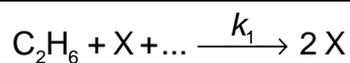
- 3.3** Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the cases:

$$1) [\text{X}]_0 > \frac{k_2}{k_1}; \quad 2) [\text{X}]_0 < \frac{k_2}{k_1}.$$

- 3.4** Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[\text{B}]_0 = [\text{D}]_0$,

$$[\text{X}]_0 > \frac{k_2}{k_1}.$$

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:



Under specific conditions this reaction displays oscillatory behavior:

Intermediates are peroxide $\text{C}_2\text{H}_6\text{O}_2$ and aldehyde $\text{C}_2\text{H}_4\text{O}$, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	E_A , kJ mol^{-1}
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

SOLUTION

3.1 The overall reaction equation



The kinetic equation for X

$$\frac{d[\text{X}]}{dt} = k_1[\text{B}][\text{X}]^2 - k_2[\text{D}][\text{X}]$$

3.2 Under the steady-state conditions

$$\frac{d[\text{P}]}{dt} = k_2[\text{D}][\text{X}] = k_1[\text{B}][\text{X}]^2,$$

whence

$$[X] = \frac{k_2[D]}{k_1[B]}$$

$$\frac{d[P]}{dt} = \frac{k_2^2[D]^2}{k_1[B]}$$

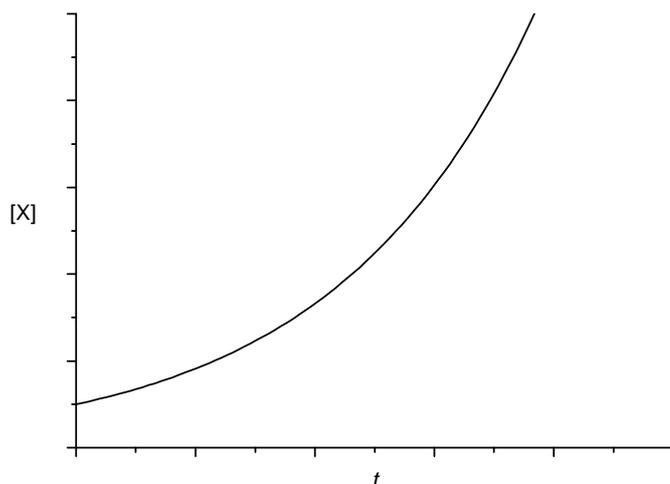
The reaction order is 2 with respect to D, and -1 with respect to B.

The overall order is 1.

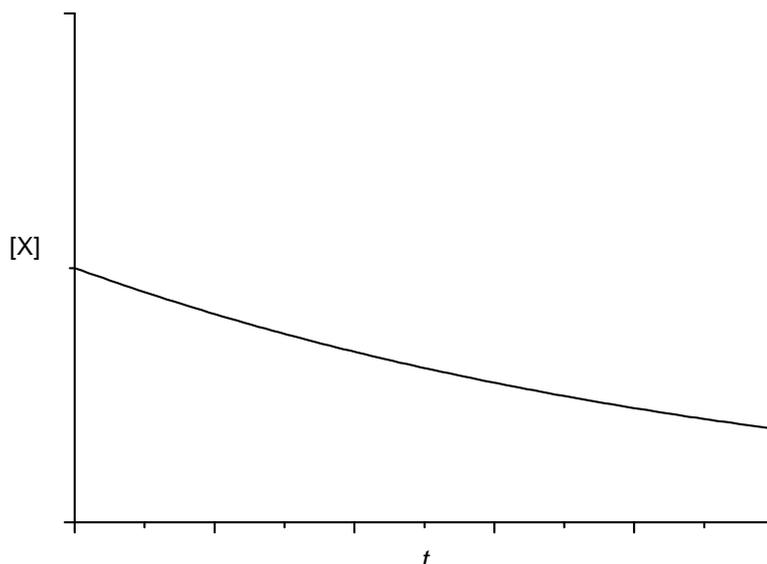
3.3 In an open system the initial reaction rate is:

$$\frac{d[X]}{dt} = [B][X](k_1[X] - k_2)$$

1) If $[X]_0 > k_2/k_1$, then $d[X]/dt > 0$ at any time, and the concentration of X monotonically increases:



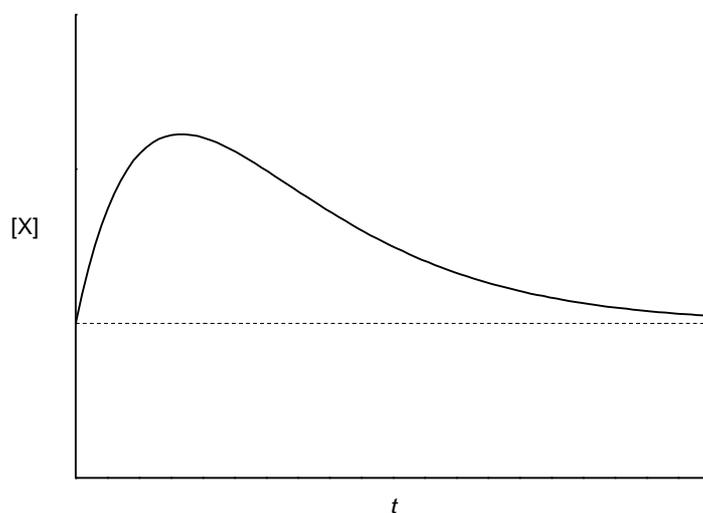
2) If $[X]_0 < \frac{k_2}{k_1}$, then $\frac{d[X]}{dt} < 0$ at any time, and the concentration of X monotonically decreases:



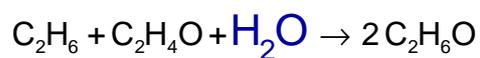
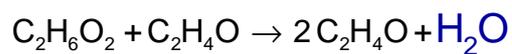
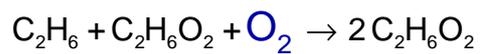
3.4 In a closed system the initial reaction rate is:

$$\left. \frac{d[X]}{dt} \right|_{t=0} = k_1[B]_0[X]_0^2 - k_2[D]_0[X]_0 = [B]_0[X]_0 (k_1[X]_0 - k_2) > 0$$

Hence, at the beginning of the reaction $[X]$ increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.5 X – C₂H₆O₂, Y – C₂H₄O, P – C₂H₆O. Dots denote O₂ and H₂O.



3.6 At the highest possible temperature the rate constants are equal:

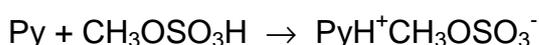
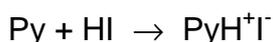
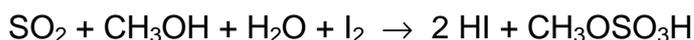
$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \frac{A_2}{A_1}} = 354 \text{ K}$$

PROBLEM 4

Determination of water by Fischer titration

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO₂ and pyridine (C₅H₅N, Py) – Fischer reagent. The following reactions occur during the titration:



Iodine content is usually expressed in mg of water reacting with 1 cm³ of the titrant solution (hereunder T, mg cm⁻³), which equals the mass of water (mg) reacting with 1.00 cm³ of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I₂ with SO₂ and H₂O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

4.2 12.20 cm³ of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate Na₂C₄H₄O₆ · 2 H₂O.

4.3 A known amount of water (21.537 g) was placed into a 1.000 dm³ volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm³ of the obtained solution, 22.70 cm³ of Fischer reagent solution were needed, whereas 2.20 cm³ of iodine were used for titration of 25.00 cm³ of methanol.

4.4 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm³ (solution **A**); 22.45 cm³ of this solution were used for titration of 15.00 cm³ of a Fischer reagent (solution **B**).

Then 25.00 cm³ of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm³ of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm³ of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound Fe₂(SO₄)₃ · x H₂O, 10.59 cm³ of iodine solution (T = 15.46 mg/cm³) were consumed.

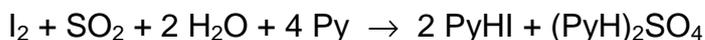
4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

4.7 Write down an equation of the overall reaction of Fe₂(SO₄)₃ · x H₂O with the Fischer reagent.

4.8 Calculate the composition of the hydrate Fe₂(SO₄)₃ · x H₂O (x = integer).

SOLUTION

4.1 Equation:



4.2 T is equal to:

$$M(\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2 \text{H}_2\text{O}) = 230.05 \text{ g mol}^{-1} \quad 2 \times M(\text{H}_2\text{O}) = 36.04 \text{ g mol}^{-1}$$

$$m(\text{H}_2\text{O}) = \frac{1.3520 \times 36.04}{230.05} = 0.2118 \text{ g} = 211.8 \text{ mg}$$

$$T = \frac{211.8}{12.20} = 17.36 \text{ mg cm}^{-3}$$

$$T = 17.36 \text{ mg cm}^{-3}$$

4.3 T is equal to:

$$\text{Volume of iodine consumed for } 10 \text{ cm}^3 \text{ of pure } \text{CH}_3\text{OH} = \frac{2.20 \times 10.00}{25.00} = 0.88 \text{ cm}^3$$

$$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.88} = 9.87 \text{ mg cm}^{-3}$$

More exactly

$$10.00 \text{ cm}^3 \text{ of the solution contains } \frac{(1000 - 21.5) \times 10.00}{1000} = 9.785 \text{ cm}^3 \text{ of methanol.}$$

$$\begin{aligned} \text{Volume of iodine consumed for } 9.785 \text{ cm}^3 \text{ of pure CH}_3\text{OH} &= \frac{2.20 \times 9.785}{25.00} = \\ &= 0.86 \text{ cm}^3 \end{aligned}$$

$$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.86} = 9.86 \text{ mg cm}^{-3}$$

$$T = 9.87 \text{ mg cm}^{-3}$$

4.4 T is equal to:

Approach 1

Let 1 cm³ of CH₃OH contains x mg H₂O, then 1 cm³ of **A** contains [(1.000 - 0.006) x + 5.624] mg H₂O.

$$15.00 T = 22.45 (0.994 x + 5.624) \quad - \text{1}^{\text{st}} \text{ titration,}$$

$$10.00 T = 25.00 x + 10.79 (0.994 x + 5.624) \quad - \text{2}^{\text{nd}} \text{ titration.}$$

Hence, x = 1.13 mg cm⁻³, T = 10.09 mg cm⁻³ (10.10 without taking into account 0.994 factor)

Approach 2

Let y cm³ of **B** be consumed for the titration of water, contained in 1 cm³ of CH₃OH.

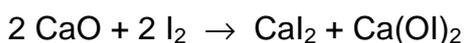
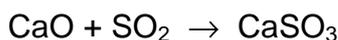
$$\text{Then } T = \frac{22.45 \times 5.624}{15.00 - 22.45 \times 0.994 \times y} \text{ (1}^{\text{st}} \text{ titration)} = \frac{10.79 \times 5.624}{10.00 - 25.00 y - 10.79 y}$$

(2nd titration).

$$\text{Hence, } y = 0.1116 \text{ and } T = 10.10 \text{ mg cm}^{-3}$$

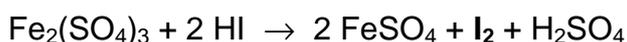
$$T = 10.09 \text{ mg cm}^{-3} \text{ (10.10 without taking into account 0.994 factor)}$$

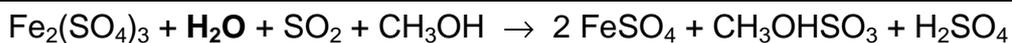
4.5 Equation(s):



(Instead of CaO, Ca(OH)₂ may be written.)

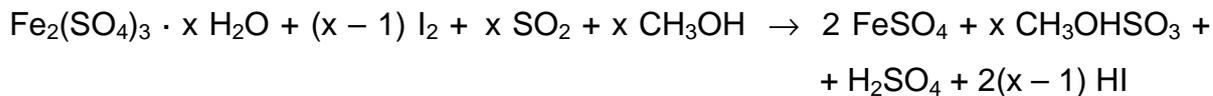
4.6 Equation(s):





(or in ionic form)

4.7 Equation:



4.8 The composition of the crystalhydrate is:

$$M(\text{Fe}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O}) = 399.9 + 18.02 x$$

$$m(\text{H}_2\text{O}) = \frac{0.6387 \times 18.02 x}{(399.9 + 18.02 x)}$$

$$m(\text{H}_2\text{O}) = 10.59 \text{ cm}^3 \times 15.46 \text{ mg cm}^{-3} \times 0.001 \text{ g mg}^{-1} \times \frac{x}{x-1}$$

$$0.1637 \times (399.9 + 18.02 x) = 11.51 x - 11.51$$

$$x = 8.994 \approx 9$$

$$\text{Formula: Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$$

PROBLEM 5

A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three colourless organic liquids **A**, **B**, **C** was treated by water containing a drop of hydrochloric acid at heating to give (after separation from water) a 1 : 2 (molar ratio) mixture of acetic acid and ethanol without any other components. A catalytic amount (one-two drops) of concentrated sulfuric acid was added to the mixture after hydrolysis and after a long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical with any of **A**, **B**, **C**.

5.1 Draw the structure of compound **D**?

5.2 Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.

5.3 Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1 : 1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85 %); b) higher than 85 %; c) lower than 85 %.

¹H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1 : 3 : 2.

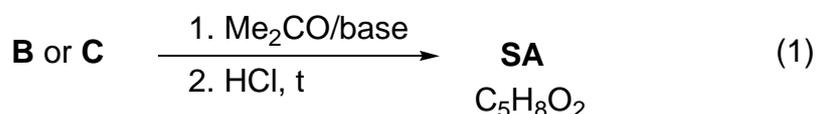
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. After acidification and short boiling the remaining solution gave 2 : 3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 dm³ (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds, except diethyl ether, could be identified after hydrogenation.

5.4 Determine and draw the structures of **A**, **B**, and **C**.

5.5 Which intermediate compounds are formed during the acidic hydrolysis of **C** and the basic hydrolysis of **B**.

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).

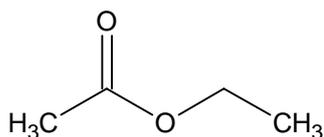


5.6 Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.

5.7 Give structure of **E**

SOLUTION

5.1 Structure of product **D**



Ethyl acetate, ethyl ethanoate

5.2 Which class of organic compounds does **D** belong to? Check the appropriate box.

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

5.3 The expected yield of **D**

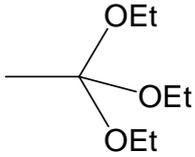
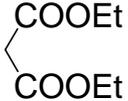
The reaction is an equilibrium without any further actions. Qualitative estimation:
The yield is lower than 85 %.

Assuming that the reaction is at equilibrium and that the equilibrium constant is supposed not to vary with temperature and composition of the reaction mixture, we can calculate:

$$K = \frac{[\text{AcOEt}][\text{H}_2\text{O}]}{[\text{AcOH}][\text{EtOH}]} = \frac{(0.85)^2}{0.15 \times 1.15} = 4.2$$

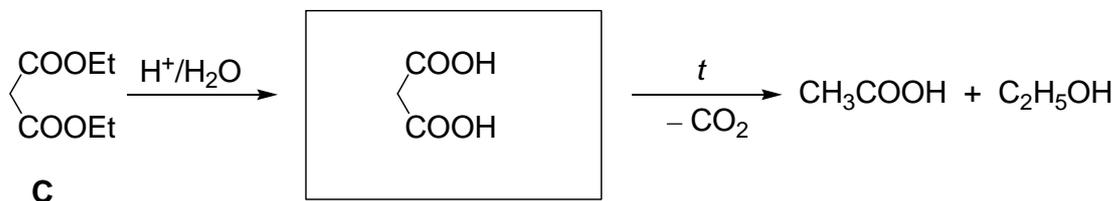
Using this constant calculation of yield in 1 : 1 mixture gives 67 %.

5.4 The structures of **A**, **B**, and **C**.

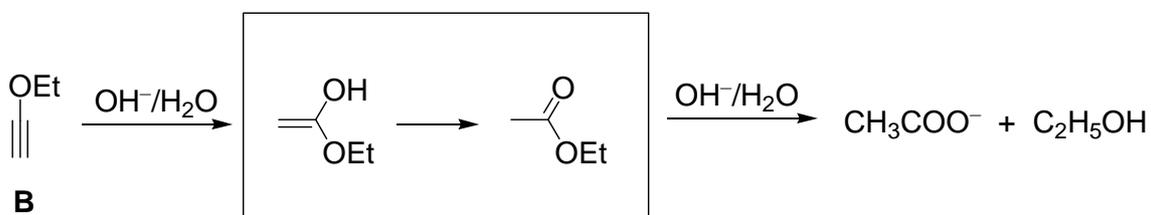
 <p>$\text{CH}_3\text{C}(\text{OEt})_3$</p> <p>triethyl orthoacetate, 1,1,1-triethoxyethane</p>	 <p>$\text{HC}\equiv\text{COEt}$</p> <p>ethoxyacetylene, ethynylethyl ether</p>	 <p>$\text{CH}_2(\text{COOEt})_2$</p> <p>diethyl malonate</p>
A	B	C

5.5 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of **C**, and basic hydrolysis of **B**.

a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate:

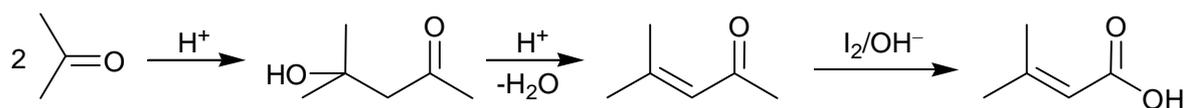


b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed



5.6 The structure of senecioic acid:

From acetone alone the synthesis includes aldol condensation and dehydration with subsequent iodoform reaction:



5.7 The structure of **E**.

Iodoform, triiodomethane, CHI_3

PROBLEM 6**Silicates as the base of the Earth crust**

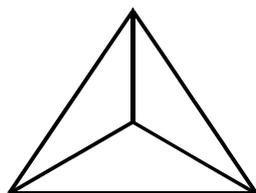
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of “liquid glass” (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the “Yes” box if it leads to changes of pH. Otherwise check the “No” box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-} , **1**):

**(1)**

For $[\text{Si}_3\text{O}_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.

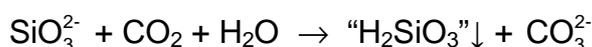
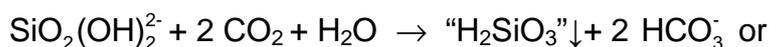
Charged monolayers with the composition $[\text{Si}_4\text{O}_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3** - **6.5**, depict a fragment of the layered structure joining 16 tetrahedra (**1**). Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

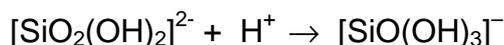
Being placed into the LGL solution, salts of transition metals give rise to fancy “trees” tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ produce “trees” of blue colour, whereas those of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ form green “trees”.

- 6.7** Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ $K_a^1 = 1 \times 10^{-7}$.
- 6.8** Write down equation of a reaction between aqueous solutions of CuSO_4 and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

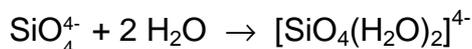
SOLUTION



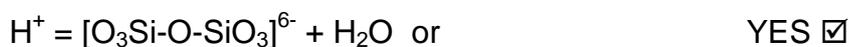
- 6.2** a) protonation of ortho-silicate ions leading to the formation of Si-OH groups:



- b) formation of hydrated $[\text{SiO}_4(\text{H}_2\text{O})_2]^{4-}$ anions NO



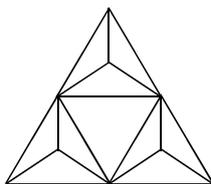
- c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds



6.3 $n = 6$ (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

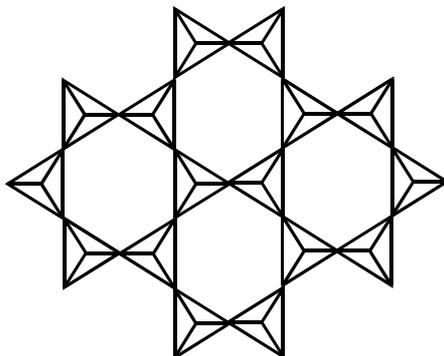
6.4 $\text{Si}_3\text{O}_9 \equiv 3 [\text{SiO}_4] - 3 \text{O}$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

6.5



6.6 $m = 4$ (assuming oxidation numbers of silicon (IV) and oxygen (-II), or taking into account its structure and the charge of orthosilicate ion (-4))

$\text{Si}_4\text{O}_{10} \equiv 4[\text{SiO}_4] - 6 \text{O}$, i. e. the formula of the tetrahedron is now $\text{SiO}_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution = 3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.7 $\text{Cu}(\text{H}_2\text{O})_4^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{H}_3\text{O}^+$,
 $[\text{H}^+] \approx (c K_a)^{1/2} = 1 \times 10^{-4}$, $\text{pH} = -\log[\text{H}^+] = 4$
 $\text{pH} = 4$

6.8 $\text{CuSO}_4 + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2\downarrow + \text{“H}_2\text{SiO}_3\text{”}\downarrow + \text{Na}_2\text{SO}_4$

or

$2 \text{CuSO}_4 + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu}_2(\text{OH})_2\text{SO}_4\downarrow + \text{“H}_2\text{SiO}_3\text{”}\downarrow + \text{Na}_2\text{SO}_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes

from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.7**).

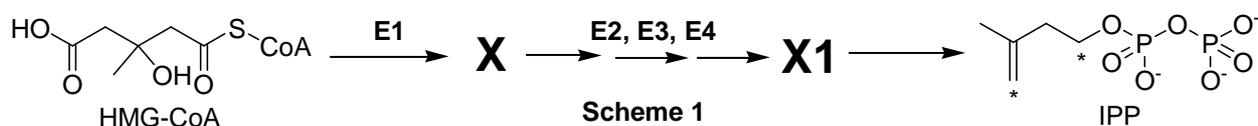
PROBLEM 7

Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

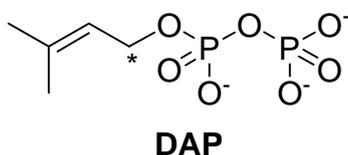
X is an optically active monocarboxylic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:



7.1 In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.

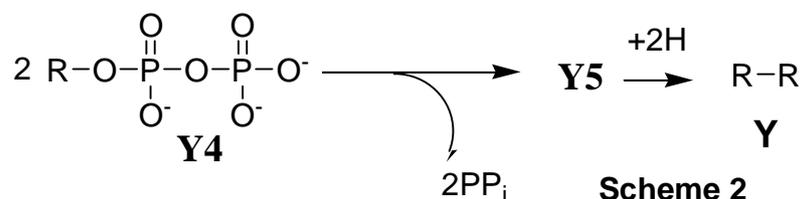
7.2 Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.

Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



7.3 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1 : 1 to the coupling product.

- 7.4** Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.
- 7.5** Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.
- 7.6** Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.

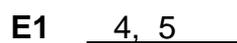
The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in trans configuration.

7.7 Draw structures of **Y** and **Y4** with stereochemical details.

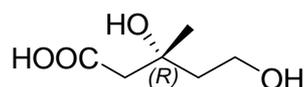
SOLUTION

7.1 **E2 - E4** catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β -oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

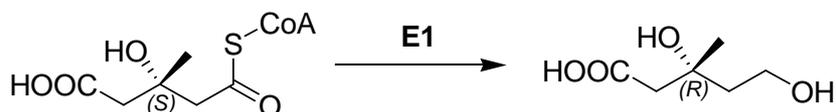


7.2 Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:

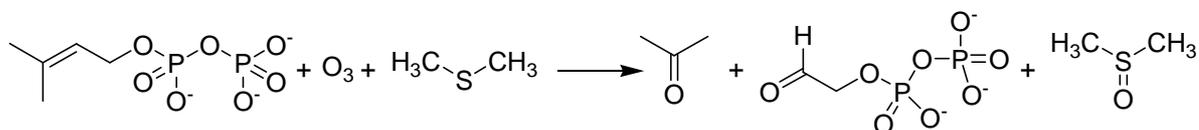


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



7.3 Reaction equation for reductive ozonolysis:



7.4 DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in 7.2.1). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(\text{C}) = 2 \cdot n_{Y1}(\text{C}) + 4 \cdot n_{Y2}(\text{C}) + n_{Y3}(\text{C}) = 2 \cdot 3 + 4 \cdot 5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$$n(\text{H}) = 2 \cdot n_Y(\text{C}) + 2 - 2 \cdot n_{\text{C}=\text{C}} = 30 \cdot 2 + 2 - 6 \cdot 2 = 50$$

Y (squalene) formula – $\text{C}_{30}\text{H}_{50}$.

Number of carbon atoms: <u>30</u>	Work: $n_Y(\text{C}) = 2 \cdot n_{Y1}(\text{C}) + 4 \cdot n_{Y2}(\text{C}) + n_{Y3}(\text{C}) = 2 \cdot 3 + 4 \cdot 5 + 4 = 30$
Number of hydrogen atoms: <u>50</u>	Work: $n(\text{H}) = 2 \cdot n_Y(\text{C}) + 2 - 2 \cdot n_{\text{C}=\text{C}} = 30 \cdot 2 + 2 - 6 \cdot 2 = 50$

Gross formula of **Y** $\text{C}_{30}\text{H}_{50}$

7.5 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

$$n(\text{IPP\&DAP}) = n_Y(\text{C})/5 = 30/5 = 6$$

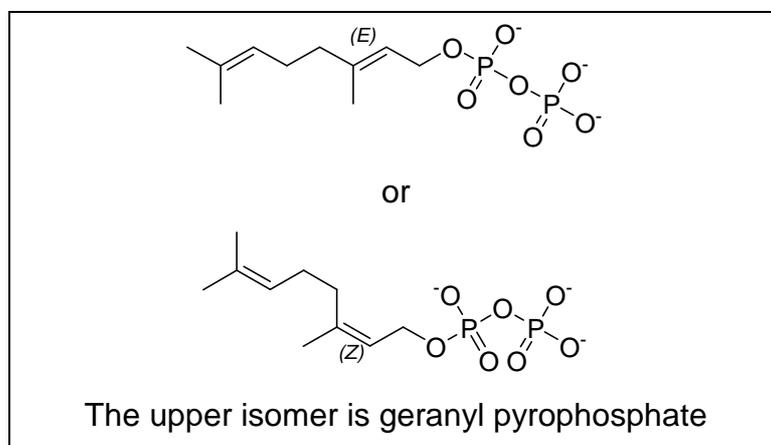
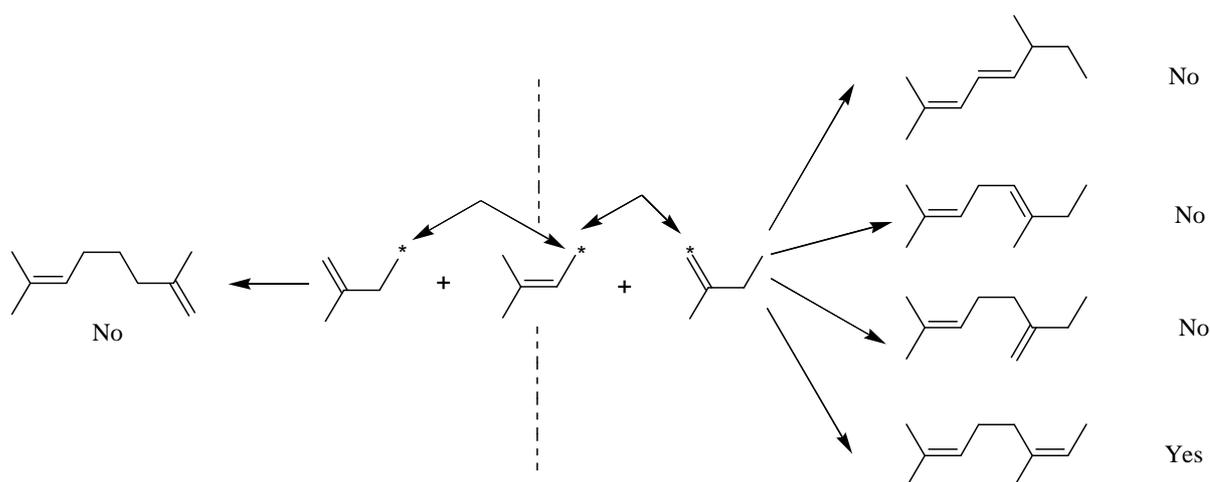
The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

$$n(\text{IPP}\&\text{DAP}) = n_{\text{Y}}(\text{C})/5 = 30/5 = 6$$

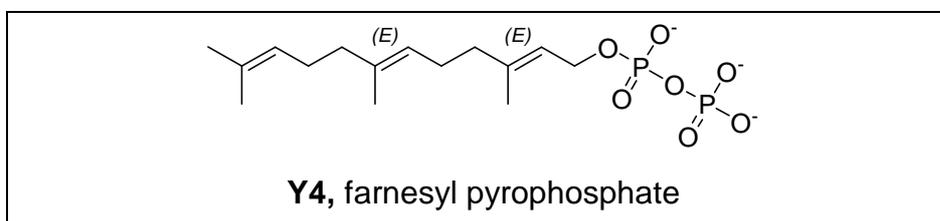
Number of DAP molecules: 2

Number of IPP molecules: 4

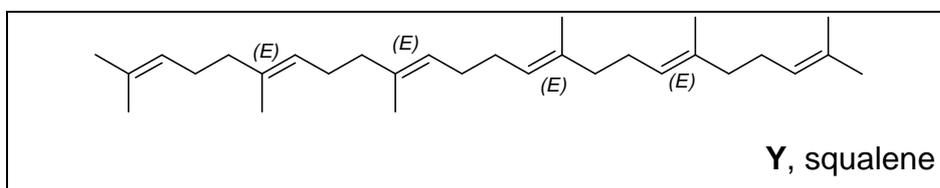
7.6 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details



7.7 It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4**, since **Y3** is formed as a result of ozonolysis in a molar ratio of 1 : 1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in trans configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



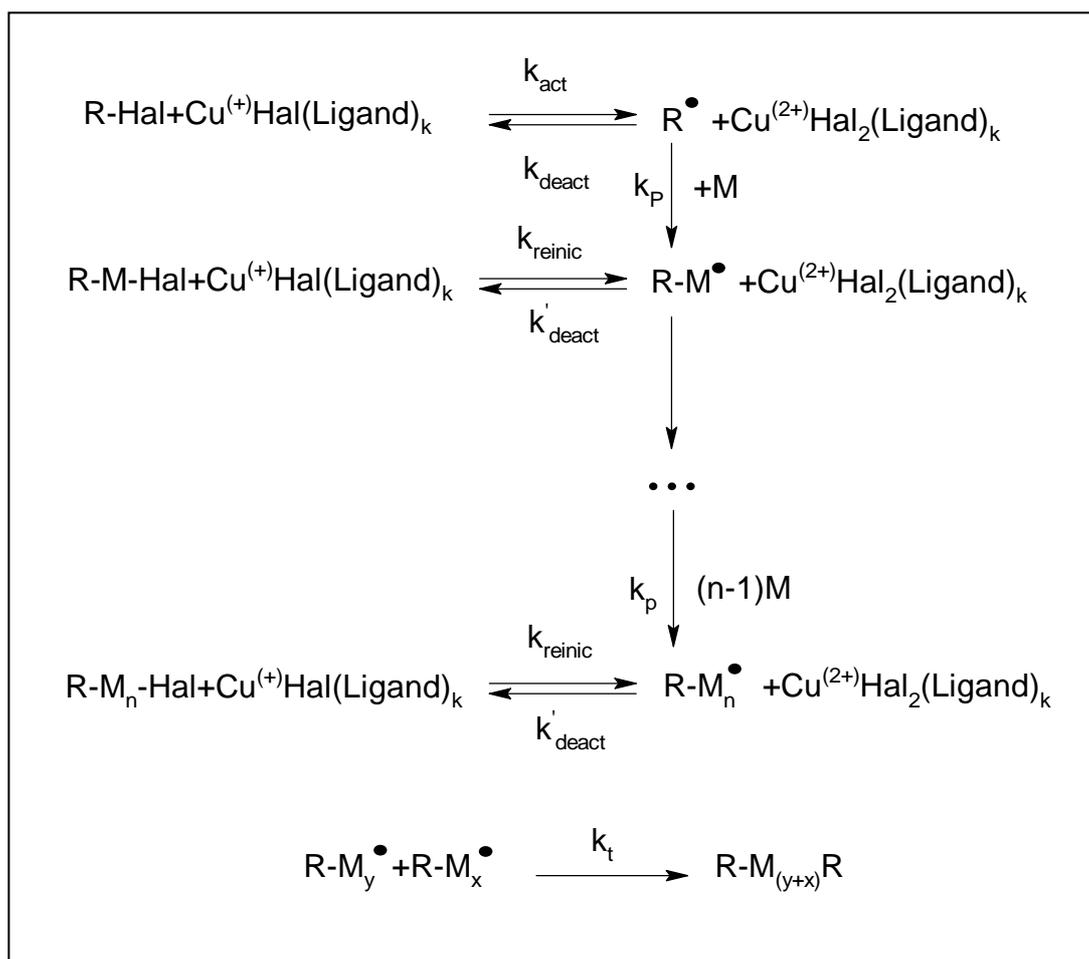
Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:



PROBLEM 8

ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

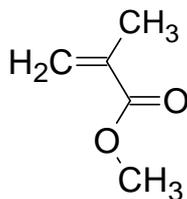
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration ($[M]$) on reaction time (t) for ATRP is:

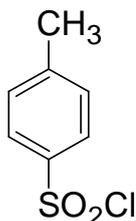
$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p [R\cdot] t,$$

$[M]_0$ - initial monomer concentration, k_p - rate constant of propagation, $[R\cdot]$ - concentration of active radicals.

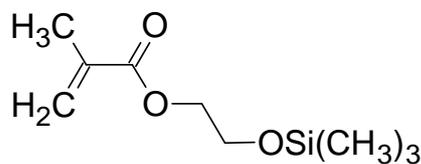
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is $1616 \text{ L mol}^{-1}\text{s}^{-1}$, and the steady state concentration of radicals is $1.76 \times 10^{-7} \text{ mol dm}^{-3}$.



MMA



TsCl



HEMA-TMS

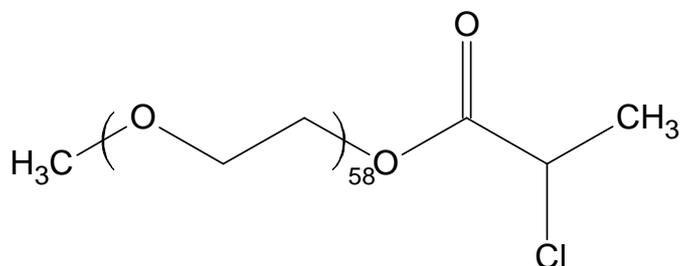
8.3 Calculate mass (m) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, (A₆₅-graft-C₁₀₀)-stat-B₃₄ means that chains of polymer C are grafted on units A in the statistical copolymer of A and B.

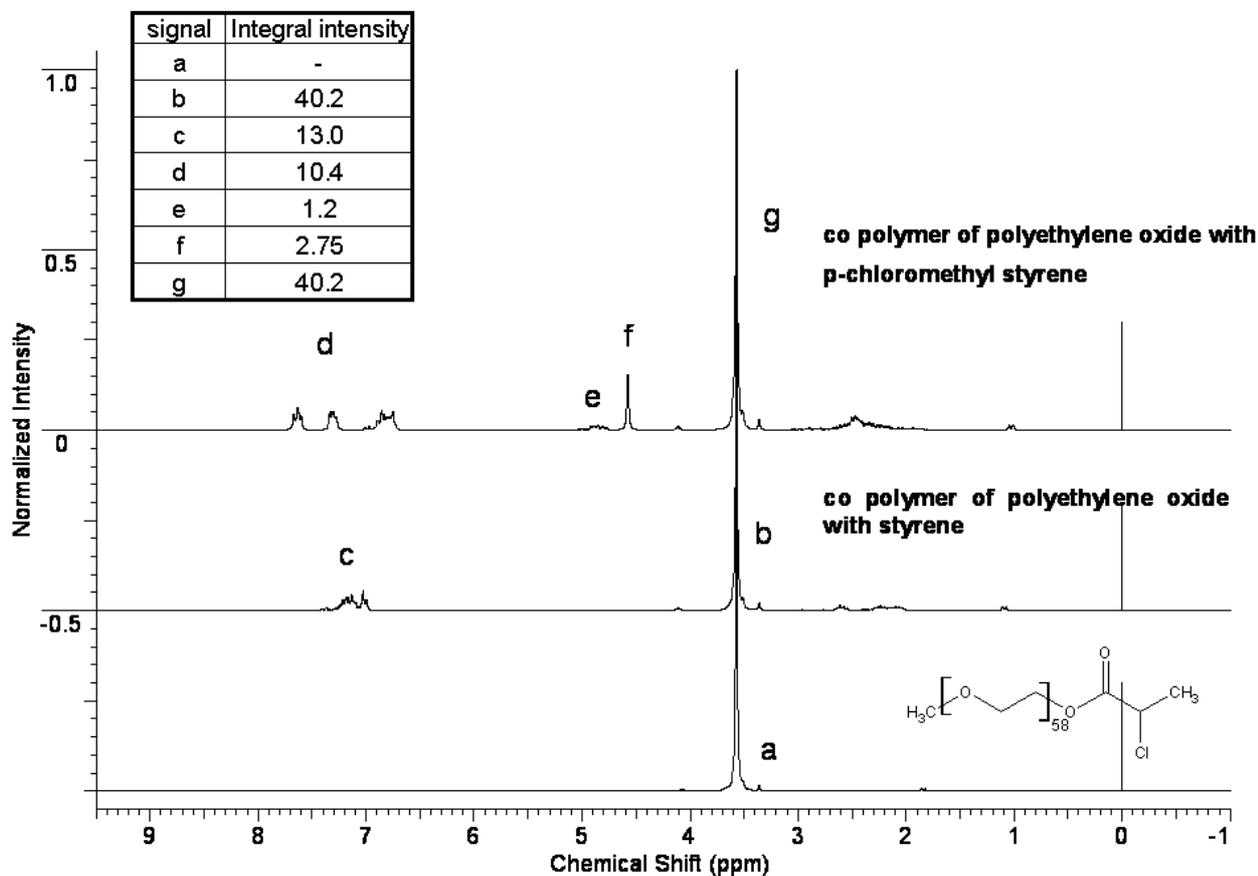
ATRP was applied to synthesize two block copolymers, P₁ and P₂. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P₁ consisted of styrene (C), and in P₂ of p-chloromethylstyrene (D) units.

¹H NMR spectra of the macroinitiator, P₁ and P₂ are given below. Integral intensities of characteristic signals can be found in the table.

- 8.6** Assign ¹H NMR signals to substructures given in the Answer Sheet.
- 8.7** Determine molar fractions of units C and D and molecular weights of P₁ and P₂.
- 8.8** Write down all possible reactions of activation occurring during the synthesis of P₁ and P₂. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.
- 8.9** Draw the structure of P₁ and one of possible structures of P₂ representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.



SOLUTION

8.1 Expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t)

$$v_{\text{act}} = k_{\text{act}} [\text{R-Hal}] [\text{CuHal}(\text{Ligand})_k]$$

$$v_{\text{deact}} = k_{\text{deact}} [\text{R}\cdot] [\text{CuHal}_2(\text{Ligand})_k]$$

$$v_p = k_p [\text{R}\cdot] [\text{M}]$$

$$v_t = 2 k_t [\text{R}\cdot]^2$$

8.2 Comparison of rates of ATRP elementary stages

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination.

Thus:

$$V_{\text{deact}} \gg V_{\text{act}}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$V_{\text{deact}} \gg V_p$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$V_{\text{deact}} \gg V_t$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$$V_{\text{deact}} \gg V_{\text{act}}$$

$$V_{\text{deact}} \gg V_p$$

$$V_{\text{deact}} \gg V_t$$

8.3 Calculation of mass (m) of the obtained polymer.

1st variant

$$[M] = [M]_0 \exp(-k_p [R\cdot] t) \text{ or } n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_p [R\cdot] t)$$

Quantity of MMA monomer remaining after polymerization during 1400 s is

$$31.0 \times \exp(-1616 \times 1.76 \times 10^{-7} \times 1400) = 20.8 \text{ mmol.}$$

Quantity of monomer consumed during polymerization: $31 - 20.8 = 10.2 \text{ mmol}$

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = \frac{10.2}{1000} \times 100.1 = 1.03 \text{ g}$$

2nd variant

$$[M] = [M]_0 \exp(-k_p [R\cdot] t) \text{ or } n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_p [R\cdot] t)$$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$$\begin{aligned} \Delta n(\text{MMA}) &= n_0(\text{MMA}) (1 - \exp(-k_p \times [R\cdot] \times t)) = 31.0 \times (1 - 1616 \times 1.76 \times 10^{-7} \times 1400) = \\ &= 10.2 \text{ mmol} \end{aligned}$$

Mass of the obtained polymer is:

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2 / 1000) \times 100.1 = 1.03 \text{ g}$$

3rd variant

$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p[R\cdot]t = -1616 \times 1.76 \times 10^{-7} \times 1400 = -0.398$$

$$\frac{[M]}{[M]_0} = e^{-0.398} = 0.672$$

$$\frac{[M]}{[M]_0} = \frac{n(\text{MMA})}{n_0(\text{MMA})}$$

$$n(\text{MMA}) = 0.672 \times n_0(\text{MMA}) = 20.8 \text{ mmol}$$

Quantity of monomer consumed during polymerization is $31 - 20.8 = 10.2$ mmol.

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2/1000) \times 100.1 = 1.03 \text{ g}$$

8.4 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73 / 100.1).

The total quantity of monomers at the beginning of the 2nd stage is $23.7 + 23.7 = 47.4$ mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$\Delta n = n_0(1 - \exp(-k_p[R\cdot]t)) = 47.4(1 - \exp(-1616 \times 1.76 \times 10^{-7} \times 1295)) = 14.6 \text{ mmol.}$$

Totally $7.3 + 14.6 = 21.9$ mmol of monomers was polymerized during two stages.

$$\text{DP} = 21.9 / 0.12 = 182.5$$

DP = 182 – 183 (all answers within this range are credited)

8.5 Structure of the obtained polymer.

The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is $7.3 / 0.12 = 60.8 \approx 61$ monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning

of the 2nd stage were equal. The DP of the 2nd block is $183 - 61 = 122$ monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A₆₁-block-(A-stat-B)₆₁-Cl or Ts-A₆₁-block-(A₆₁-stat-B₆₁)-Cl

8.6 Assignment of NMR signals to substructures given in the Answer Sheet.

	a, b, g
	c
	d
	e
	f

8.7 Determination of molar fractions of units C and D and molecular weights of P₁ and P₂.

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is $40.2 / 4 / 58 = 0.173$ for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to $13.0 / 0.173 = 75$ protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is $75 / 5 = 15$.

Molar fraction of styrene units in P₁ is $15 / (15 + 58) = 20.5\%$

Intensity of multiplet d is 10.4, which is equivalent to $10.4 / 0.173 = 60$ protons. Since each monomer unit of p-chloromethylstyrene has 4 protons, DP of PCS is $60 / 4 = 15$.

Molar fraction of D is $15 / (15 + 58) = 20.5\%$

$$M(P_1) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 104.15 + 35.45 = \mathbf{4240}$$

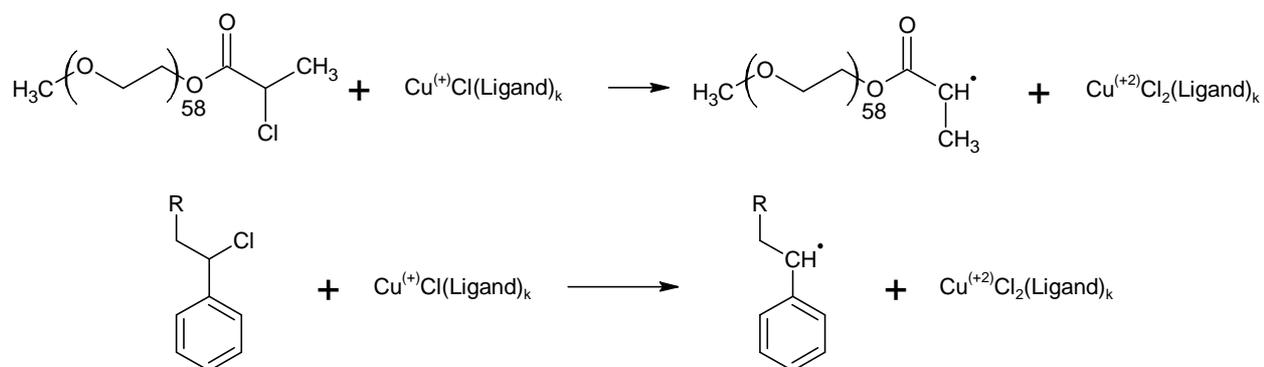
$$M(P_2) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 152.62 + 35.45 = \mathbf{4967}$$

$$M(P_1) = 4240 \quad ; \quad M(P_2) = 4967$$

$$n(C) = 20.5\% ; \quad n(D) = 20.5\%$$

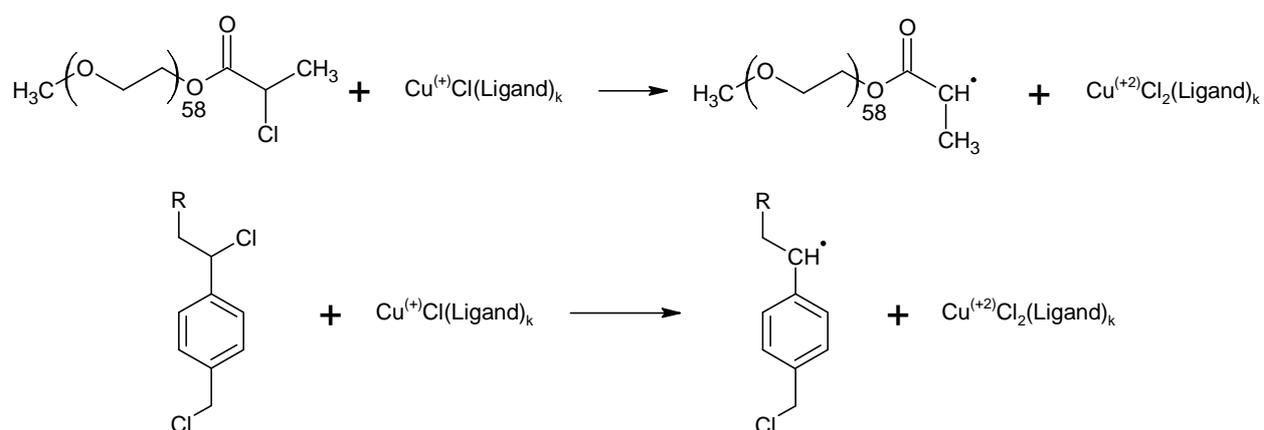
8.8 All possible reactions of activation occurring during the synthesis of P₁ and P₂.

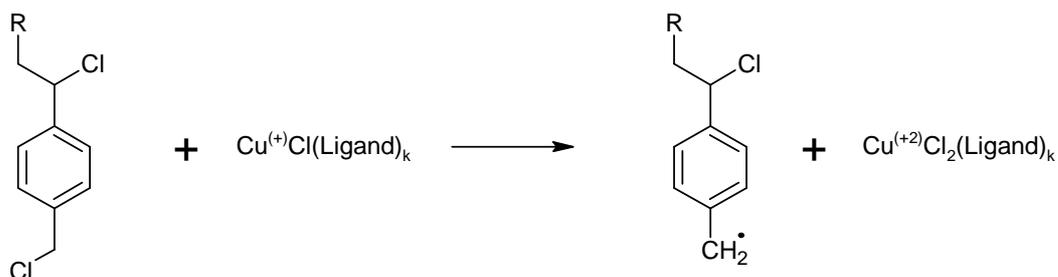
P₁:



Here R is used for the macroinitiator fragment with one or several styrene units attached.

P₂:





Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

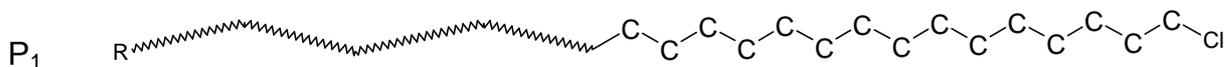
8.9 The structure of P₁ and one of possible structures of P₂

P₁ is a block copolymer of PEO and PS. The PS block contains 15 units.

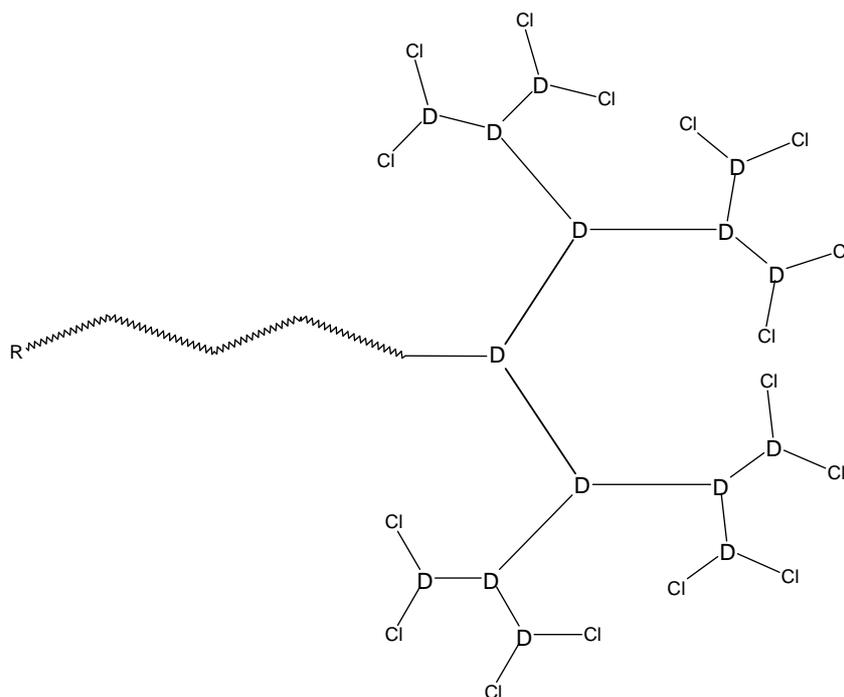
P₂ is a block copolymer composed of PEO block and branched styrene block.

The integral intensity of multiplet f is 2.75, so $2.75/0.173=15.9$, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P₂, it would contain 15 chloromethyl groups. Each branching reduces the number of such groups by 1. Thus P₂ has $15 - 8 = 7$ branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units



P₂

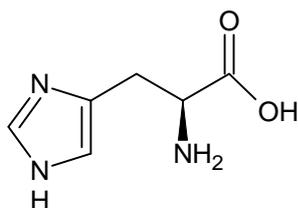


PRACTICAL PROBLEMS

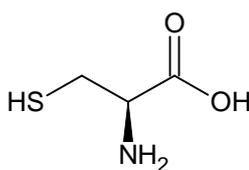
PROBLEM 1 (Practical)

Ion-exchange chromatography of amino acids

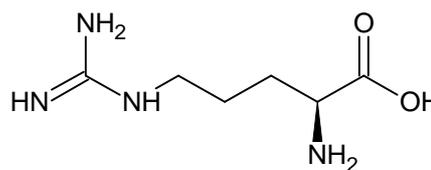
Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.



His



Cys



Arg

Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (*pH* 4.9).

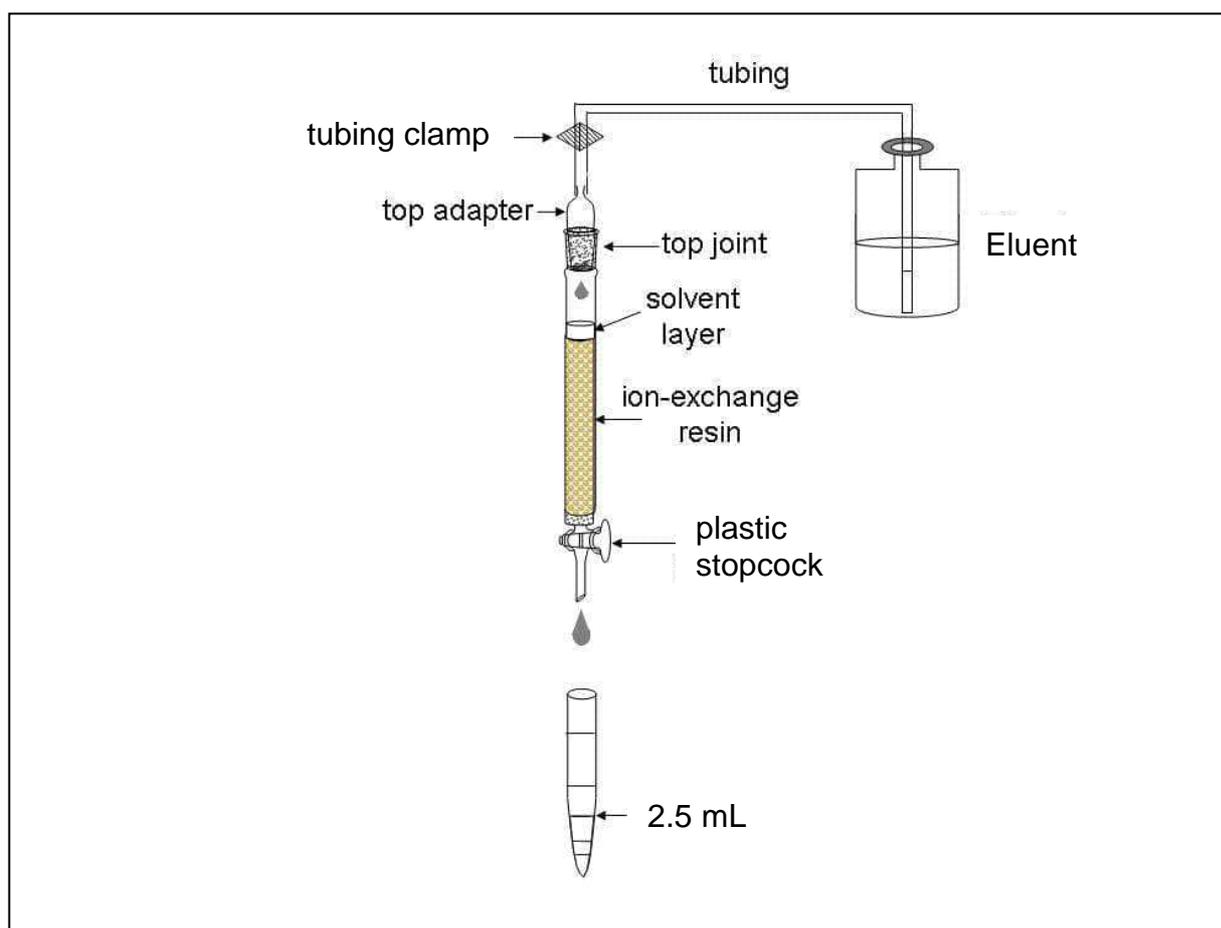
Procedure

Chromatography. Step 1

Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labelled "Waste" so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the "Waste" flask). Close the stopcock and add about 1 cm³ of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the

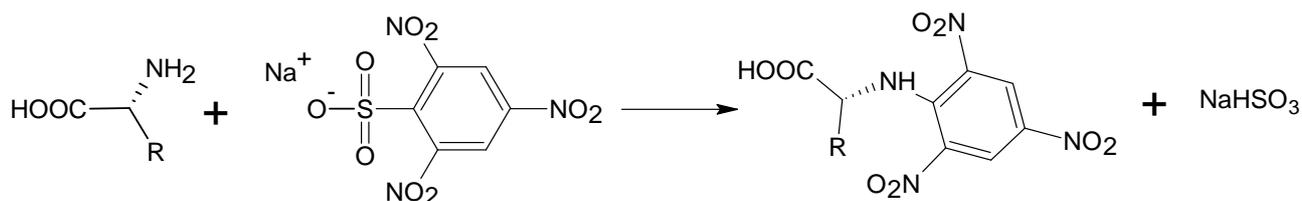
tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always pen the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 cm³ (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α -amino groups with sodium 2,4,6-trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 cm³ of TNBS solution with 10 cm³ of carbonate buffer solution and place 0.1 cm³ of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 cm³ of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 cm³ should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1 a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1 b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.

1.1 Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.

1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labelled "Peak 1", "Peak 2", "Peak 3". Prepare samples for quantitative spectrophotometric analysis as described below.

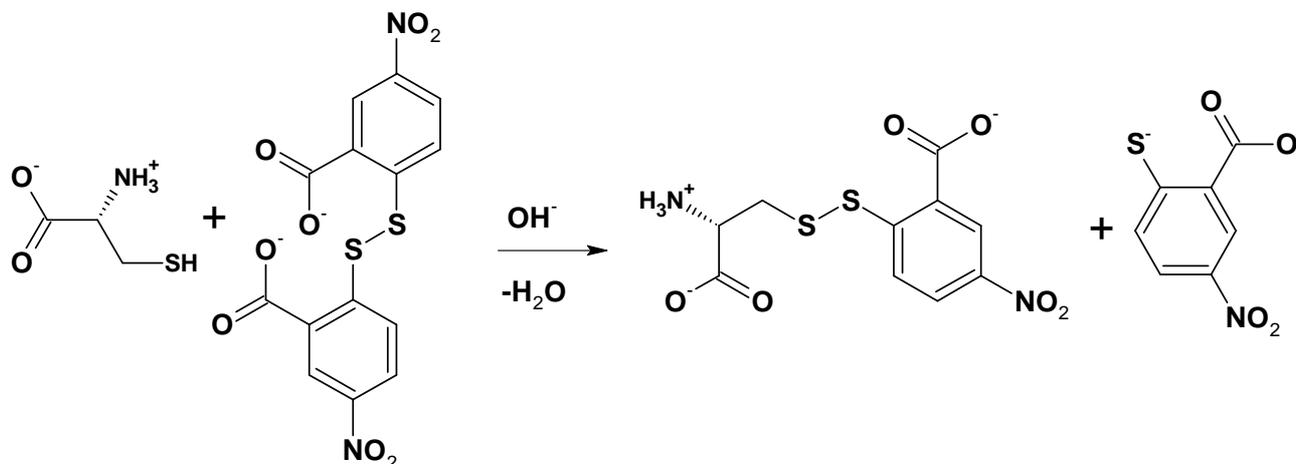
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cells to the operator. Prepare the probes as follows.

Important! When storing, always put cell in the cell holder! All cells have 2 ribbed and 2 working vertical surfaces. While operating with cells, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A₁ (Reference).

Place 0.1 cm³ of Eluent 1 from plastic microtube into a test tube and add 2.9 cm³ of Ellmann reagent (DTNB).

Test tube B₁ (Sample).

Place 0.1 cm³ of the analyzed solution into a test tube and add 2.9 cm³ of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A₁ (for reference) and B₁ (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A₂ (Reference).

Place 2.8 cm³ of Tris-HCl buffer solution into a test tube, add 0.1 cm³ of Eluent 2 from plastic microtube and 0.1 cm³ of Pauli reagent.

Test tube B₂ (Sample).

Place 2.8 cm³ of Tris-HCl buffer solution into a test tube, add 0.1 cm³ of the analyzed solution and 0.1 cm³ of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A₂ (for reference) and B₂ (for sample).

Assay 3 (peak 3). Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions

(Sakaguchi reaction).

Test tube A₃ (Reference).

Place 0.1 cm³ of Eluent 3 into a test tube and add 1.5 cm³ of 10 % NaOH solution, 1 cm³ of 8-hydroxyquinoline solution and 0.5 cm³ of sodium hypobromite solution.

Test tube B₃ (Sample).

Place 0.1 cm³ of the analyzed solution into a test tube and add 1.5 cm³ of 10 % NaOH solution, 1 cm³ 8-hydroxyquinoline solution and 0.5 cm³ of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange colour. Add 0.2 cm³ of 8 M urea solution to each test tube, mix the contents and transfer about 3 cm³ of each mixture to the corresponding cells labelled A₃ (for reference) and B₃ (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cells to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:

The values of extinction coefficients: Product of Ellmann reaction: 13600 M ⁻¹ cm ⁻¹ at 410 nm Product of Pauli reaction: 6400 M ⁻¹ cm ⁻¹ at 470 nm Product of Sakaguchi reaction: 7700 M ⁻¹ cm ⁻¹ at 500 nm	Molar masses of the amino acids. Cysteine: 121 g mol ⁻¹ Histidine: 155 g mol ⁻¹ Arginine: 174 g mol ⁻¹
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1.4 Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

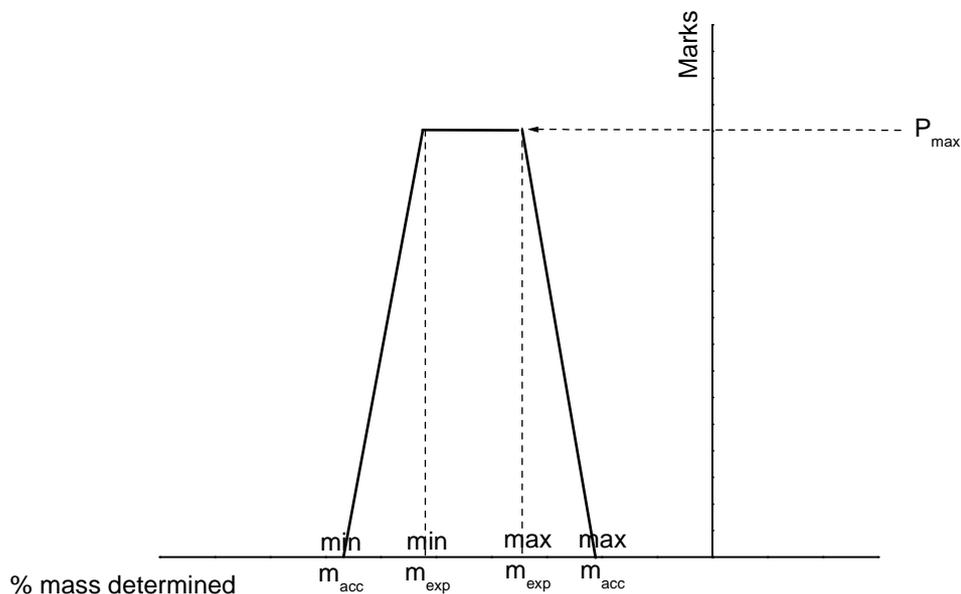
SOLUTION

1.2 – 1.3

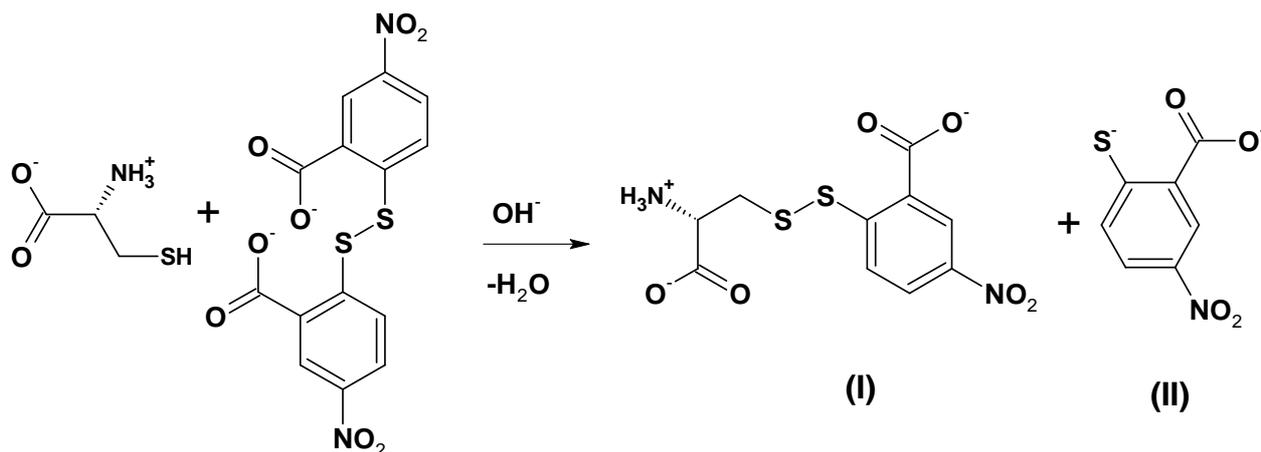
$$\text{Content of an amino acid} = \frac{A_{\lambda} n V M}{\epsilon l},$$

A_{λ} is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 cm³) and the final volume of the sample in the cells, V is the volume of the combined fraction from the corresponding peak, and M is the molar mass of the amino acid.

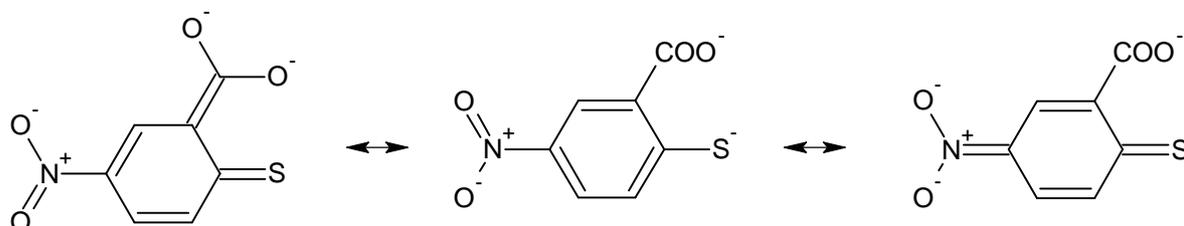
Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer).



1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.



Under slightly alkaline conditions, thiol group of (II) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:



The electronic structure of asymmetrical disulfide (I) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing C=S bond).

PROBLEM 2 (Practical)

Determination of Carbonate and Hydrogen Phosphate in an Abrasive Sample

Na_2CO_3 , CaCO_3 and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4 , whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to H_2PO_4^- ion, the endpoint lying in slightly acidic medium (pH of ~ 4.5). It corresponds to the colour change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colourless to blue (moderately alkaline medium, pH of ~ 10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

- the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
- the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. Dissolution of the sample and removal of CO_2

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 cm^3 (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. 1 mol dm^{-3} HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat

carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2 – 3 min.

Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1 – 2 cm³ of 15 % K₂C₂O₄ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 cm³ of HCl solution into a 100 cm³ volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 cm³ of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1 – 2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5 – 10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 cm³. Report all the final volume values with 0.01 cm³ accuracy.

2.1 a Complete the table in the Answer Sheet.

2.1 b Calculate the concentration of NaOH solution (in mol dm⁻³).

Step 4. Filtering off calcium oxalate

After the most part of CaC₂O₄ precipitates filter the precipitate off collecting the filtrate into a 100 cm³ volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 cm³ aliquot of the sample solution coming from the

step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15 – 20 cm^3 of distilled water. Titrate the sample solution with NaOH solution until the colour coincides with that of the reference solution.

2.2 Complete the table in the Answer Sheet.

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5 – 10 s appears.

2.3 Complete the table in the Answer Sheet.

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+} .

2.6b A list of mistakes possible at different steps is given in the table in the answer sheet.

Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+” or “–” if the result is higher (positive error) or lower (negative error) than the true one.

SOLUTION

2.1 a, 2.2, 2.3

The values of the final volumes $V_{1,f}$, $V_{2,f}$, and $V_{3,f}$, (as reported in the Answer Sheet) were graded according to a scheme approved by the International Jury.

The values of $\Delta V_{\text{expected}}$ and $\Delta V_{\text{acceptable}}$ (in cm^3) are listed in the table below.

	$\Delta V, \text{cm}^3$	
	expected	acceptable
$V_{1,f}$	0.10	0.25
$V_{2,f}$	0.15	0.40
$V_{3,f}$	0.15	0.40

2.1 b Calculation of NaOH concentration

$$c(\text{NaOH}) = \frac{c(\text{HCl}) \times V(\text{HCl}) \times V(\text{aliquot})}{V(\text{flask}) \times V(\text{NaOH})} = \frac{1.214 \text{ mol dm}^{-3} \times 10.00 \text{ cm}^3 \times 10.00 \text{ cm}^3}{100.0 \text{ cm}^3 \times V_{1,f} \text{ cm}^3}$$

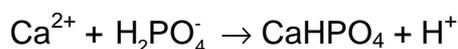
2.4 Calculation of the mass of CO_3^{2-}

$$\begin{aligned} m(\text{CO}_3^{2-}) &= M(\text{CO}_3^{2-}) \times 1/2 \times \frac{c(\text{NaOH}) \times (V_{1,f} - V_{3,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\ &= 60.01 \text{ g mol}^{-1} \times 1/2 \times \frac{c(\text{NaOH}) \text{ mol dm}^{-3} \times (V_{1,f} - V_{3,f}) \text{ cm}^3 \times 100.0 \text{ cm}^3}{10.00 \text{ cm}^3} \times 0.001 \text{ dm}^3/\text{cm}^3 = \end{aligned}$$

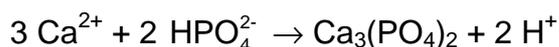
2.5 Calculation of the mass of HPO_4^{2-}

$$\begin{aligned} m(\text{HPO}_4^{2-}) &= M(\text{HPO}_4^{2-}) \times \frac{c(\text{NaOH}) \times (V_{3,f} - V_{2,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\ &= 95.98 \text{ g mol}^{-1} \times \frac{c(\text{NaOH}) \text{ mol dm}^{-3} \times (V_{3,f} - V_{2,f}) \text{ cm}^3 \times 100.0 \text{ cm}^3}{10.00 \text{ cm}^3} \times 0.001 \text{ dm}^3/\text{cm}^3 = \end{aligned}$$

2.6 a



or



40th



International Chemistry Olympiad

**9 theoretical problems
3 practical problems**

THE FORTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 12–21 JULY 2008, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A pH meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

1.1 Give the formulae of four acids that could have been in the solution if the pH changed one unit after a tenfold dilution.

1.2 Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $pK_{a2} = 1.99$

Yes No

If yes, calculate the pH (or at least try to estimate it) and show your work.

1.3 Could it be possible that the solution contained acetic acid?

Acetic acid: $pK_a = 4.76$

Yes No

If yes, calculate the pH (or at least try to estimate it) and show your work.

1.4 Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$

Yes No

If yes, calculate the concentration.

SOLUTION

1.1 Any univalent, strong acid (HCl , HBr , HI , HNO_3 , $HClO_4$) is acceptable. HF is not!

1.2 Yes No

No, the first dissociation step can be regarded as complete in aqueous solutions, thus $[H^+] > c_{\text{acid}}$.

No text or calculations are needed.

1.3 Yes No

Yes, but it can happen only in quite dilute solutions.

$$c = [HA] + [A^-] = [H^+]$$

$$[H^+] = [A^-] + [OH^-]$$

This means that $[HA] = [OH^-]$

$$K = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]([H^+] - [OH^-])}{[OH^-]} = \frac{[H^+]^3}{K_w} - [H^+]$$

The *pH* of the solution must be acidic, but close to 7.

6.5 is a good guess.

A good approximation is: $[H^+] = \sqrt[3]{(K K_w)}$

The full equation can be solved through iteration: $[H^+] = \sqrt[3]{(K + [H^+])K_w}$

Starting with a neutral solution two cycles of iteration give identical results:

$5.64 \times 10^{-7} \text{ mol dm}^{-3}$ as the required concentration. Exact *pH* is 6.25.

1.4 Yes No

We can suppose that this solution would be quite acidic, so the 3rd and 4th dissociation steps can be disregarded. The following equations are thus true:

$$c = [H_4A] + [H_3A^-] + [H_2A^{2-}] = [H^+]$$

$$[H^+] = [H_3A^-] + 2 [H_2A^{2-}]$$

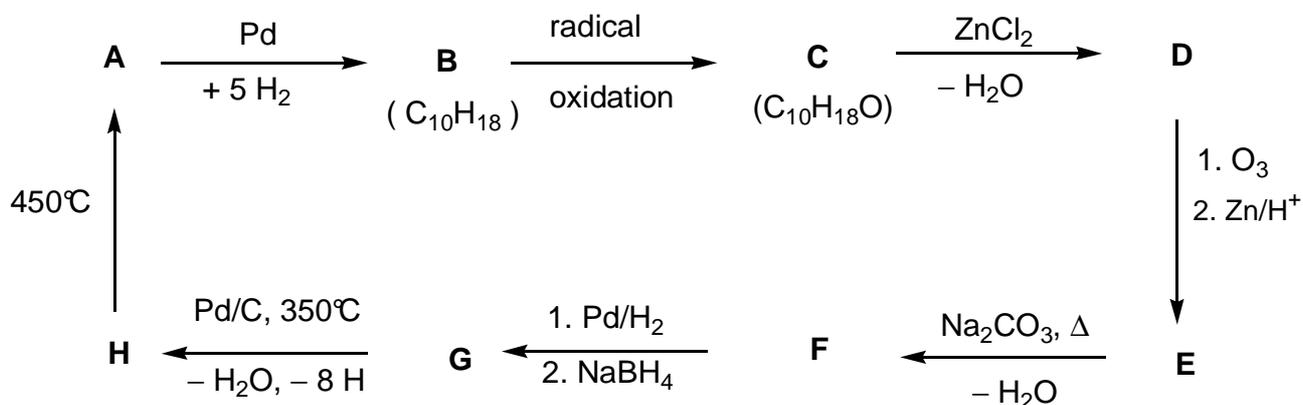
This means that $[H_4A] = [H_2A^{2-}]$

$$K_1 K_2 = \frac{[H^+]^2 [H_2A^{2-}]}{[H_4A]} = [H^+]^2 \quad (\text{or } pH = (pK_1 + pK_2) / 2 = 2.15)$$

$$c = 0.0071 \text{ mol dm}^{-3}$$

PROBLEM 2

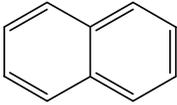
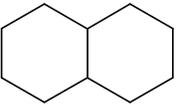
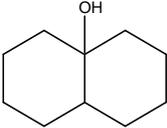
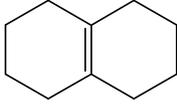
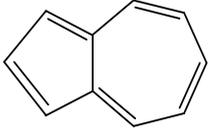
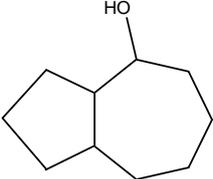
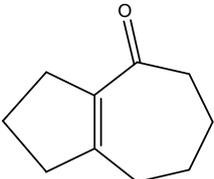
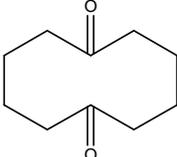
Determine the structure of the compounds **A - H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

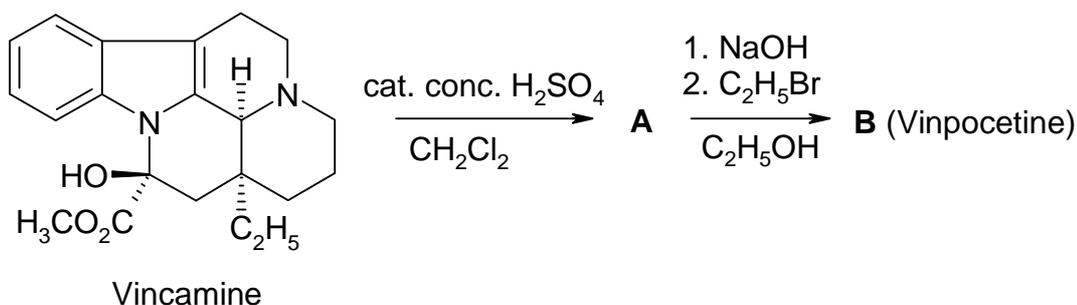
- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ¹³C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH₂ groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

SOLUTION

A 	B 	C 	D 
H 	G 	F 	E 

PROBLEM 3

Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine (C₂₁H₂₆ N₂O₃), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in two steps depicted below.



All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

3.1 Propose structures for the intermediate **A** and vinpocetine (**B**).

A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Hints:

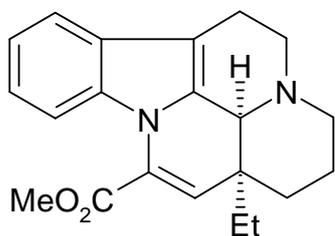
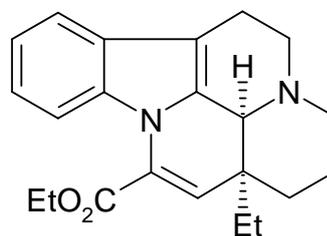
- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**: C 72.11 %, H 7.15 %, N 7.64 %, O 13.10 %.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

3.2 Propose one possible structure for each of the metabolites **C**, **D**, **E** and **F**!

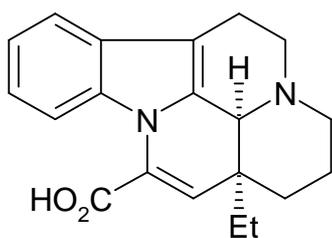
3.3 Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.

SOLUTION

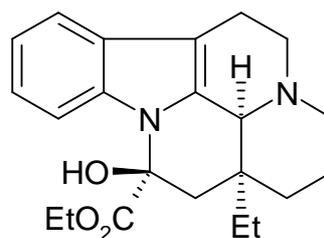
3.1

**A****B**

3.2

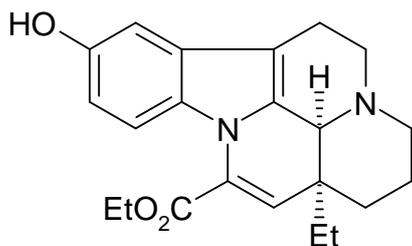
C

apovincaminic acid

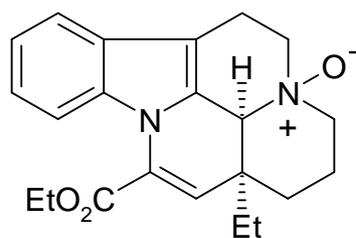
D

ethyl vincamate

Both stereoisomers around the new chiral center are acceptable.

E

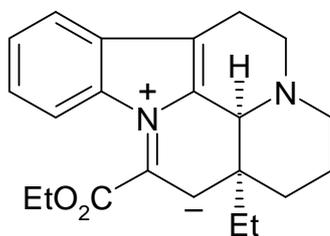
10-hydroxyvinpocetine

F

vinpocetine N-oxide

All aromatic positions for the OH are acceptable in **E**.

3.3



All aromatic positions for the OH are acceptable in **E**.

PROBLEM 4

A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

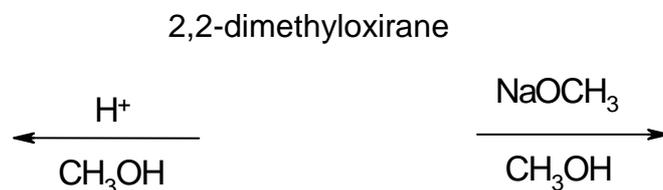
On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

On base catalysis the sterically less hindered C–O bond is cleaved predominantly. Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the \blacktriangleleft \cdots — bond symbols and nothing else where necessary.

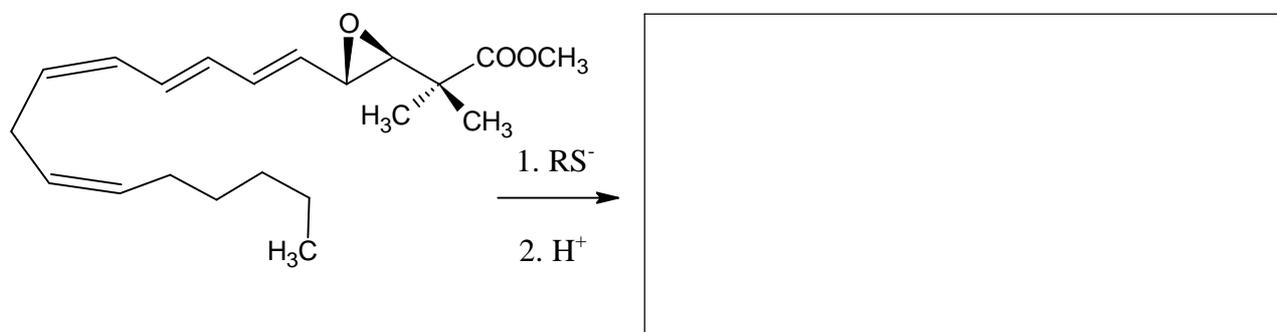
4.1 Draw the structure of the reactant and the predominant products when 2,2-dimethyloxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by

(i) sulphuric acid

(ii) NaOCH₃.



4.2 Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS[−]).



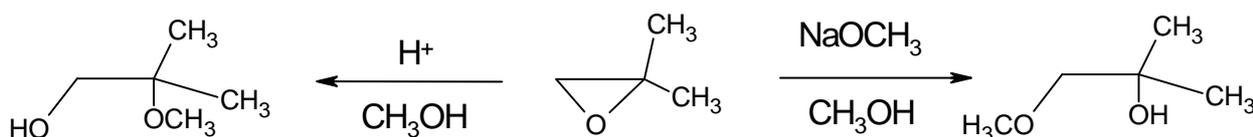
Different porous acidic aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

- 4.3** Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (*S*)-2-methyloxirane ((*S*)-1,2-epoxypropane). Give the structure of the reactant as well.
- 4.4** Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (*R*)-1,2-epoxy-2-methylbutane ((*R*)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.
- 4.5** Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).

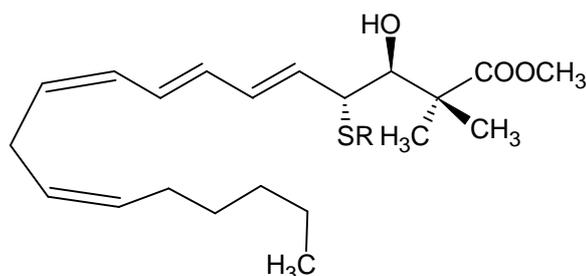
SOLUTION

4.1

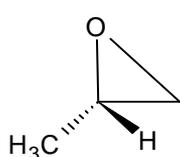
2,2-dimethyloxirane



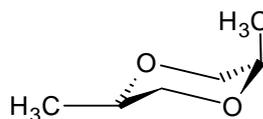
4.2



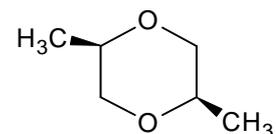
4.3



(S)-2-methyloxirane

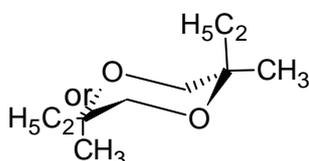
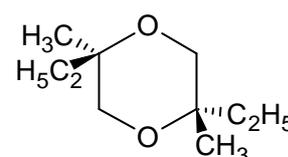
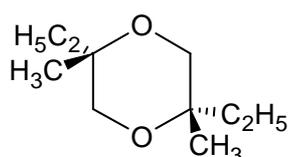
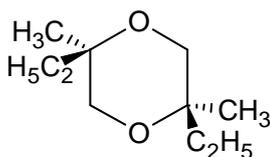
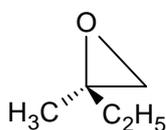


or

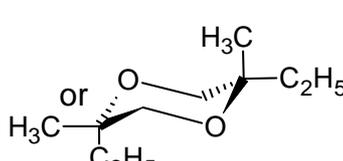


product

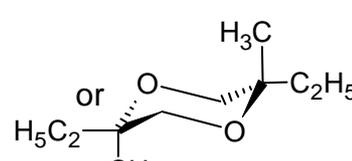
4.4 (R)-1,2-epoxy-2-methylbutane:



R,R

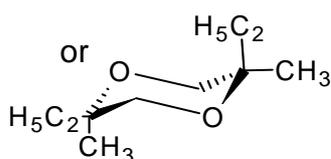
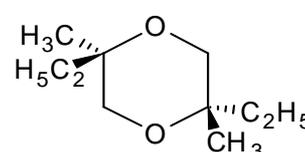
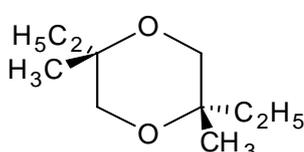
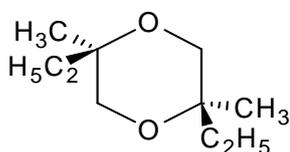


S,S

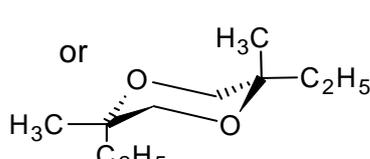


R,S

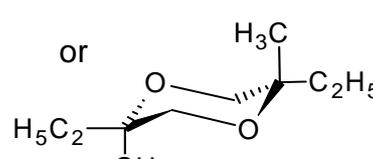
4.5



R,R



S,S



R,S

PROBLEM 5

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 °C) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, $pH \approx 8.5-9$) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, $pH \approx 4.5-5$) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 °C produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 °C is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

5.1 Give the formulae of the substances **A - F**

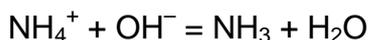
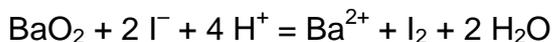
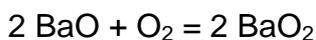
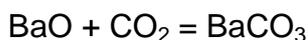
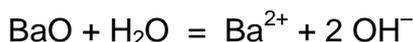
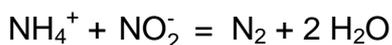
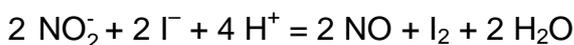
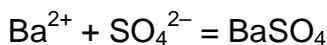
5.2 Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

SOLUTION

5.1 The formulae of the substances **A - F**:

A Ba(NO ₂) ₂	B (NH ₄) ₂ SO ₄	C BaSO ₄
D BaO	E BaCO ₃	F BaO ₂

5.2 Equations:



Detailed solution:

The problem contains quite a number of clues to the identification of the compounds. It is clear that **A**, **D**, **E**, and **F** all contain the same element; with a water-soluble solid compound stable at 1400 °C, probably a metal. The aqueous solution of a metal compound giving a precipitate and pure water upon standing in the air strongly hints at the formation of a carbonate, possibly from a soluble hydroxide. A likely conclusion is that **D** is an oxide, limiting the choice of the metal to Sr or Ba. (One might also consider Li, Ca, or Tl which are less satisfactory because Ca(OH)₂ is poorly soluble while the solubilities of Li₂CO₃ and Tl₂CO₃ are quite significant.) If **E** is an alkaline earth metal carbonate, then the molar mass of **F** could be either $M_{\text{Ca}} + 45.8$, or $M_{\text{Sr}} + 39.05$, or $M_{\text{Ba}} + 32$. Since **F** is formed by heating the oxide in air, the former two do not make any sense while the latter is consistent with BaO₂. This is confirmed by the oxidative capability of **F**.

The odour appearing in the reaction of **B** with Ba(OH)₂ indicates that the former might be an ammonium salt. Assuming that the reaction of **A** and **B** is a simple precipitation between a barium salt and an ammonium salt, we get an equivalent mass of 48 for the anion of the precipitate. This might be either SO₄²⁻ or HPO₄²⁻ but the acidity of **B** is consistent with the former and, in addition, (NH₄)₂HPO₄ would not

give the same BaHPO_4 precipitate with Ba(OH)_2 as with $\text{Ba(NO}_2)_2$. If we accept that **B** is $(\text{NH}_4)_2\text{SO}_4$, we obtain an equivalent mass of 46 for the anion of **A**. This and the surrounding chemistry are consistent with the nitrite ion.

PROBLEM 6

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates. The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm. There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

- 6.1 How many type **A** cavities can be found in a unit cell?
- 6.2 How many water molecules are there in a unit cell?
- 6.3 If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?
- 6.4 Methane hydrate is formed with the structure in **c)** at temperatures between 0-10 °C. What is the density of the clathrate?
- 6.5 The density of chlorine hydrate is 1.26 g/cm³. What is the ratio of the number of water and guest molecules in the crystal?
- Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

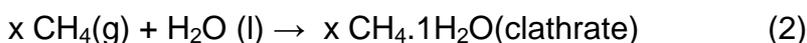
Some **A** Some **B** All **A** All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Non-bonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modelled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

6.6 Based on the covalent and non-bonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes



6.7 What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a -, 0 or +.

	sign
$\Delta G_m(1)$	
$\Delta G_m(2)$	
$\Delta H_m(1)$	
$\Delta H_m(2)$	
$\Delta S_m(1)$	
$\Delta S_m(2)$	
$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta H_m(2) - \Delta H_m(1)$	

SOLUTION

6.1 The number of A cavities in a unit cell: 2

6.2 The number of water molecules in a unit cell?

$$46 = 20 \times 2 \text{ (dodecahedra)} + 6 \times 2 / 2 \text{ (faces)}$$

6.3 The number of water to the number of guest molecules?

$$46 : 8 = 5.75$$

6.4 A unit cell has a volume of $1.182^3 \text{ nm}^3 = 1.651 \text{ nm}^3$.

It contains 8 methane and 46 water molecules with a mass of $957 \text{ g mol}^{-1} / N_A = 1.589 \times 10^{-21} \text{ g}$.

The density is $1.589 / 1.651 = 0.962 \text{ g/cm}^3$.

6.5 The mass of a unit cell with this density is: $1.651 \text{ nm}^3 \times 1.26 \text{ g cm}^{-3} = 2.081 \times 10^{-21} \text{ g}$, meaning 1253 g/mol for the contents.

Subtracting the waters, this means 424.3 g mol^{-1} for the chlorine atoms, giving 11.97 chlorine atoms in a unit cell.

The ratio is then 6 (5.98) chlorine molecules for the 46 waters, or a ratio of 7.68.

It is expected that only the 6 larger B type cavities contain chlorine. Thus:

Some A Some B All A All B

6.6 Methane fits in both cavities, its radius is approximately $37 + 77 + 120 \text{ pm} = 234 \text{ pm}$.

The chlorine molecule, with a radius of $180 + 99 \text{ pm} = 279 \text{ pm}$, fits only in B.

Thus $234 \text{ pm} < r(\text{A}) < 279 \text{ pm}$ and $279 \text{ pm} < r(\text{B})$

6.7

	sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	-
$\Delta H_m(1)$	-
$\Delta H_m(2)$	-
$\Delta S_m(1)$	-
$\Delta S_m(2)$	-
$\Delta S_m(2) - \Delta S_m(1)$	-
$\Delta H_m(2) - \Delta H_m(1)$	-

Under these conditions, methane clathrate forms, while ice melts to water, so the Gibbs energy changes are of opposite signs.

Freezing is an exothermic process with an entropy decrease in both cases.

The entropy decrease of the clathrate formation is larger in magnitude, as it involves a gas-solid transition.

The relation of the reaction enthalpies can be inferred from these facts:

$$\Delta G_m(1) > \Delta G_m(2)$$

$$\Delta H_m(1) - T \Delta S_m(1) > \Delta H_m(2) - T \Delta S_m(2)$$

$$T (\Delta S_m(2) - \Delta S_m(1)) > \Delta H_m(2) - \Delta H_m(1)$$

$$\text{a negative quantity} > \Delta H_m(2) - \Delta H_m(1)$$

PROBLEM 7

The dithionate ion ($\text{S}_2\text{O}_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

7.1 Write the balanced chemical equations for the two reactions.

After the reaction is complete, $\text{Ba}(\text{OH})_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3 .

7.2 Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3 .

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with BaCl_2 solution. When the solid is heated and maintained at $130\text{ }^\circ\text{C}$, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with BaCl_2 solution. When another sample of the original crystals is kept at $300\text{ }^\circ\text{C}$ for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with BaCl_2 solution.

7.3 Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At $75\text{ }^\circ\text{C}$, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

7.4 Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at $75\text{ }^\circ\text{C}$.

$[\text{Br}_2]_0$ (mmol dm^{-3})	$[\text{Na}_2\text{S}_2\text{O}_6]_0$ (mol dm^{-3})	$[\text{H}^+]_0$ (mol dm^{-3})	v_0 ($\text{nmol dm}^{-3}\text{s}^{-1}$)
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

7.5 Determine the order of the reaction with respect to Br_2 , H^+ and $\text{S}_2\text{O}_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are 2.53×10^{-5} (Cl_2), 2.60×10^{-5} (BrO_3^-), 2.56×10^{-5} (H_2O_2), and 2.54×10^{-5} ($\text{Cr}_2\text{O}_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

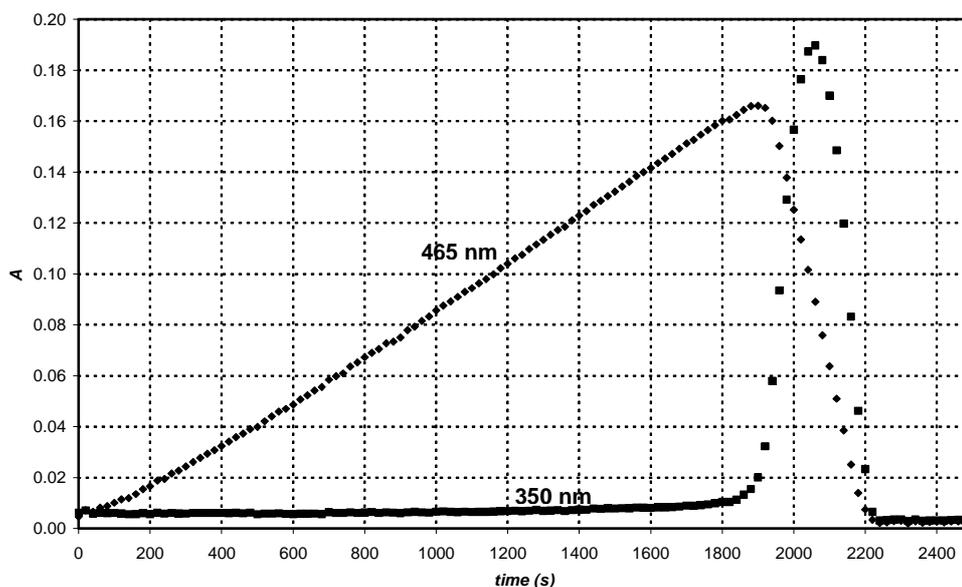
7.6 Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0022 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.70 \text{ mol dm}^{-3}$, and the temperature was 75 °C. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

7.7 Calculate the rate constant of the reaction.

Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as H_4IO_6^- in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 °C in the same experiment at two different wavel engths. The initial concentrations were $[\text{H}_4\text{IO}_6^-] = 5.3 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0519 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.728 \text{ mol dm}^{-3}$. At 465 nm, only I_2 absorbs and its molar absorption coefficient is $715 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is $11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The optical path length was 0.874 cm.

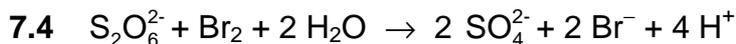
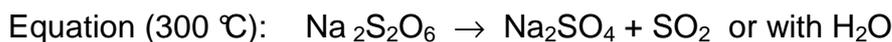
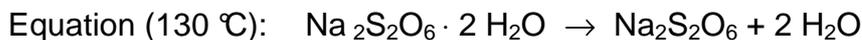
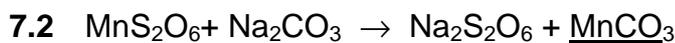
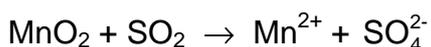


7.8 Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

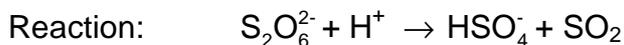
Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm.

SOLUTION



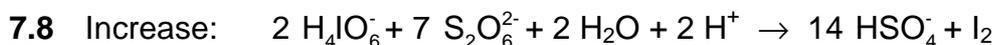
$$k = 2.56 \cdot 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

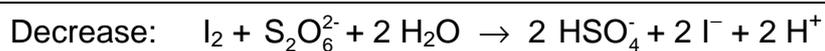


7.7 $t_{1/2} = 10 \text{ h } 45 \text{ min} = 3.87 \cdot 10^4 \text{ s}$

$$k_{\text{obs}} = \ln 2 / t_{1/2} = 1.79 \times 10^{-5} \text{ s}^{-1}$$

$$k = k_{\text{obs}} / [\text{H}^+] = 2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$





The expected time for the maximum absorbance of the kinetic curve measured at 465 nm:

$$t_{\max} = \frac{7}{2} \frac{[\text{H}_4\text{IO}_6^-]_0}{k[\text{S}_2\text{O}_6^{2-}]_0[\text{H}^+]_0} = \frac{7 \times 5.3 \times 10^{-4} \text{ M}}{2 \times 2.56 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1} \times 0.0519 \text{ M} \times 0.728 \text{ M}} = 1900 \text{ s}$$

The expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm: 1; -7 (it reflects the stoichiometry).

PROBLEM 8

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-VIS absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified CeCl₃ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c_{NaCl} (mol/dm ³)	E (mV)
0.1000	26.9
1.000	-32.2

8.1 Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

Ms. Z also determined the molar absorption coefficient for Ce³⁺ ($\epsilon = 35.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 295 nm, and, as a precaution, also for Ce⁴⁺ ($\epsilon = 3967 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

8.2 Give a formula to calculate the Ce³⁺ concentration from an absorbance reading at 295 nm (A) measured in a solution containing CeCl₃ (cuvette path length: 1.000 cm).

Ms. Z prepared a solution which contained 0.0100 mol/dm³ CeCl₃ and 0.1050 mol/dm³ HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

8.3 What were the expected initial absorbance ($A_{295\text{nm}}$) and voltage (E) readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

8.4 Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectrophotometric measurements is ± 0.002 and the accuracy of the voltage measurements is ± 0.3 mV.

time (min)	0	120	240	360	480
$A_{295\text{ nm}}$	0.349	0.348	0.350	0.348	0.349
	6	8	4	9	9
E (mV)	19.0	18.8	18.8	19.1	19.2

8.5 Estimate the average rate of change in the concentrations of Ce^{3+} , Cl^- , and H^+ .
 $d[\text{Ce}^{3+}]/dt = d[\text{Cl}^-]/dt = d[\text{H}^+]/dt = ?$

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic CeCl_3 solution she had used before. She measured the molar absorption coefficient for Ce^{3+} ($\epsilon = 2400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 254 nm.

8.6 What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3 . The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was $22.0 \text{ }^\circ\text{C}$.

8.7 Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

- 8.8 Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.
- 8.9 What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?
- 8.10 Estimate the quantum yield of product formation in the Ce(III) solution.

SOLUTION

$$8.1 \quad [\text{Cl}^-] = 10^{-(E+32.2\text{mV})/59.1\text{mV}}$$

$$8.2 \quad [\text{Ce}^{3+}] = \frac{A_{295\text{nm}}}{35.2\text{dm}^3\text{mol}^{-1}}$$

$$8.3 \quad [\text{Ce}^{3+}] = 0.0100\text{ mol/dm}^3 \Rightarrow A_{295\text{nm}} = 0.352$$

$$[\text{Cl}^-] = 3 \cdot 0.0100\text{ mol/dm}^3 + 0.1050\text{ mol/dm}^3 = 0.1350\text{ mol/dm}^3 \Rightarrow E = 19.2\text{ mV}$$

8.4 HCl, Cl₂, (O₃, ClO₂) (no oxidation of indicator)

$$8.5 \quad d[\text{Ce}^{3+}]/dt = ? \quad d[\text{Cl}^-]/dt = ? \quad d[\text{H}^+]/dt = ?$$

No significant change in either Cl⁻ or Ce³⁺ concentrations.

$$[\text{H}^+] = [\text{Cl}^-] - 3[\text{Ce}^{3+}], \text{ no significant change.}$$

All three values are zero.

8.6 What percentage of the light is absorbed in this experimental setup?

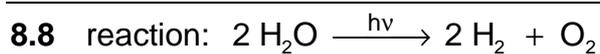
$$A = 2400\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 5\text{ cm} \times 0.0100\text{ M} = 120 \Rightarrow (100 - 10^{-118})\% \approx 100\%$$

$$8.7 \quad p_{\text{partial}} = p_{\text{final}} - p_{\text{initial}} = 114075\text{ Pa} - 102165\text{ Pa} = 11910\text{ Pa}$$

$$n = p_{\text{partial}} V / (RT) = 11910\text{ Pa} \cdot 0.000068\text{ m}^3 / (8.314\text{ J mol}^{-1}\text{ K} \times 295.15\text{ K}) =$$

$$= 3.3 \times 10^{-4}\text{ mol}$$

identity of gases: H₂, O₂



8.9 Final pressure: 104740 Pa (saturated water vapour)

8.10 Quantum yield:

3.3×10^{-4} mol gas formed altogether: 2.2×10^{-4} mol H_2 and 1.1×10^{-4} mol O_2 .

$$\text{Light beam intensity } 0.0500 \text{ J s}^{-1} \Rightarrow \frac{0.0500 \text{ J s}^{-1} \lambda}{h c N_A} = 1.06 \times 10^{-7} \text{ mol s}^{-1} \text{ photon}$$

Total time 18.00 h = 64800 s

Total number of absorbed photons: $64800 \text{ s} \times 1.06 \times 10^{-7} \text{ mol s}^{-1} = 6.87 \times 10^{-3} \text{ mol}$

Quantum yield for H_2 production: $\Phi = 2.2 \times 10^{-4} \text{ mol} / 6.87 \times 10^{-3} \text{ mol} = 0.032$

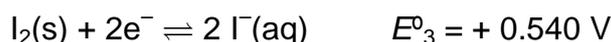
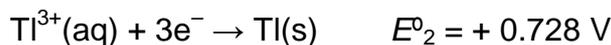
Quantum yield for O_2 production: $\Phi = 1.1 \times 10^{-4} \text{ mol} / 6.87 \times 10^{-3} \text{ mol} = 0.016$

Either value or the quantum yield of the gas production (0.048) is acceptable when demonstrated in a calculation.

PROBLEM 9

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+} . Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

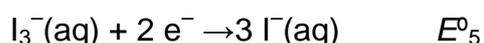
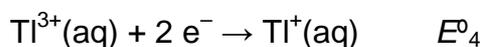
The standard redox potentials for some relevant reactions are:



The equilibrium constant for the reaction $\text{I}_2(\text{s}) + \text{I}^-(\text{aq}) \rightarrow \text{I}_3^-(\text{aq})$: $K_1 = 0.459$.

Use $T=25 \text{ }^\circ\text{C}$ throughout this problem.

9.1 Calculate the redox potentials E°_4 and E°_5 for the following reactions:



9.2 Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one? Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $\text{Tl}^{3+} + 4\text{I}^- \rightarrow \text{TlI}_4^-$ is $\beta_4 = 10^{35.7}$

9.3 Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant K_2 for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

9.4 What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

SOLUTION

$$9.1 \quad E_4^0 = \frac{3E_2^0 - E_1^0}{2} = 1.26 \text{ V}$$

$$E_5^0 = E_3^0 + 0.059 / 2 \log(1 / K_1) = 0.550 \text{ V}$$

9.2 Tl I, Tl I₃, Tl I₅, Tl I₇, Tl I₉

Tl I₃ can be either Tl³⁺(I⁻)₃ or Tl⁺(I₃⁻)

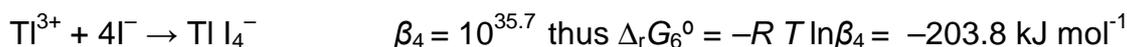
More stable: Tl⁺(I₃⁻)

as $E_4^0 > E_5^0$ or E_3^0 ,

Isomerisation: Tl³⁺ + 3 I⁻ = Tl⁺ + I₃⁻

9.3 Reaction: Tl⁺ + I₃⁻ + I⁻ → Tl I₄⁻

This reaction could be regarded as sum of three reactions:



The net free enthalpy change is $\Delta_r G_7^0 = \Delta_r G_4^0 + \Delta_r G_5^0 + \Delta_r G_6^0 = -66.8 \text{ kJ mol}^{-1}$

$$\text{Thus } K_2 = \exp\left(-\frac{\Delta_r G_7^0}{RT}\right) = 4.96 \cdot 10^{11}$$

9.4 Supposing that the substance contains Tl and an anion, the formula of the compound is Tl_aX_b and the following equation holds:

$$\frac{a \cdot 204.4}{a \cdot 204.4 + bM_X} = 0.895$$

From the values $b = 1, 3$ and $a = 1, 2, 3$ only $b = 3, a = 2$ gives a realistic:

$$M_X = 16.0 \text{ g mol}^{-1}.$$

X is oxygen.

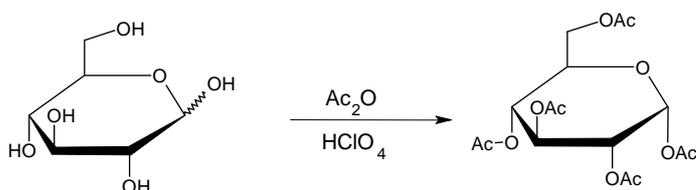
Formula: Tl₂O₃.

Equation: 2 Tl I₃ + 6 OH⁻ → Tl₂O₃ + 6 I⁻ + 3 H₂O

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of α -D-glucopyranose pentaacetate

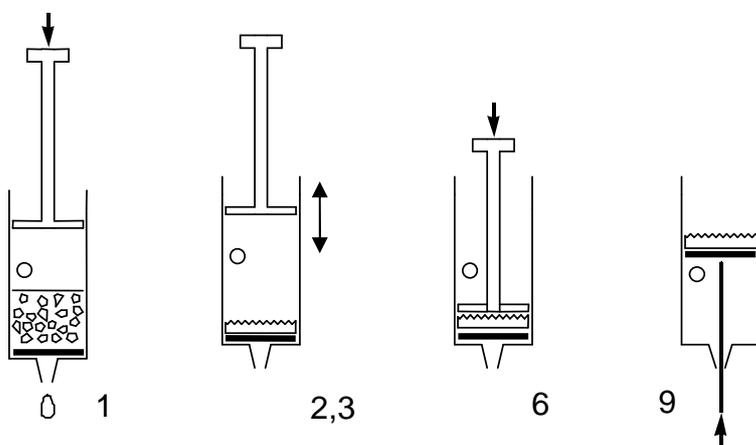


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm³ of pure acetic acid to 12 cm³ of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is in excess). Add with a Pasteur-pipette 5 drops of 30% HClO₄ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm³ of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm³ of water using the syringe and the porous polypropylene filter disc.

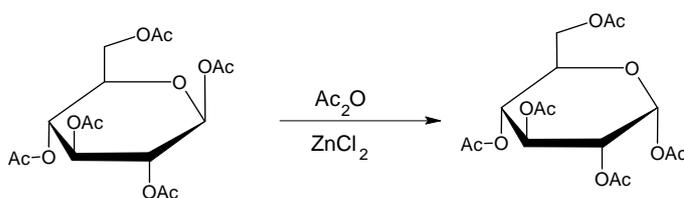
Filtration using a plastic syringe



1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
 2. Cover the hole with your finger and press in the piston as far as the hole.
 3. Open the hole and draw the piston back. Do not draw in air through the filter.
 4. Repeat steps 2-3 a few times to expel the liquid.
 5. Repeat steps 1-4 until all solids are on the filter.
 6. Press the piston against the filter cake and squeeze out the liquid.
 7. Wash the product twice with 10 cm³ of water repeating steps 1-4.
 8. Press the piston against the filter cake and squeeze out the water.
 9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)
- 1.1 Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.
 - 1.2 Calculate the theoretical yield (mass) of your product in g. ($M(C) = 12 \text{ g mol}^{-1}$, $M(O) = 16 \text{ g mol}^{-1}$, $M(H) = 1.0 \text{ g mol}^{-1}$)

Synthesis of α -D-glucopyranose pentaacetate from β -D-glucopyranose pentaacetate

An alternative synthesis of α -D-glucopyranose pentaacetate starts from readily available β -D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm³ acetic anhydride to 50 mg of anhydrous ZnCl₂ (preweighed in a test tube). Add 100 mg of pure β -D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm³ methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70°C. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture

with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm³ of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun (under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

1.3 Copy your plate on the answer sheet and place your plate in the labelled zip lock bag.

1.4 Interpret your experiment and choose the correct answer.

The acetylation reaction of glucose is exothermic.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

The isomerisation reaction of β -D-glucopyranose pentaacetate can be used for the preparation of pure α -D-glucopyranose pentaacetate.

- a) Yes
 - b) No
 - c) Cannot be decided based on these experiments
-

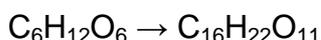
SOLUTION

1.1 Yield of the product in g, measured by the organizer.

The samples are dried by the organisers. The typical yield is 70 %.

Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.

1.1 Calculation of the theoretical yield of the product in g:



$$m = \frac{3.00 \text{ g} \times 390 \text{ g mol}^{-1}}{180 \text{ g mol}^{-1}} = 6.50 \text{ g}$$

1.3 The developed TLC plate was expected to be sketched on the answer sheet.

Full points were given if both standards and all samples are present.

1.4 Solutions: a), a).

PROBLEM 2 (Practical)

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6] \cdot 3H_2O$ ($M = 422.41$ g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm³ volumetric flask. Take 10.00 cm³ portions of the hexacyanoferrate(II) solution. Add 20 cm³ 1 mol/dm³ sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the 0.05136 mol/dm³ Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming Ce(III).

2.1 Report the Ce^{4+} solution volumes consumed.

2.2 Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6] \cdot 3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm³ of the hexacyanoferrate(II) solution and add 20 cm³ 1 mol/dm³ sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

2.3 Report the zinc solution volumes consumed.

2.4 Interpret the titration answering the questions on the answer sheet.

Mark the correct answer:

The diphenyl amine indicator changes in colour at the end point

- a) because the concentration of the Zn^{2+} ions increases.
- b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.
- c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.
- d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

- a) Oxidized
 b) Reduced
 c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

- a) True
 b) False

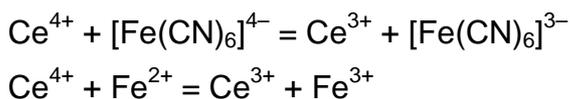
2.5 Determine the formula of the precipitate.

SOLUTION

2.1 Ce^{4+} consumptions:

Full marks if V_1 is within 0.15 cm^3 of the expected value recalculated from the $\text{K}_4[\text{Fe}(\text{CN})_6]$ mass. Zero marks if deviation is more than 0.50 cm^3 . Linear scale is applied in between.

2.2 The titration reaction:



2.3 Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $\text{K}_4[\text{Fe}(\text{CN})_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3 . Linear scale is applied in between.

2.4 Solutions: b), b), a)

2.5 Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc : hexacyanoferrate(II) in the precipitate can be evaluated as:

$$\frac{n(\text{Zn})}{n(\text{Fe}(\text{CN})_6)} = \frac{10 c(\text{Zn}) V_2 M}{m}$$

Values for $c(\text{Zn})$ are distributed according to a certain plan.

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio:

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($\text{H}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ or $\text{KHZn}_3[\text{Fe}(\text{CN})_6]_2$) is also acceptable.

PROBLEM 3 (Practical)

Caution:

Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.

The heat gun heats the expelled air up to 500 °C. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.

Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+ , NH_4^+ , Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Sr^{2+} , Ag^+ , Sn^{2+} , Sn^{4+} , Sb^{3+} , Ba^{2+} , Pb^{2+} , Bi^{3+}

Anions: OH^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , NO_3^- , F^- , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , HSO_4^- , S^{2-} , HS^- , Cl^- , ClO_4^- , MnO_4^- , Br^- , I^-

You have test tubes and heating at your disposal but no additional reagents apart from distilled water and *pH* paper.

Identify the compounds in the solutions **1-8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks: The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

SOLUTION

The solutions received by the students contain the following compounds in eight test-tubes: AgNO_3 , BaI_2 , KHCO_3 , MgSO_4 , NaHS , NaOH , NH_4ClO_4 , $\text{Pb}(\text{CH}_3\text{COO})_2$ ($\text{Pb}(\text{OAc})_2$). There were eight sets of samples differing in order of the compounds in particular test tubes.

The problem can be approached in many ways. A systematic solution is given here for one of the sets of test tubes with the following order of the compounds:

Test tube No	1	2	3	4	5	6	7	8
Compound	AgNO_3	KHCO_3	NH_4ClO_4	NaOH	NaHS	$\text{Pb}(\text{OAc})_2$	BaI_2	MgSO_4

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (pH paper reading about 5-6). Solution **2** is basic ($\text{pH} = 9$) while solutions **4** and **5** are very strongly basic ($\text{pH} > 11$).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and MnO_4^- . (In principle we should also exclude Mn^{2+} but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H^+ , Sn^{2+} , Sn^{4+} , Sb^{3+} , Bi^{3+} , and HSO_4^- with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH_4^+ , Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Mn^{2+} , Zn^{2+} , Sr^{2+} , Ag^+ , Ba^{2+} , Pb^{2+} .

Anions: OH^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , NO_3^- , F^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , S^{2-} , HS^- , Cl^- , ClO_4^- , Br^- , I^- .

The unknown solutions react with each other as follows (\downarrow = precipitate; \uparrow = volatile product; "no change" means even when boiled, unless indicated otherwise):

	1	2	3	4	5	6	7	8
	AgNO ₃	KHCO ₃	NH ₄ ClO ₄	NaOH	NaHS	Pb(OAc) ₂	BaI ₂	MgSO ₄
1 AgNO ₃	—	—	—	—	—	—	—	—
2 KHCO ₃	↓ light yellow ↑ neutral, odourless	—	—	—	—	—	—	—
3 NH ₄ ClO ₄	no change	↓ white crystals (*)	—	—	—	—	—	—
4 NaOH	↓ brown-black	no change	boiling: ↑ basic, odour of ammonia	—	—	—	—	—
5 NaHS	↓ black solution turns acidic	no change	boiling: ↑ basic, odour of NH ₃ , H ₂ S	no change	—	—	—	—
6 Pb(OAc) ₂	↓ white crystals	↓ white ↑ neutral, odourless	no change	↓ white	↓ black	—	—	—
7 BaI ₂	↓ yellow	↓ white ↑ (**)	no change	no change	no change	↓ yellow	—	—
8 MgSO ₄	↓ white crystals	no change (***)	no change	↓ white	no change (****)	↓ white	↓ white	—

(*): upon boiling, the formation of NH₃ is detectable by its odour and by *pH* paper.

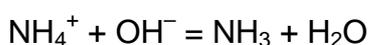
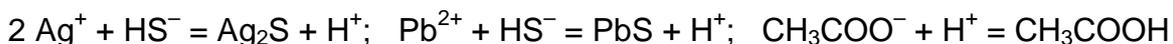
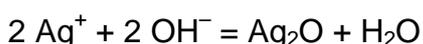
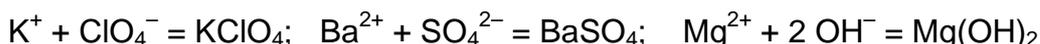
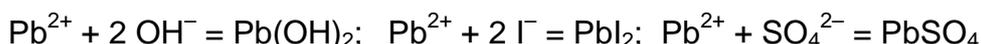
(**): gas bubbles are usually not observed when **2** is in excess.

(***): upon boiling, an odourless gas evolves and a white precipitate forms.

(****): upon boiling, a white precipitate forms and the odour of H₂S appears.



$\text{Mg}^{2+} + 2 \text{HCO}_3^- = \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ (more accurately, basic carbonates of variable composition are formed)



Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2 . Thus **2** contains CO_3^{2-} or HCO_3^- .

Second, there are only 3 dark precipitates that can be formed from the given ions: Ag_2O , Ag_2S , and PbS . This fact, together with the *pH* of the solutions, instantly identifies the cation of **1** as Ag^+ , the cation of **6** as Pb^{2+} , the anion of **4** as OH^- , and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the *pH* of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is HS^- .

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as HCO_3^- . (in accord with the moderately basic *pH*)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is NH_4^+ .

2+4 form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+ .

2+5 do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+ . Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+ . Thus the anion of **3** is ClO_4^- and the cation of **2** is K^+ . **4** does not give a precipitate with NH_4ClO_4 . The cation of **4** is Na^+ .

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of KHCO_3 and NaOH (Li^+). The cation of **5** is **Na^+** .

7 forms no precipitate or ammonia with NaOH but gives a precipitate with KHCO_3 . **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is **Ba^{2+}** and the anion of **7** is I^- .

At room temperature **8** gives a precipitate with OH^- but not with HS^- which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one between Ba^{2+} and the anion of **8**. The latter is very likely SO_4^{2-} but HCO_3^- and H_2PO_4^- are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+ . This excludes both HCO_3^- and H_2PO_4^- . Thus the anion of **8** is **SO_4^{2-}** . This instantly identifies the cation of **8** as **Mg^{2+}** .

6 is a soluble compound of lead. The anion could be CH_3COO^- , NO_2^- , NO_3^- , or ClO_4^- . The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with HS^- does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+ . It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with HS^- would also be noticeable). The absence of these reactions indicates that the anion of **6** is **CH_3COO^-** .

Soluble salts of silver are even less numerous, the only choices are NO_3^- , F^- , and ClO_4^- . The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH . The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out F^- . The solubility of KClO_4 is quite significant; therefore the absence of a precipitate with KHCO_3 is inconclusive. The anion of **1** is therefore either **NO_3^-** or **ClO_4^-** .

QUANTITIES AND THEIR UNITS USED IN THIS PUBLICATION

SI Basic Units

Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol

Special names and symbols for certain derived SI Units

Force	F	Newton	N
Pressure	p	pascal	Pa
Energy	E	joule	J
Power	P	watt	W
Electric charge	Q	coulomb	C
Electric potential difference	U	volt	V
Electric resistance	R	ohm	Ω

Other derived SI Units used in chemistry

Area	S	square metre	m^2
Volume	V	cubic metre	m^3
Density	ρ	kilogram per cubic metre	$kg\ m^{-3}$
Concentration	c	mole per cubic metre	$mol\ m^{-3}$ ($mol\ dm^{-3}$)
Molar mass	M	kilogram per mole	$kg\ mol^{-1}$ ($g\ mol^{-1}$)

Some other quantities and constants

Relative atomic mass of an element	A_r
Relative molecular mass of a compound	M_r
Molar fraction	x
Mass fraction	w
Volume fraction	φ
Enthalpy	H
Entropy	S
Gibbs energy	G
Temperature in Celsius scale	$^{\circ}\text{C}$

Elementary charge, e	$1.6021892 \times 10^{-19} \text{ C}$
Planck constant, h	$6.626176 \times 10^{-34} \text{ J s}$
Avogadro constant, A	$6.022045 \times 10^{23} \text{ mol}^{-1}$
Faraday constant, F	$9.648456 \times 10^4 \text{ C mol}^{-1}$
Gas constant, R	$8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$
Zero of Celsius scale, T_0	$273.15 \text{ K (exactly)}$
Normal pressure, p_0	$1.01325 \times 10^5 \text{ (exactly)}$
Standard molar volume of ideal gas, V_0	$2.241383 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$

Abbreviations and Mathematical symbols

IChO	International Chemistry Olympiad
STP	Standard temperature and pressure (T_0, p_0)
M	molar, mol dm^{-3}
N	normal
$\hat{=}$	corresponds to
\approx	approximately equal to
\sim	proportional to
\Rightarrow	implies