21st

6 theoretical problems
2 practical problems

THE TWENTY-FIRST
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THEORETICAL PROBLEMS

PROBLEM 1

To determine the solubility product of copper(II) iodate, $Cu(IO_3)_2$, by iodometric titration in an acidic solution (25 °C) 30.00 cm^3 of a 0.100 molar sodium thiosulphate solution are needed to titrate 20.00 cm^3 of a saturated aqueous solution $Cu(IO_3)_2$.

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

1.1 $2\ Cu^{2+} + 4\ IO_3^- + 24\ I^- + 24\ H^+ \rightarrow 2\ CuI + 13\ I_2 + 12\ H_2O$ (1)

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$ (2)

1.2 From (2):

$n(S_2O_3^{2-}) = c\ V = 0{,}100 \text{ mol dm}^{-3} \times 0{,}03000 \text{ dm}^3 = 3.00\times10^{-3} \text{ mol}$

From (2) and (1):

$n(I_2) = 1.50\times10^{-3}$ mol

$$n(Cu^{2+}) = \frac{1.50\times10^{-3}\text{ mol}}{13}\times 2 = 2.31\times10^{-4}\text{ mol}$$

$$c(Cu^{2+}) = \frac{2.31\times10^{-4}\text{ mol}}{0.02000\text{ dm}^3} = 1.15\times10^{-2}\text{ mol}$$

$[Cu^{2+}] = 1.15\times10^{-2}$

$[IO_3^-] = 2\,[Cu^{2+}]$

$K_{sp} = [Cu^{2+}]\,[IO_3^-]^2 = 4\,[Cu^{2+}]^3 = 4 \times (1.15\times10^{-2})^3 = 6.08\times10^{-6}$

PROBLEM 2

A mixture of gases containing mainly carbon monoxide and hydrogen is produced by the reaction of alkanes with steam:

$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$ $\Delta H = 36$ kJ mol^{-1} (1)

$CH_4 + H_2O \rightarrow CO + 3 H_2$ $\Delta H = 216$ kJ mol^{-1} (2)

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.

$CO + H_2O \rightarrow CO_2 + H_2$

2.3 Calculate the number of moles of each gas leaving the reactor.

SOLUTION

2.1 $6 CH_4 + 3 O_2 \rightarrow 6 CO + 12 H_2$ $\Delta H = – 216$ kJ mol^{-1}

$CH_4 + H_2O \rightarrow CO + 3 H_2$ $\Delta H = 216$ kJ mol^{-1}

$7 CH_4 + 3 O_2 + H_2O \rightarrow 7 CO + 15 H_2$ $\Delta H = 0$ kJ mol^{-1}

a) For a pressure increase in two steps under the conditions given, the work of compression is:

$$W_2 = n_1\, RT \ln\frac{p_1}{p_2} + n_2\, RT \ln\frac{p_2}{p_1} = n_1\, RT (\ln\frac{p_1}{p_0} + 2\ln\frac{p_2}{p_1})$$

$$= 100\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 500\ \text{K} \times \left(\ln\frac{3.0\ \text{MPa}}{0.1\,\text{MPa}} + 2\ln\frac{6.0\ \text{MPa}}{3.0\ \text{MPa}}\right) = 1.99\ \text{MJ}$$

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:

$$K = \frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}} = \frac{(18 + x)\,(40 + x)}{(40 - x)\,(200 - x)}$$

$x_{1/2} = 184 \pm 151.6$; $x_1 = 33.2$; $x_2 = 336.4$

The composition of the leaving gas is:

6.8 mol CO, 51.2 mol CO_2, 2.0 mol CH_4 and N_2, 73.2 mol H_2 and 166.8 mol H_2O.

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 m^3/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 m^3 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 $K_{a,1}(H_2SO_3) = 10^{-2.25}$.

Assume ideal gases and a constant temperature of 0 °C at standard pressure.

$M(CaCO_3) = 100 \text{ g mol}^{-1}$; $M(CaSO_4) = 172 \text{ g mol}^{-1}$.

SOLUTION

3.1 $SO_2 + CaCO_3 + ½\, O_2 + 2\, H_2O \rightarrow CaSO_4 \,.\, 2\, H_2O + CO_2$

$SO_2 + Ca(OH)_2 + ½\, O_2 + H_2O \rightarrow CaSO_4 \,.\, 2\, H_2O$

3.2 Under given conditions:

$n(SO_2)/h = v(SO_2/h) \,/\, V = 669.34 \text{ mol h}^{-1}$

$m(CaCO_3/d) = n(SO_2/h) \times M(CaCO_3) \times 24 \text{ h} \cdot \text{d}^{-1} \times 0.95 = 1.53\times10^3 \text{ kg/d}$

$$m(\text{CaSO}_4 \,.\, 2\,\text{H}_2\text{O}) = \frac{M(\text{CaSO}_4 \,.\, 2\,\text{H}_2\text{O})}{M(\text{CaCO}_3)} \times m(\text{CaCO}_3)\,/\,\text{d} = 2.63\times10^3\ \text{kg/d}$$

3.3 $pH = -\log[H_3O^+]$; $K_a = \frac{[H_3O^+]^2}{[SO_2] - [H_3O^+]}$

$$[H_3O^+]_{1/2} = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_A\,[SO_2]}$$

Solving for $[H_3O^+]$:

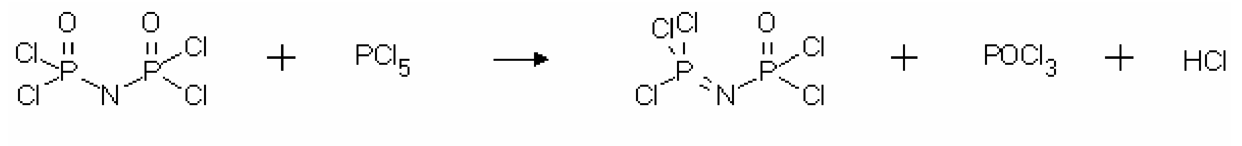
If $[SO_2] = n(SO_2) / V = 1.34\times10^{-4}$ and $K_a = 1\times10^{-2.25}$, then $[H_3O^+] = 1.32\times10^{-4}$ and $pH = 3.88$

3.4 $SO_2 + Na_2SO_3 + H_2O \rightarrow 2\ NaHSO_3$

Possibilities to increase the recovery of SO_2 are: temperature rise, reduced pressure, lower *pH*-value.

PROBLEM 4

^{32}P 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.



I II III IV

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 $Mg(NH_4)PO_4$

III. 28 Bq for 153 mg of $Mg(NH_4)PO_4$

IV. 2627 Bq for 142 mg of $Mg(NH_4)PO_4$

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 $Mg(NH_4)PO_4$: $pK_s = 12.6$

Equilibrium concentration of NH_4^+ = 0.1 mol dm^{-3}

4.6 Calculate the solubility for $Mg(NH_4)PO_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

SOLUTION

4.1 $2\ {}^{32}P + 5\ Cl_2 \rightarrow 2\ {}^{32}PCl_5$

4.2 $PCl_5 + 2\ OH^- \rightarrow POCl_3 + 2\ Cl^- + H_2O$

$POCl_3 + 6\ OH^- \rightarrow PO_4^{3-} + 3\ Cl^- + 3\ H_2O$

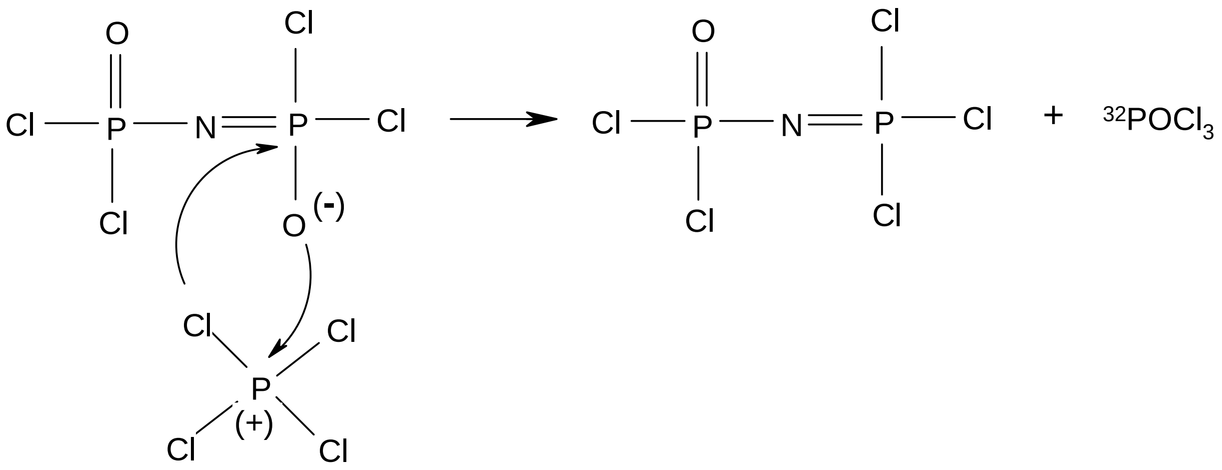
$PCl_5 + 8\ OH^- \rightarrow PO_4^{3-} + 5\ Cl^- + 4\ H_2O$

$Cl_3PNPOCl_2 + 11\ OH^- \rightarrow 2\ PO_4^{3-} + NH_3 + 5\ Cl^- + 4\ H_2O$

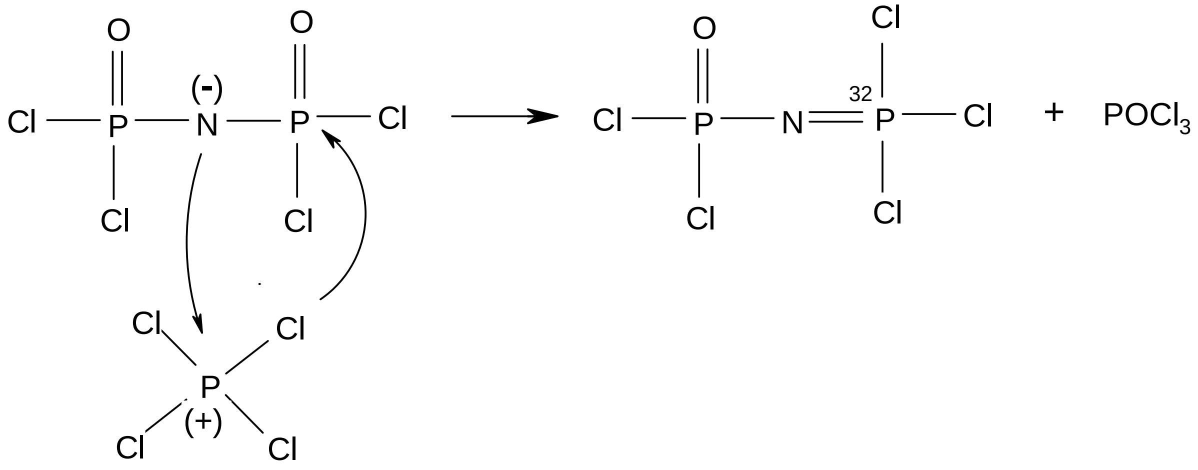
4.3 $A = A_0\ e^{-\lambda t}$ $t_{1/2}$: $A = 0.5\ A_0 \Rightarrow \lambda = \ln 2 / t_{1/2}$ $A = 10^{-3}\ A_0$

$$t = \frac{\ln A \;\; \ln A_0}{\lambda} = \frac{\ln 10^3}{\frac{\ln 2}{14.3}}\ \text{d} = 142.5\ \text{d}$$

4.4



1st mechanism



2nd mechanism

4.5 Specific activities $A_{sp}(\mathbf{II})$ = 18.6 Bq/mg,

$A_{sp}(\mathbf{III})$ = 0.18 Bq/mg,

$A_{sp}(\mathbf{IV})$ = 18.5 Bq/mg.

Because of $A_{sp}(\mathbf{II}) \approx A_{sp}(\mathbf{IV})$ the first mechanism, proposed in d), is probable and therefore it is PCl_4^+ that attacks the O-atom.

4.6 Given data: $K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}] = 10^{-12.6}$; $[NH_4^+] = 0.1$; $pH = 10$; $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$.

Exact solution:

$$2\,[Mg^{2+}] + [NH_4^+] + [H_3O^+] = [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}] + [OH^-]$$

$$[HPO_4^{2-}] = \frac{[PO_4^{3-}]\,[H^+]}{K_3}$$

$$[H_2PO_4^-] = \frac{[HPO_4^{2-}]\,[H^+]}{K_2} = \frac{[PO_4^{3-}]\,[H^+]^2}{K_2\,K_3}$$

$$[PO_4^{3-}] = \frac{K_{sp}}{[NH_4^+]\,[Mg^{2+}]}$$

$$\Rightarrow\ 2\,[Mg^{2+}] = \left(\frac{[H^+]^2}{K_1\,K_3} + \frac{2\,[H^+]}{K_3} + 3\right)\frac{K_{sp}}{[NH_4^+]} - [Mg^{2+}]\left([NH_4^+] + [H^+] - [OH^-]\right)$$

etc.

A simpler solution:

At pH = 10 the main component is HPO_4^{2-} :

$$[HPO_4^{2-}] = \frac{[PO_4^{3-}]\,[H^+]}{K_3} = 10^{2.4}\ [PO_4^{3-}]$$

$$[H_2PO_4^-] \ = \ \frac{[HPO_4^{2-}][H^+]}{K_2} \ = \ 10^{-2.8}\ [HPO_4^{2-}]$$

$S = [Mg^{2+}]\ [HPO_4^{2-}]$ and $K_{sp} = [NH_4^+] \times S \times K_3 \times \dfrac{S}{[H^+]}$

$pS = 0.5\ (pK_{sp} + pH - pK_3 - p[NH_4^+] = 0.5\ (12.6 + 10.0 - 12.4 - 1.0) = 4.6$;

$S = 2.5 \times 10^{-5}$ 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?

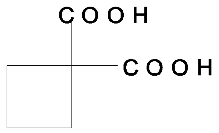
5.4 Which reaction can be used to determine the relative configuration of diastereoisomers?

5.5 How may the enantiomers of cyclobutane-1,2-dicarboxylic acid be separated?

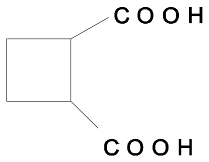
5.6 Indicate the absolute configurations of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (*R,S* system).

SOLUTION

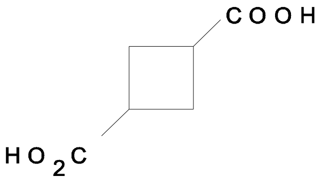
5.1 Constitutional isomers:



1,1 - cyclobutane - dicarboxylic acid



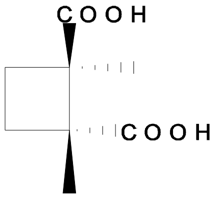
1,2 - cyclobutane - dicarboxylic acid



1,3 - cyclobutane - dicarboxylic acid

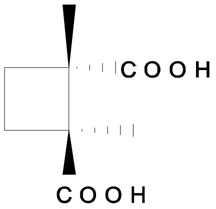
5.2 Stereoisomers:

I



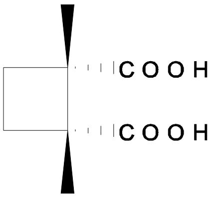
trans

II



trans

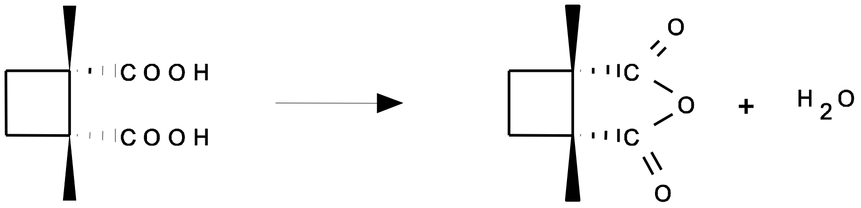
III



cis

5.3 Diastereomers are **I**, **III** and **II**, **III**. Enantiomeric pairs are **I** and **II**.

5.4 On loosing water the *cis*-diastereomer forms the corresponding anhydride according to:



5.5 The trans-diastereomer can be precipitated with a 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).

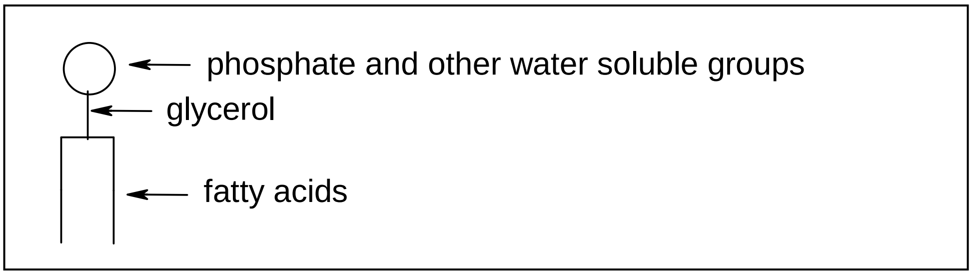
6.2 Using these three fatty acids in part 6.1 draw one possible structure of a triacyl glyceride.

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:



i) Mark the hydrophilic and hydrophobic groups on a copy of the above diagram.

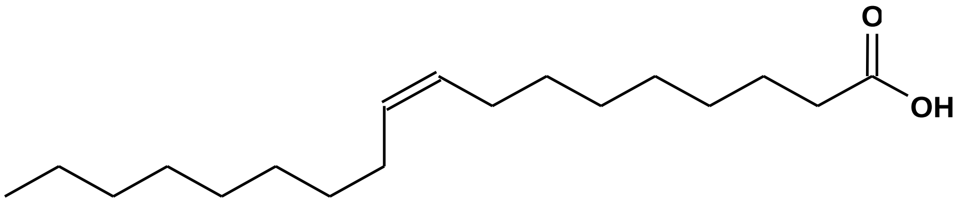
ii) Draw two possibilities for the association of six identical molecules of a phospholipid in water using the above diagram.

iii) Biomembranes consist of a phospholipid bi-layer. Draw such a model for a membrane using the above diagram.

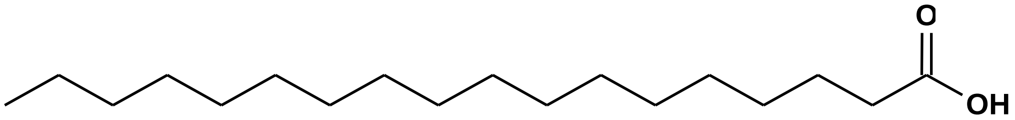
iv) Such a model (iii) is incomplete. What other bio-macromolecules are contained in such biomembranes?

SOLUTION

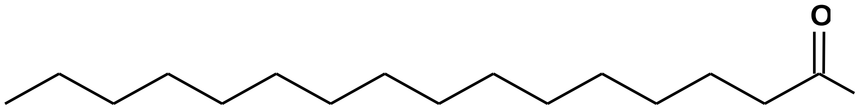
6.1



oleic acid

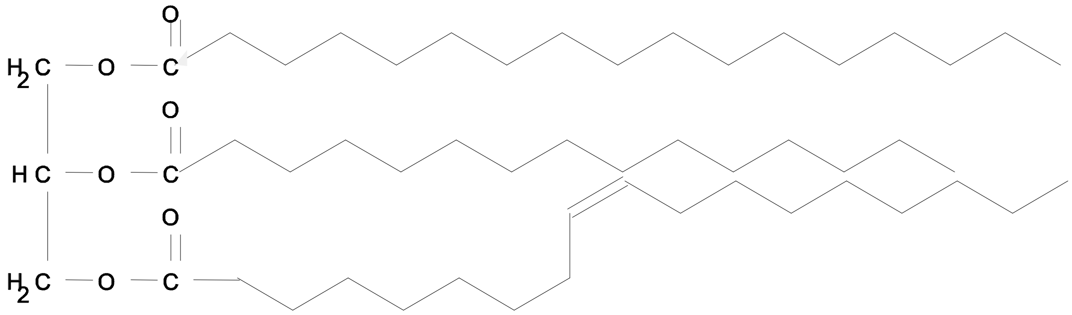


stearic acid

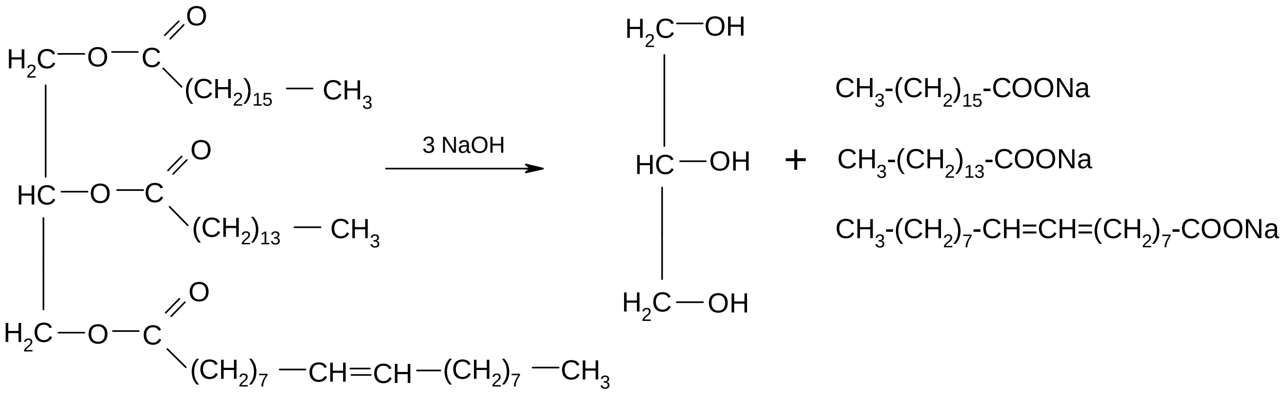


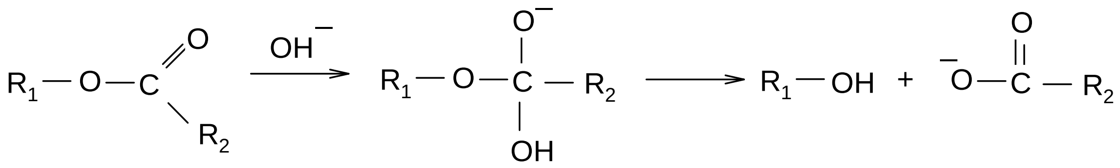
palmitic acid

6.2 A possible structure of a triacyl glyceride with the fatty acids mentioned is:



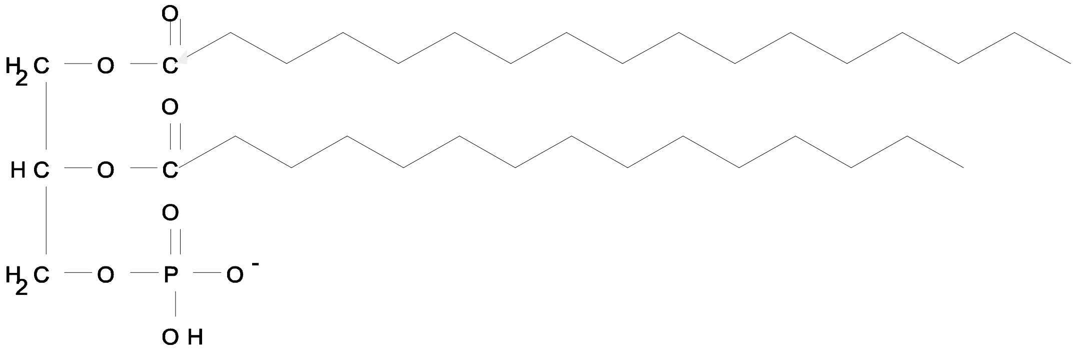
6.3



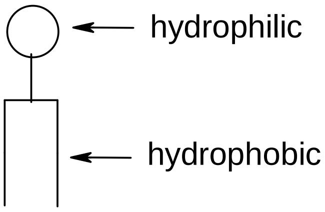


6.4 It is $C_{21}H_{43}COOH$.

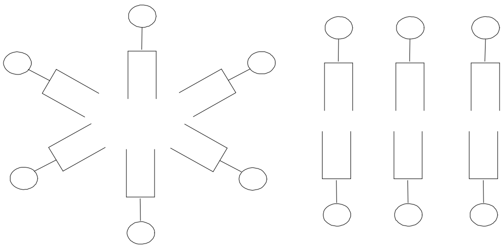
6.5 An example for a phospholipid is:



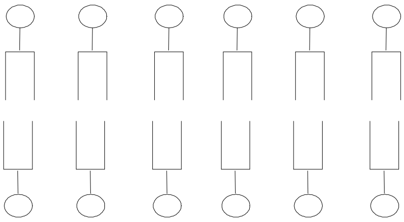
6.6 i)



ii)



iii)



phospholipid bilayer

iv) For example, proteins (enzymes)

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis

Preparation of 2-Ethanoyloxybenzoic Acid (Acetylsalicylic Acid, also known as Aspirin) by Ethanoylation (Acetylation) of 2-Hydroxybenzoic Acid (Salycilic 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 % H_3PO_4)
Ethanol
Deionised/distilled water

Procedure

In a 100 cm^3 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 cm^3 of deionised water to the still hot flask; then immediately add 20 cm^3 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 cm^3 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.

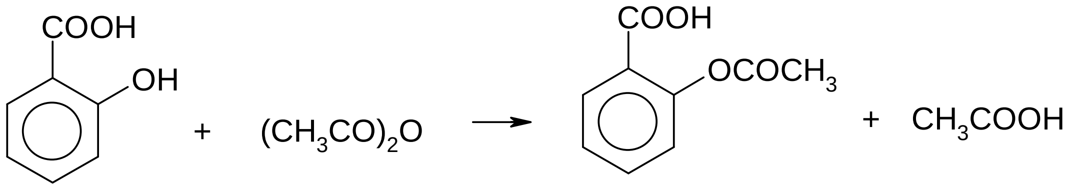
A technician should then weigh the cooled dish containing your product in your presence. Record the mass. The melting point will subsequently be taken by a technician to check the purity of your product.

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 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 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:

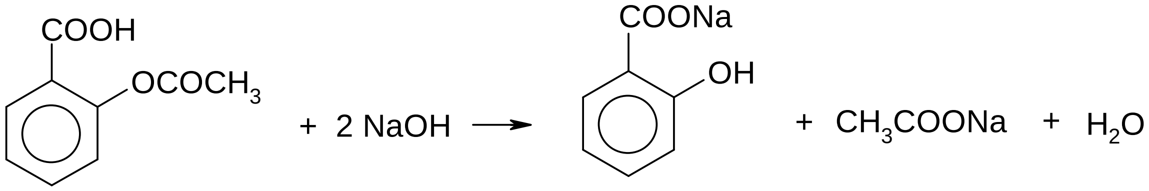
Pipette 50.00 cm^3 of your standardized sodium hydroxide solution into the Erlenmeyer flask I (with a ground glass joint) which contains your unknown mass of aspirin. Add 3 – 5 boiling stones to the flask and boil the reaction mixture for 15 minutes using a reflux condenser and the electrical hot plate. 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 cm^3 volumetric flask and fill it exactly to the mark with deionised water. Pipette 20.00 cm^3 of this solution into a 300 cm^3 Erlenmeyer flask and dilute to about 100 cm^3 with deionised water. Back titrate the residual sodium hydroxide with the standard hydrochloric acid solution (0.4975 mol dm^{-3}) using a 10 cm^3 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 cm^3 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, $Ca_3(PO_4)_2$, calcium sulphate, calcium fluoride, calcium carbonate and silica.

For uses as fertilizer the calcium bis(dihydrogenphosphate), $Ca(H_2PO_4)_2$, 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_2O_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 cm^3 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, $Ca(H_2PO_4)_2$, 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 ℃, then filtered, dried and weighed. The mass of the residue obtained is m_2. This new residue is mainly containing gypsum, $CaSO_4 \cdot 2\ H_2O$, whose solubility can be considered as constant between 20 ℃ and 50 ℃ 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 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 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: $\frac{HSO_4^-}{SO_4^{2-}} = 2$ $\frac{HF}{F^-} = 3$ $\frac{H_3PO_4}{H_2PO_4^-} = 2$ $\frac{H_2PO_4^-}{HPO_4^{2-}} = 7$ $\frac{HPO_4^{2-}}{PO_4^{3-}} = 12$

SOLUTION

1.1 $Ca_3(PO_4)_2 + 4\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2\ HF$

$CaCO_3 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CO_2\uparrow + H_2O$

$Ca_3(PO_4)_2 + 2\ H_2SO_4 + 4\ H_2O \rightarrow 2\ CaSO_4 + 2\ H_2O + Ca(H_2PO_4)_2$

$CaF_2 + H_2SO_4 + 2\ H_2O \rightarrow CaSO_4 \cdot 2\ H_2O + 2\ HF\uparrow$

$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2\ H_2O + CO_2\uparrow$

1.2 1 g of apatite contains $\frac{0.284}{142} = 2.00\times10^{-3}$ mol of $Ca_3(PO_4)_2$

$\frac{0.034}{2+19} = 0.89\times10^{-3}$ mol of CaF_2

$\frac{0.061}{44} = 1.39\times10^{-3}$ mol of $CaCO_3$

$\frac{0.035}{80} = 0.44\times10^{-3}$ mol of $CaSO_4$

$\frac{0.473}{56} - \frac{3\times0.284}{142} - \frac{0.034}{38} - \frac{0.061}{44} - \frac{0.035}{80} = 2.72\times10^{-4}$ mol CaO that remain.

The amount of H_3PO_4 needed to react with 1 g of apatite is equal to $n(H_3PO_4) = 4\ n(Ca_3(PO_4)_2 + 2\ n(CaF_2) + 2\ n(CaCO_3) = 12.56\times10^{-3}$ mol.

50 cm^3 of the acid contains 25×10^{-3} mol of H_3PO_4, therefore 25 / 12.56 = <u>1.99 g</u> 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:

$n(H_2SO_4) = 2\ n(Ca_3(PO_4)_2) + n(CaF_2) + n(CaCO_3) = 6.28\times10^{-3}$ mol. 50 cm^3 of the acid contains 5.00×10^{-3} mol of sulphuric acid. Therefore 5 / 6.28 = 0.80 g of apatite is needed to neutralize the H_2SO_4.

The total amount of apatite is m_0 = 1.99 + 0.80 = <u>2.79 g</u>

1.3 Formation of $Ca(H_2PO_4)_2$:

1.99 g of apatite needed to neutralize the H_3PO_4 contains $1.9 \times 2.00\times10^{-3}$ mol of $Ca_3(PO_4)_2$, thus $3 \times 2 \times 2\times10^{-3} = 1.2\times10^{-2}$ mol of dihydrogen phosphate is being formed.

From CaF_2, 1.99 × 0.89 = 1.80 mol and from $CaCO_3$, 1.99 × 1.39 = 2.77 mol of $Ca(H_2PO_4)_2$ are formed.

0.8 g of apatite that reacts with 50 cm^3 of the sulphuric acid yields $2 \times 0.8\times10^{-3} = 1.6\times10^{-3}$ mol of $Ca(H_2PO_4)_2$.

$m(Ca(H_2PO_4)_2 = 18.07\times10^{-3}$ mol = 4.230 g

Formation of gypsum: $n(CaSO_4) = n(H_2SO_4) = 5.00\times10^{-3}$ mol $\triangleq$ 0.86 g

The amount of $CaSO_4$ that was already present in 1 g of apatite and yielded gypsum is $0.434\times10^{-3} \times 172 = 0.075$ g. There remain also 0.034 g of silica, and thus the theoretical mass of the residue should be:

$m_{th} = 4.230 + 0.86 + (0.0753 + 0.034) \times 2.79 = \underline{5.39\text{ g}}$

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 $Ca(H_2PO_4)_2$, 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 $Ca(H_2PO_4)_2$ it would correspond to 0.856 / 234 = 3.66×10^{-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 $Ca_3(PO_4)_2$ in 2.79 g apatite is 0.00558 mol (equals 0.00558 mol P_2O_5). So, $r_{exp} = 100 \times [0.0201/(0.0125 + 0.00558)] = \underline{111\ \%}$

Since 50 cm^3 water dissolve 0.115 g of gypsum, the real quantity of $Ca(H_2PO_4)_2$ is 0.856 – 0.115 = 0.741 mol, so that the real yield gives: $r_{exp} = 100 \times [0.0174/(0.0125 + 0.00558)] = \underline{96\ \%.}$

1.6 The theoretical value for r_{exp} is: $r_{exp} = 100 \times [4.23/234 / (0.0125 + 0.00558)] = 100\ \%$, 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 1.00×10^{-2} 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 $K_{sp} = 1\times10^{-20}$.

2.3 At what *pH* value hydroxide $Cu(OH)_2$ 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:

Couple 1: $Cu^+ + e^- \rightleftharpoons Cu$

Standard electrode potential $E_1^0 = + 0.52$ V

Couple 2: $Cu^{2+} + e^- \rightleftharpoons Cu^+$

Standard electrode potential $E_2^0 = + 0.16$ V

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 1.00×10^{-2} 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 1.00×10^{-2} mol dm^{-3} solution of Cu^{2+} ions. The solubility product of copper(I) oxide is $K_{sp} = [Cu^+][OH^-] = 1\times10^{-15}$

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 $[Cu(NH_3)_2]^+$ is $K_D = 1\times10^{-11}$. Calculate the standard electrode potential of the couple:

$$[Cu(NH_3)_2]^+ + e^- \rightleftarrows Cu + 2\,NH_3$$

2.9 The standard electrode potential of the couple

$$[Cu(NH_3)_4]^{2+} + 2\,e^- \rightleftarrows Cu + 4\,NH_3$$

$E_3^0 = -\,0{,}02$ V.

Calculate the dissociation constant for the complex ion $[Cu(NH_3)_4]^{2+}$.

2.10 Deduce from it the standard electrode potential of the couple:

$$[Cu(NH_3)_4]^{2+} + e^- \rightleftarrows [Cu(NH_3)_2]^+ + 2\,NH_3$$

Does the disproportionation of the cation $[Cu(NH_3)_2]^+$ take place?

SOLUTION

2.1 $[Cu(H_2O)_4]^{2+} + H_2O \rightarrow H_3O^+ + [Cu(OH)(H_2O)_3]^+$

2.2 $$K_a = \frac{[H_3O^+]\left[[Cu(OH)(H_2O)_3]^+\right]}{\left[[Cu(H_2O)_4]^{2+}\right]} = \frac{[H_3O^+]^2}{\left[[Cu(H_2O)_4]^{2+}\right]} = \frac{(2.24\times10^{-5})^2}{1\times10^{-2}} = 5.01\times10^{-8}$$

$pK_a = 7.30$

2.3 $[Cu^{2+}][OH^-]^2 = 1\times10^{-20}$; $[Cu^{2+}] = 1\times10^{-2}$ $\Rightarrow$ $[OH^-] = 1\times10^{-9}$; <u>*pH* = 5</u>

$$\left[[Cu(OH)(H_2O)_3]^+\right] : \left[[Cu(H_2O)_4]^{2+}\right] = K_a : 10^{-pH} = 1\times10^{-7.3} : 1\times10^{-5} = 1 : 200$$

2.4 $2\ Cu^+ \rightarrow Cu^{2+} + Cu$

$$K = \frac{[Cu^{2+}]}{[Cu^+]^2}$$

$0.52 - 0.16 = 0.059 \log K$ (Nernst equation) $\Rightarrow K = 1\times10^6$

2.5 At equilibrium: $[Cu^+] + 2\,[Cu^{2+}] = 1\times10^{-2}$ and $[Cu^{2+}] = 1\times10^6\,[Cu^+]$ so that the following equation is obtained:

$2\times10^6\,[Cu^+]^2 + [Cu^+] - 1\times10^{-2} = 0$

with the solution

$[Cu^+] = \underline{7.07\times10^{-5}}$ and $[Cu^{2+}] = \underline{4.96\times10^{-3}}$.

2.6 Other disproportionation reactions:

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ (catalyzed by $KMnO_4$, Fe^{3+} etc.)

$Cl_2 + OH^- \rightarrow HCl + ClO^-$ (basic conditions)

2.7 $Cu_2O + 2\ H_3O^+ + 2\ e^- \rightarrow 2\ Cu + 3\ H_2O$ $\qquad [Cu^+] = \dfrac{1\cdot10^{-15}}{[OH^-]}$

$$E_1 = 0.52 + \frac{0.059}{2}\log\left([Cu^+][H_3O^+]^2\right) = 0.49 - 0.0885\ pH$$

$2\ Cu^{2+} + 3\ H_2O + 2\ e^- \rightarrow Cu_2O + 2\ H_3O^+$

$$E_2 = 0.16 + \frac{0.059}{2}\log\frac{1\times10^{-4}}{[Cu^+][H_3O^+]^2} = 0.07 + 0.0885\ pH$$

Cu_2O is stable when $E_2 > E_1$ i.e. $0.42 < 0.177$ pH, or 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.

2.8 $[Cu(NH_3)_2]^+ \rightleftharpoons Cu^+ + 2\ NH_3$

$$K_D = \frac{[Cu^+]\,[NH_3]^2}{\left[[Cu(NH_3)_2{}^+]\right]} = 1\times10^{-11}$$

Knowing $E_0(Cu^+/Cu) = 0.52$ V, the $E^0([Cu(NH_3)_2]^+ / Cu^+)$ becomes:

$E_{f1} = 0.52 - 0.06\ pK_D = -\ \underline{0.14\ V}$

2.9 The standard *emf* of a Cu^{2+}/Cu cell is thus: $E^0 = (0.5 + 0.16)/2 = 0.33$ V and $E_3^0 = 0.33 – 0.03\ pK_2$.

Thereout: $pK_2 = (0.33 – E_3^0) / 0.03 = (0.33 – (– 0.02)) / 0.03 = \underline{12}$

$[Cu(NH_3)_4]^{2+} + 2\ e^– \rightarrow Cu + 4\ NH_3 \quad E_0 = – 0.02$ V

$[Cu(NH_3)_2]^{+} + e^– \rightarrow Cu + 2\ NH_3 \quad E_0 = – 0.14$ V

$[Cu(NH_3)_4]^{2+} + e^– \rightarrow [Cu(NH_3)_2]^{+} + 2\ NH_3$

Since only ΔG^0 is additive and from $\Delta G^0 = – n\ F\ E^0$ it follows:

$E_{f2} = 2 \times (– 0.02) – (– 0.14) = 0.10$ V

2.10 $[Cu(NH_3)_2]^{+} + e^– \rightarrow Cu + 2\ NH_3 \qquad E_{f1} = – 0.14$ V

$[Cu(NH_3)_4]^{2+} + e^– \rightarrow [Cu(NH_3)_2]^{+} + 2\ NH_3 \qquad E_{f2} = 0.10$ V

Since $E_{f1} < E_{f2}$ the $[Cu(NH_3)_2]^{+}$ ion doesn't disproportionate (the *emf* would be – 0.14 – 0.10 = – 0.24 V)

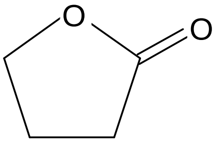
PROBLEM 3

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** ($C_{10}H_{10}OFCl$).

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?

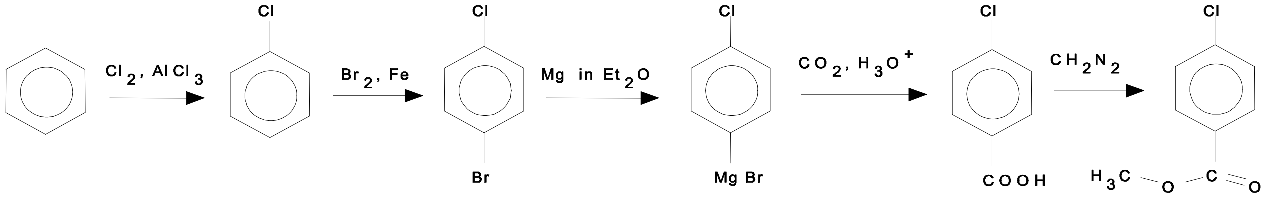
P reacts with **O** in basic media in a 1 : 1 molar ratio to give **H** that contains only one chlorine atom on the aromatic ring.

3.7 Give the structure of **H** which is haloperidol.

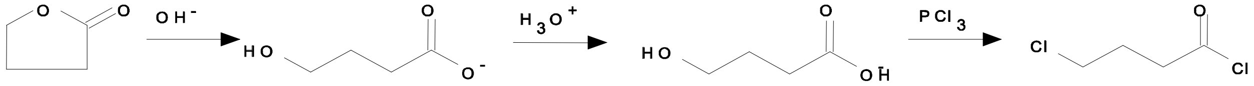
3.8 State the multiplicity of each resonance in the ^{1}H NMR spectrum of **K**. Assume that all coupling constants between protons and adjacent carbons are identical.

SOLUTION

3.1



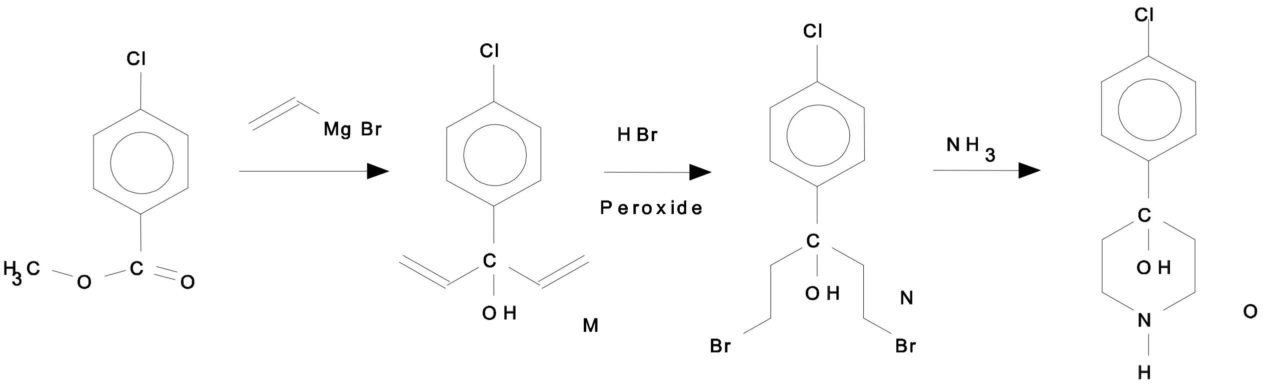
3.2 and **3.3**



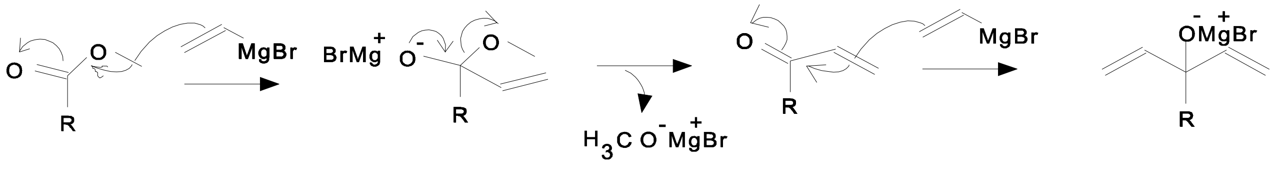
J **K**

L

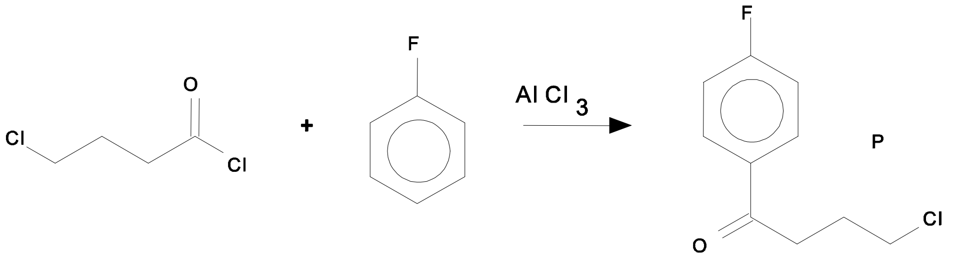
3.4

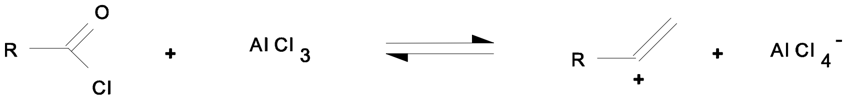


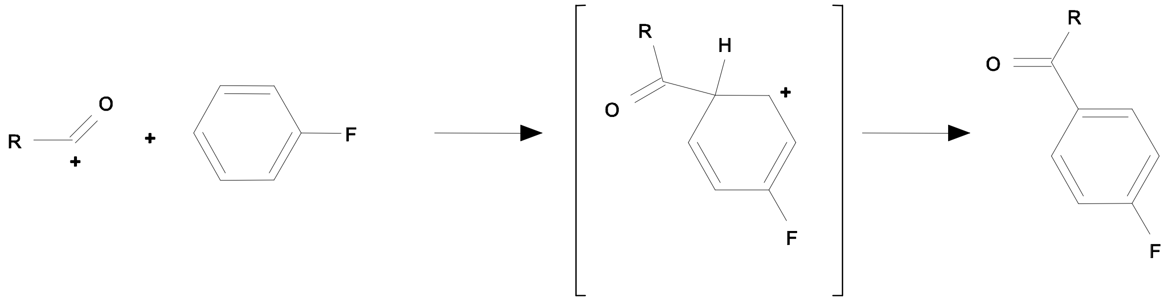
Mechanism of the Grignard reaction:



3.5





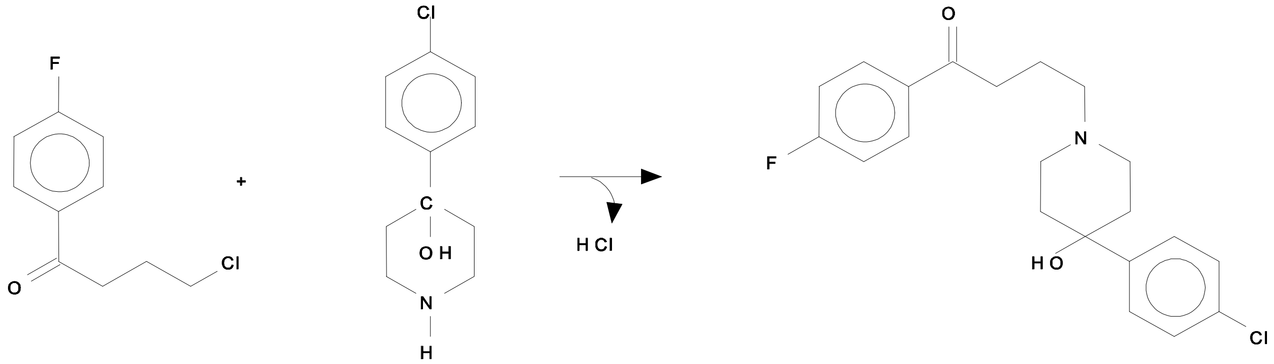


3.6 Chemical test: carbonyl groups react with phenylhydrazines to phenylhydrazones with a sharp, specific melting point.

Physical test: IR-absorption at 1740 cm^{-1}

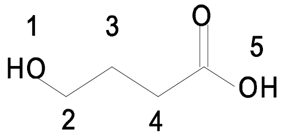
A possibility to distinguish between ketones and aldehydes is the Tollens-test (silver mirror). Ketones cannot be reduced whereas aldehydes easily reduce the silver ions to elementary silver.

3.7



Haloperidol

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:

$$ZnS(s) + 3/2\ O_2(g) \rightarrow ZnO(s) + SO_2(g) \qquad \Delta_r H^0_{1350} = -\ 448.98\ \text{kJ mol}^{-1}$$

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 SiO_2.

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 is 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 O_2 and 6 mol of N_2. Therefore:

$$\Delta_r H^0_{1350} = \int_{298}^{T} [c_p(\text{ZnS}) + 1.5\, c_p(\text{O}_2) + 6\, c_p(\text{N}_2)]\, dT = 293.3(T - 298) = 448\,980 \text{ J mol}^{-1}$$

Thus $\underline{T \approx 1830 \text{ K}}$, which indicates that the reaction is self-sustaining.

4.2 If *n* denotes the quantity (in moles) of SiO_2 per mol of ZnS, the heat given off heats 1 mol of ZnS, *n* mol of SiO_2, 1.5 mol of O_2 and 6 mol of N_2 from 298 to 1350 K:

$$\Delta_r H^o = \int_{298}^{1350} \sum(n_i \times c_{p(i)})\, dT = \int_{298}^{1350} (293.3 + 72.5 n)\, dT$$

Wherefrom: 448 980 = (293.3 + 72.5 *n*)(1350 - 298), so $\underline{n = 1.84 \text{ mol}}$

4.3 By mass, we have 110.6 g of SiO_2 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 $\underline{46.9\ \%}$.

PROBLEM 5

CHEMICAL KINETICS

Nitramide NO_2NH_2 decomposes slowly in aqueous solution according to the reaction:

$$NO_2NH_2 \rightarrow N_2O(g) + H_2O$$

The experimental kinetic law is as follows:

$$\frac{d[N_2O]}{dt} = k\,\frac{[NO_2NH_2]}{[H_3O^+]}$$

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:

$NO_2NH_2 \xrightarrow{k_1} N_2O + H_2O$ (rate limiting step)

Mechanism 2:

$NO_2NH_2 + H_3O^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO_2NH_3^+ + H_2O$ (rapid equilibrium)

$NO_2NH_3^+ \xrightarrow{k_3} N_2O + H_3O^+$ (rate limiting step)

Mechanism 3:

$NO_2NH_2 + H_2O \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} NO_2NH_3^- + H_3O^+$

$NO_2NH^- \xrightarrow{k_5} N_2O + OH^-$ (rate limiting step)

$H_3O^+ + OH^- \xrightarrow{k_6} 2\ H_2O$ (very fast reaction)

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(min)	0	5	10	15	20	25
p(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

$$k` = \frac{k}{[H_3O^+]}\,.$$

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 $[H_3O^+]$ is constant and the reaction is of the first order:

$v = k' [NO_2NH_2]$

5.2 The rate laws of the three mechanisms proposed are:

$v_1 = k_1 [NO_2NH_2]$

$$v_2 = k_3 [NO_2NH_3^+] = \frac{k_3k_2}{k_{-2}} [NO_2NH_2] [H_3O^+]$$

$$v_3 = k_5 [NO_2NH^-] = \frac{k_5k_4}{k_{-4}} \frac{[NO_2NH_2]}{[H_3O^+]}$$

Thus, it is the third mechanism that is correct.

5.3 $k = \dfrac{k_5k_4}{k_{-4}}$

5.4 Noting that $[H_3O^+] = K_e / [OH^-]$ it follows that $v = k / K_e [NO_2NH_2] [OH^-]$, which shows the catalytic role of OH^-.

5.5 $d[N_2O]$ can be expressed by the change of pressure $dp(N_2O)/RT$ (according to $pV = nRT$). We obtain:

$$v = \frac{d[N_2O]}{dt} = \frac{1}{RT}\,\frac{dp(N_2O)}{dt} = \frac{1}{RT}\,\frac{dp}{dt} = k\,\frac{[NO_2NH_2]}{[H_3O^+]}$$

We also know that $V\,[NO_2NH_2] = n(NO_2NH_2)_{init} - n(N_2O) = n(N_2O)_\infty - n(N_2O)$ from which

$$\frac{dp}{dt} = \frac{k}{[H_3O^+]} \times \frac{RT}{V} \times (n(N_2O)_\infty - n(N_2O))$$

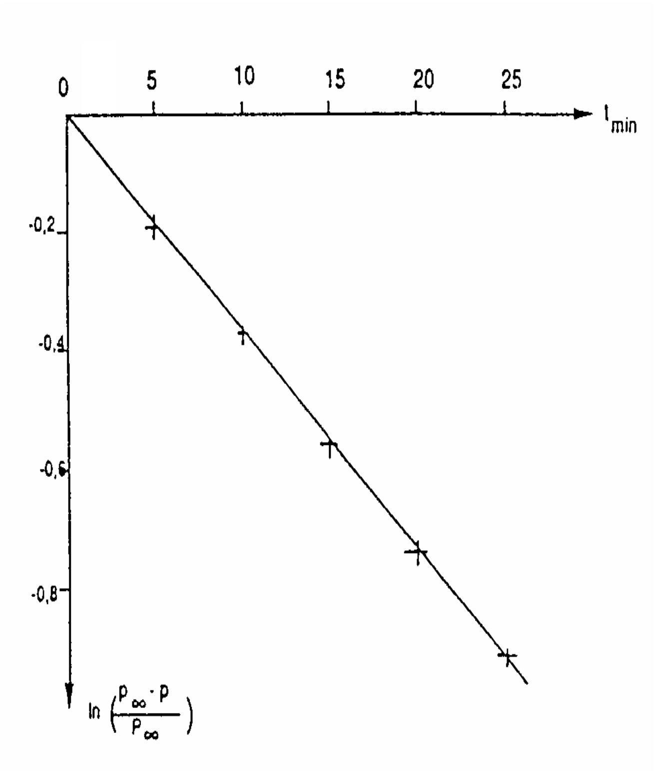
and thus

$$\frac{dp}{dt} = \frac{k}{[H_3O^+]} \times (p_\infty - p) = k'(p_\infty - p)$$

Integration gives $p = p_\infty\,(1 - e^{-k't})$

wherefrom: $e^{-k't} = 1 - p/p_\infty$

5.6

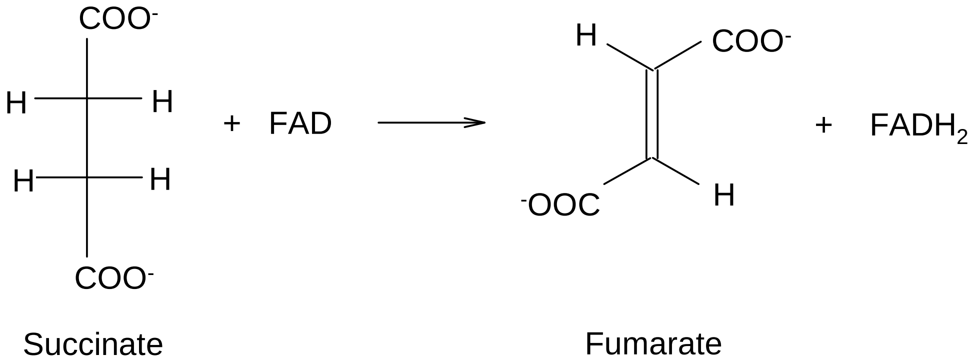


5.7 The graph of $f(x) = \ln(1 - p/p_\infty) = -k't$ is a straight line with the slope k' shown in Fig. k' was determined to be 3.7×10^{-2} min^{-1}.

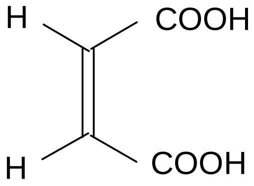
PROBLEM 6

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.



Maleic acid

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*.

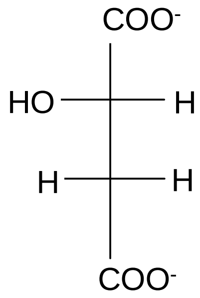
6.2 On the basis of the Newman projections of the most stable conformations of each isomer and the above facts, determine the percentage of dideuterated fumarate formed by *syn* and *anti* dehydrogenation.

(Assume that the percentages of dideuterated fumarate are 0 or 50 %, respectively.)

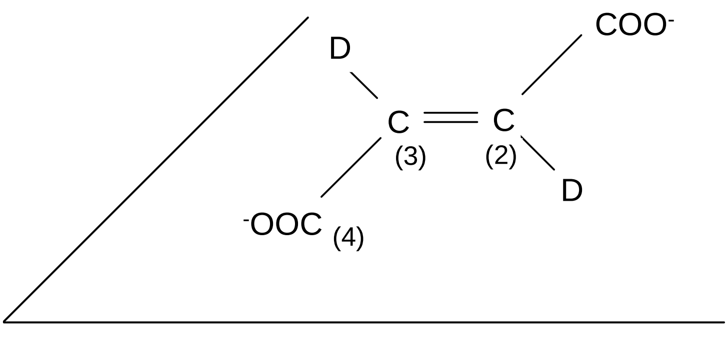
6.3 Show the stereochemistry of the enzymatic dehydrogenation.

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).

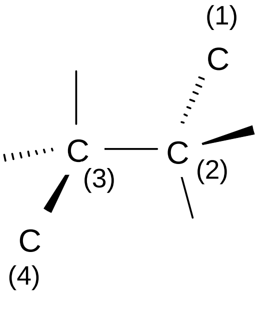
Fischer projection of (*S*)-malate:



6.4 The 2,3-dideuterofumarate reacts with fumarase to (2*S*,3*S*)-2,3-dideuteromalate (through addition of water). Show the stereochemical pathway of the reaction. Use the schematic drawing below to answer this question.

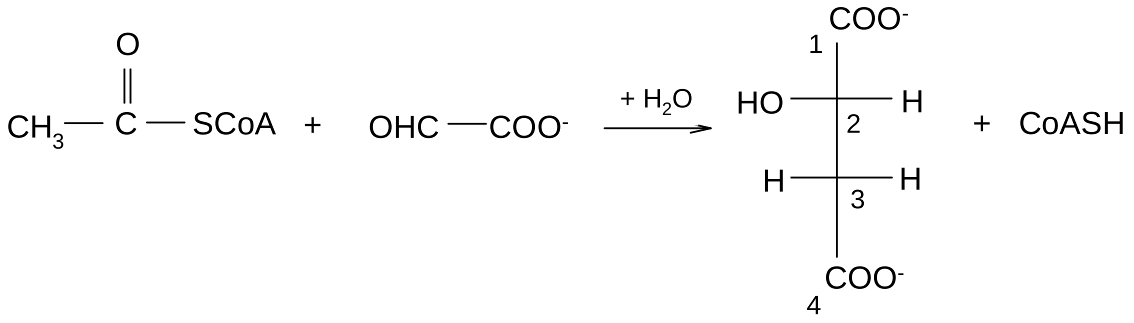


2,3-dideuteriofumarate

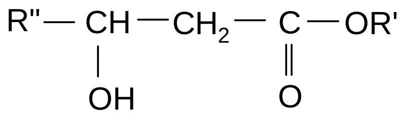


(2S,3S)-2,3-dideuteriomalate

The acetylcoenzyme A, $CH_3COSCoA$ reacts with glyoxylate, $OHC\text{-}CO_2$-, in the presence of malate synthetase enzyme to (*S*)-malate.



A similar reaction can proceed between an ester CH_3COOR' (similar to the thioester $CH_3COSCoA$) and an aldehyde R"CHO (similar to the glyoxylate) in the presence of $R'-O^-$ ions. It leads to a β-hydroxyester.

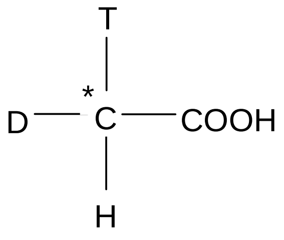


$R''-CH(OH)-CH_2-C(=O)-OR'$

($R'-O^-$ 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 CHDTCOOH having R-configuration.



(tritium T = ^3_1H, deuterium D = ^2_1H)

The formed (*S*)-malate is dehydrated (the reverse reaction of question 6.4) by an enzymatic reaction.

6.6 What enzyme can be used?

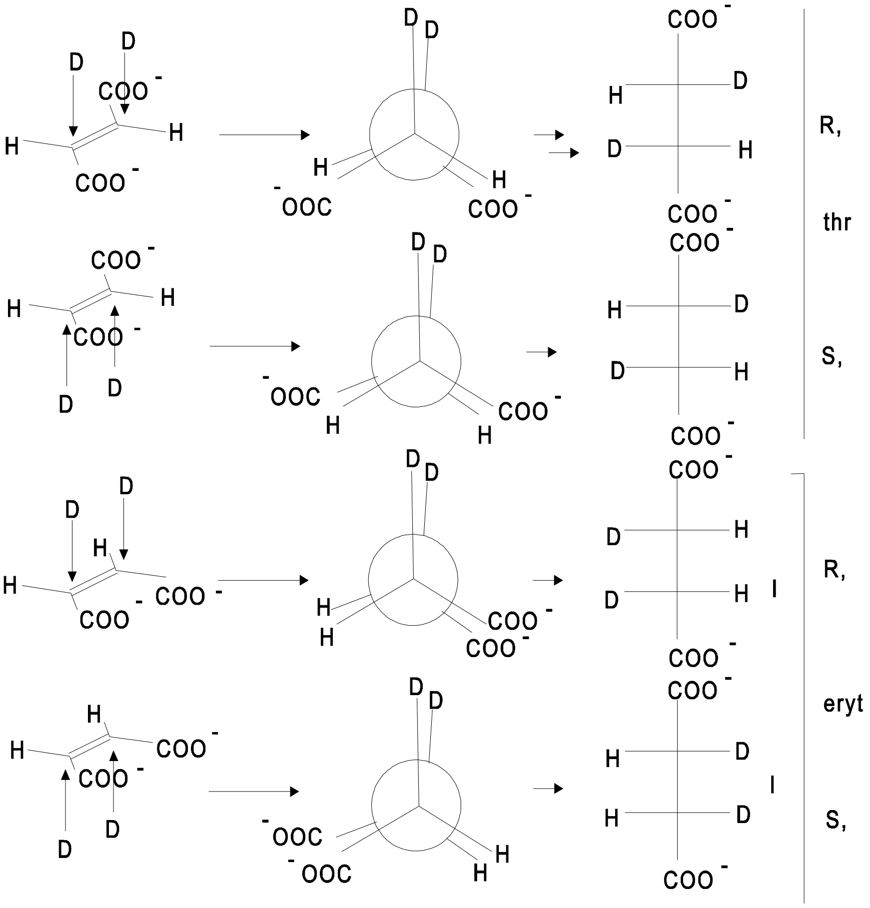
The major product is monotritiated fumarate (79%) with 21 % untritiated fumarate.

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.

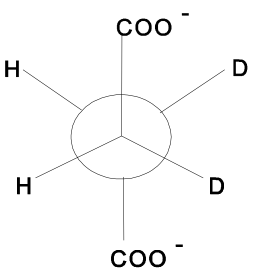
6.8 What would be the products if the starting material has a labelled acetyl group with *S*-configuration?

SOLUTION

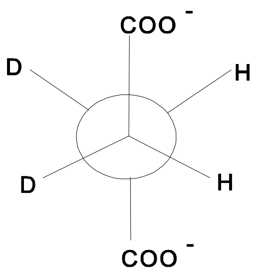
6.1 There are three isomers. The catalytic deuteration is a syn deuteration.



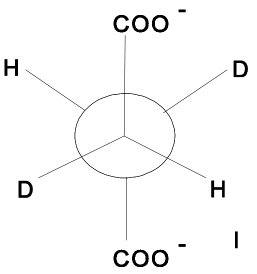
The most stable conformation for succinates is the anti form, since the distance between the bulky COO$^-$ groups is maximal:



I



II

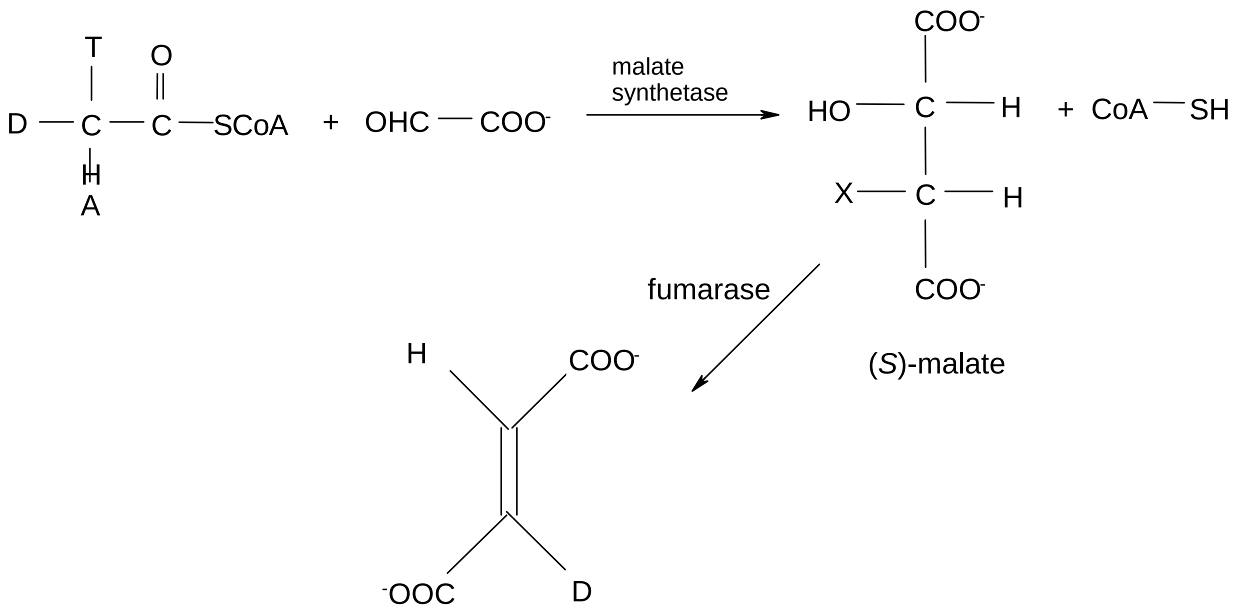


III

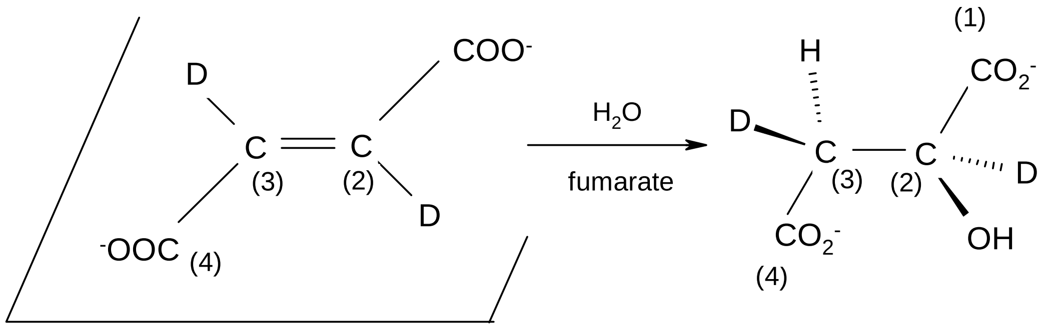
I and II are enantiomeres, II and III are a meso isomer, thus there are in total three isomers (two enantiomers and one meso form). Each threo and the meso form are diastereomers.

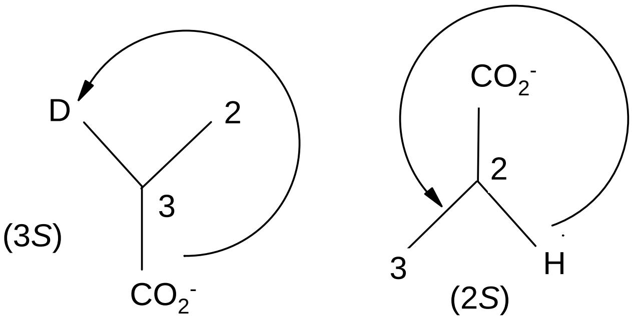
6.2 Considering the Newman projections of the three isomers it is clear that *syn* elimination of I and II leads either to fumarate containing no D or to dideuterated fumarate (percentage of dideuterated fumarate is thus 50 %) whereas *anti* elimination leads to monodeuterated fumarate. Concerning the 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.



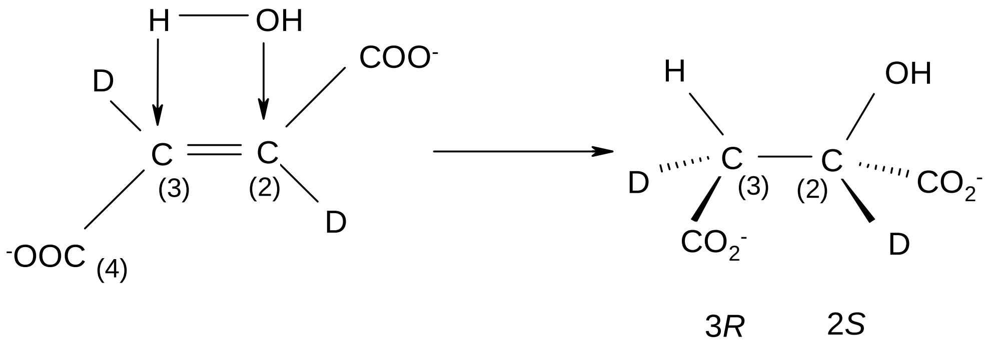
6.4





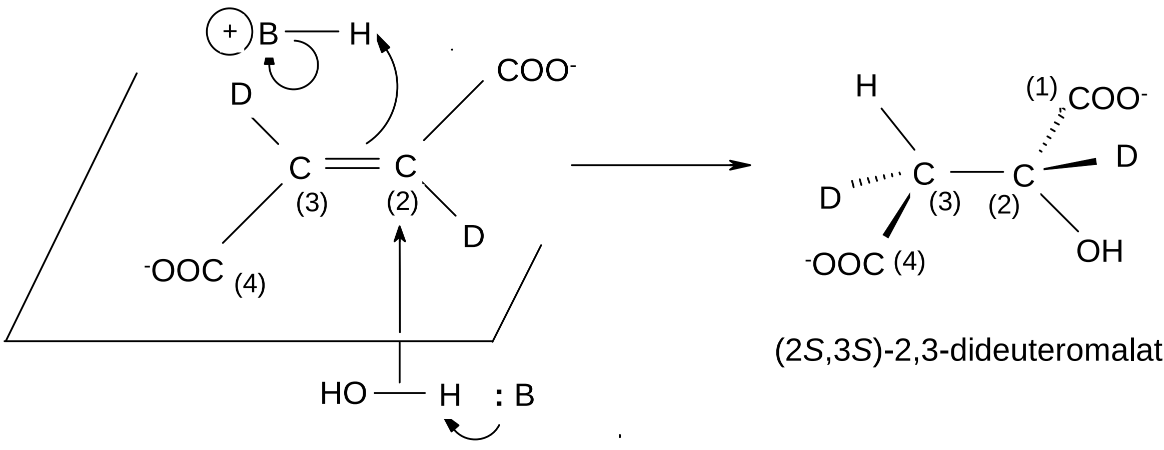
Stereospecific addition, *syn* or *anti*

Syn addition:



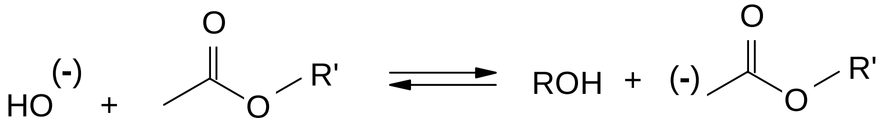
Syn addition would yield 2*S*, 3*R* or 2*R*, 3*S*

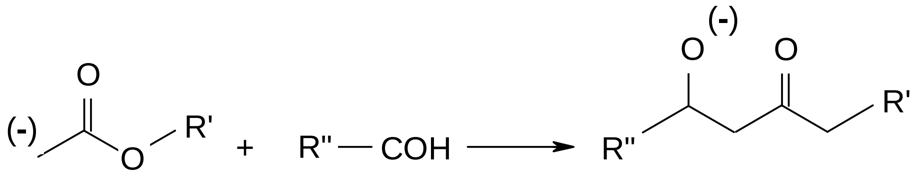
Anti addition:

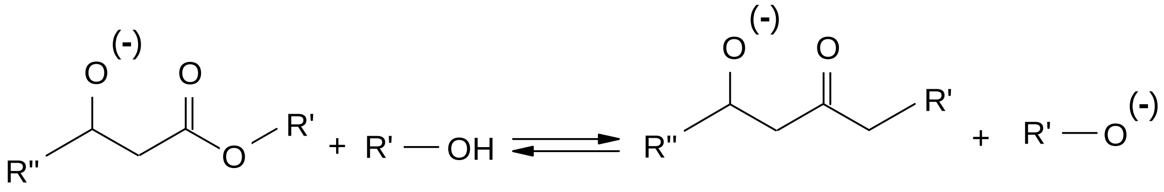


(2*S*,3*S*)-2,3-dideuteromalate

6.5

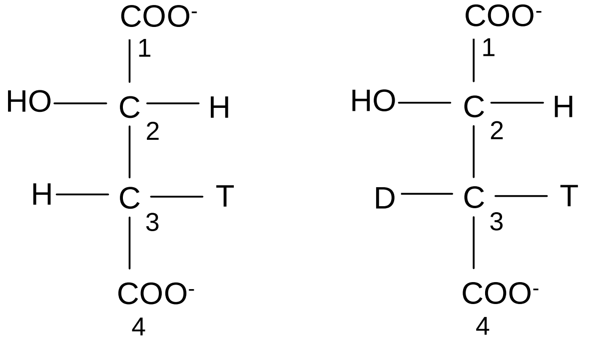




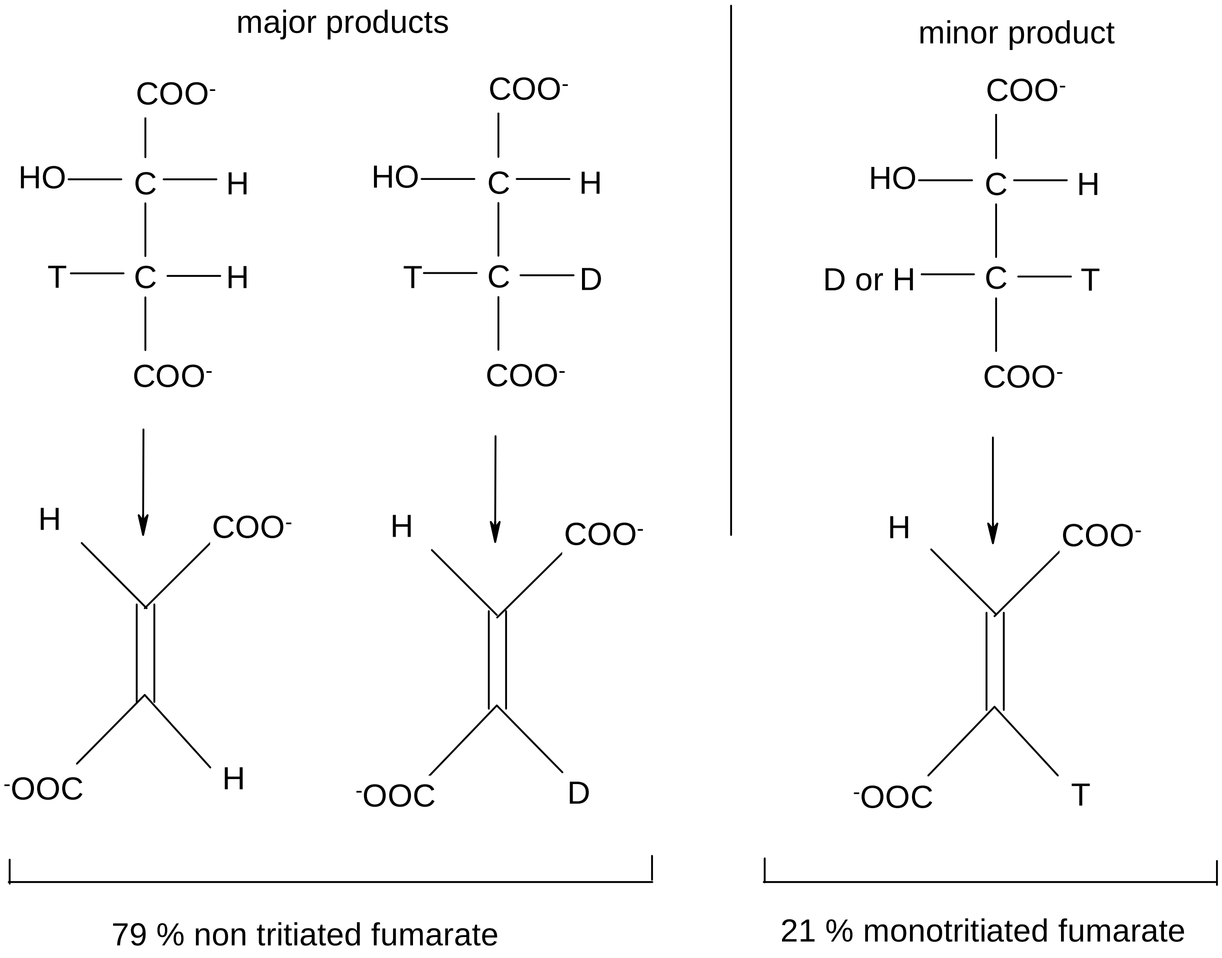


6.6 We would have (2*R*) (3*R*) if the enzyme did not produce enantiospecific addition. Thus: enantiospecific addition *anti*.

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:


major products
minor product
79 % non tritiated fumarate
21 % monotritiated fumarate

PROBLEM 7

<u>In this problem tick the appropriate box in the tables of the answer sheet.</u>

Hydrogenation of benzene to cyclohexane is performed in continuous reactors. The reaction is as follows:

$C_6H_6 + 3\ H_2 \rightleftarrows C_6H_{12}$ (catalyst) $\Delta H^0 = 214$ kJ mol^{-1} at 200 °C

Two basic types of continuous reactors are examined: a continuous plug flow reactor and a continuous stirred reactor.

<u>The continuous plug flow reactor (Fig. 1)</u>

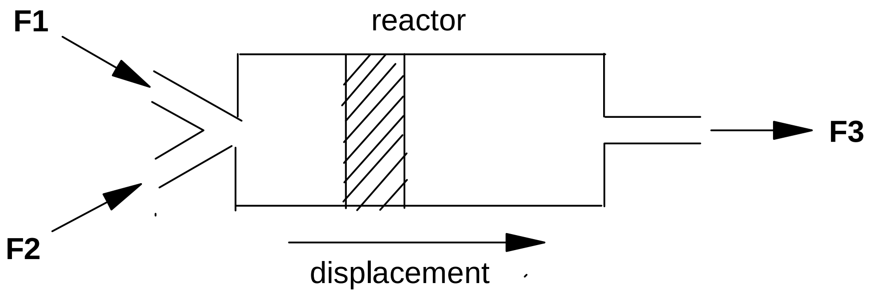


Fig. 1

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.

<u>The continuous stirred reactor (Fig. 2)</u>

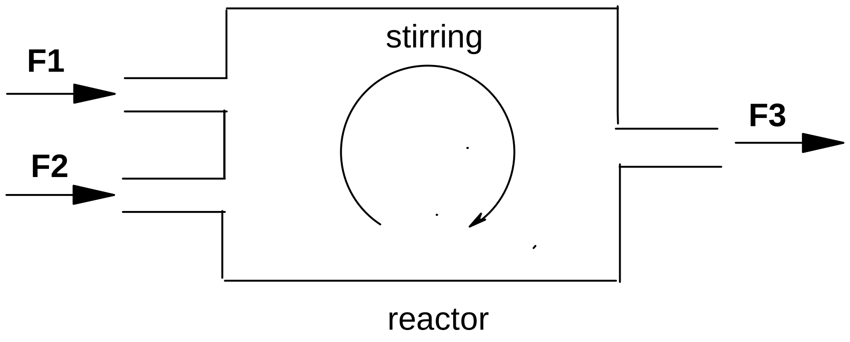


Fig. 2

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 = $-\dfrac{d([C_6H_{12}])}{d([C_6H_6])}$.

The proportion of benzene already hydrogenated is given by p = $\dfrac{[C_6H_{12}]}{[C_6H_{12}]+[C_6H_6]}$.

The relationship between p and Y is shown in Fig. 3.

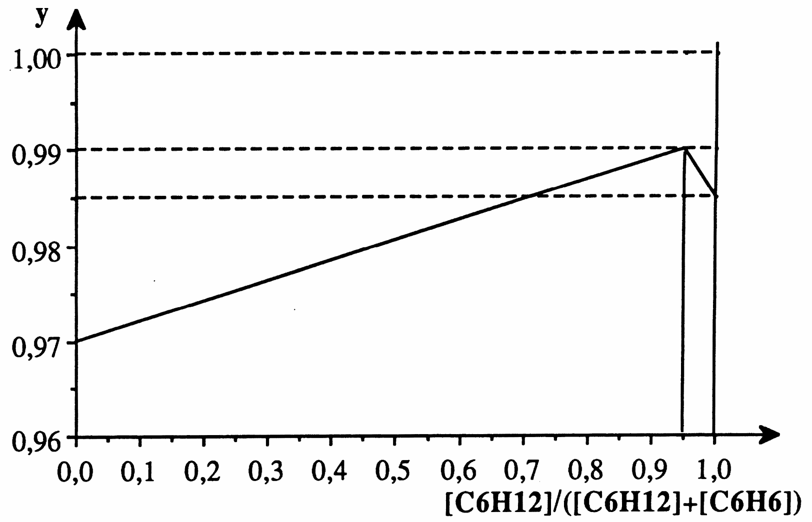


Fig. 3

The aim is to hydrogenate almost all the benzene, i.e. 0.9 ≤ p ≤ 1 with the best mean yield

Y = $-\dfrac{\Delta[C_6H_{12}]}{\Delta[C_6H_6]}$.

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 ≤ p ≤ 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.

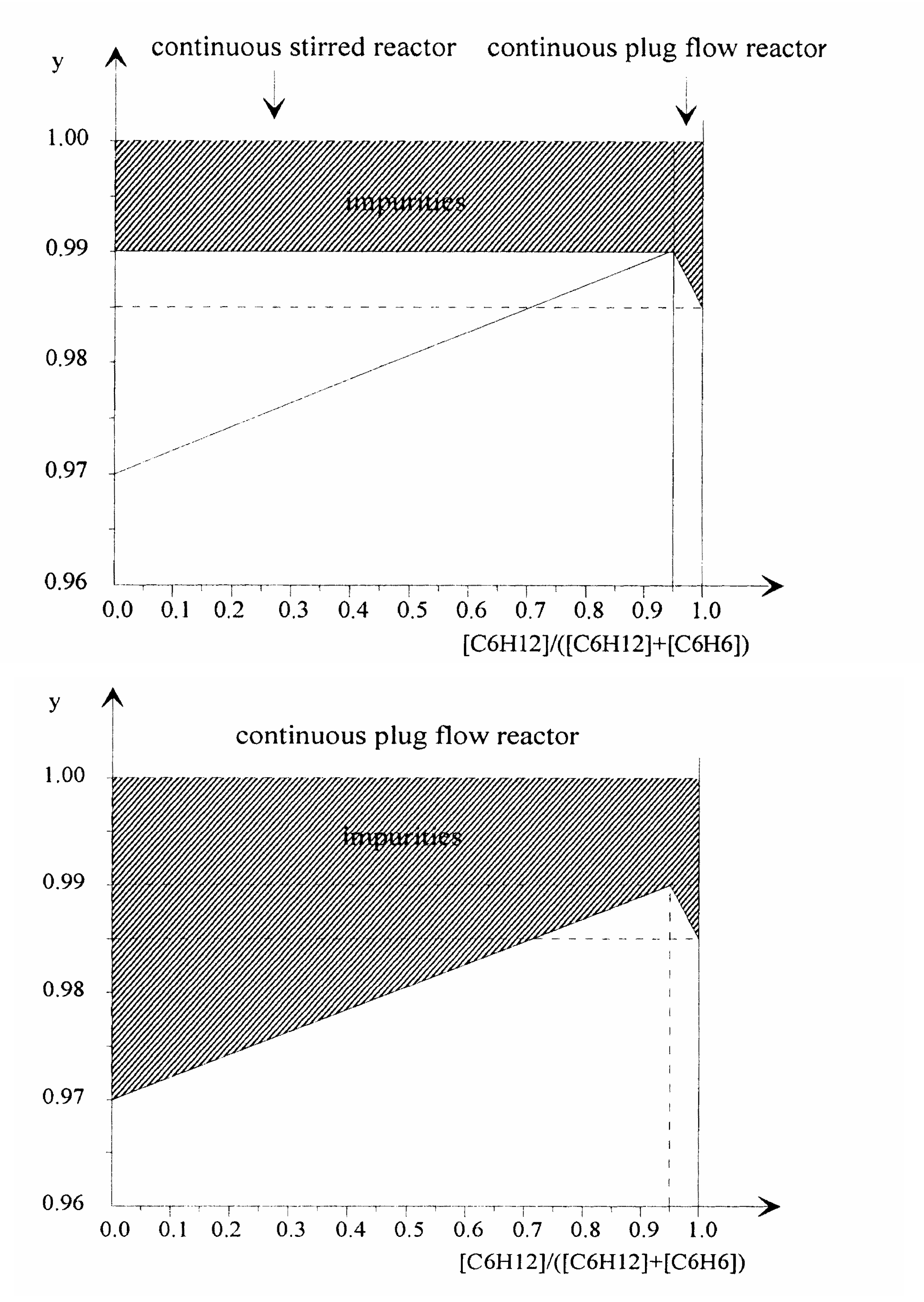
7.3 In the plug flow reactor, the quantity of benzene lost (not hydrogenated) is 1 – p. Fig. 1 shows the area that represents the amount of benzene that is not hydrogenated and therefore lost. For the installation MP we first have the amount of benzene lost in the continuous stirred reactor which is 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

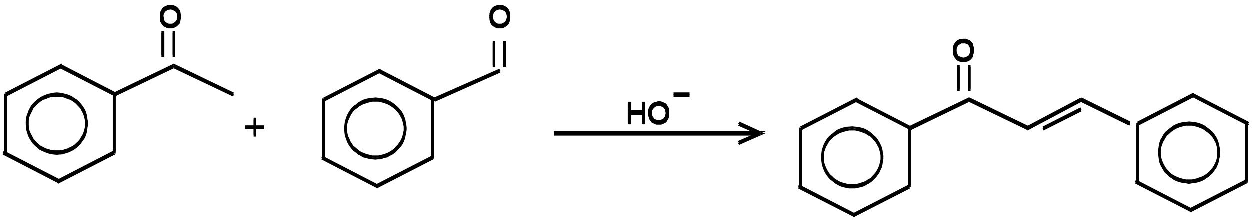

y
continuous stirred reactor
continuous plug flow reactor
1.00
0.99
0.98
0.97
0.96
impurities
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
[C6H12]/([C6H12]+[C6H6])
y
continuous plug flow reactor
1.00
0.99
0.98
0.97
0.96
impurities
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
[C6H12]/([C6H12]+[C6H6])

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 dehydratation, an α,β - unsaturated ketone is obtained: the chalcone, 1,3-diphenylprop-2-en-1-on.



a) *Starting the condensation reaction*

In a 250 cm^3 ground neck Erlenmeyer (conical) flask, dissolve about 5 g of potassium hydroxide, KOH, (50 pellets) in 30 cm^3 of water, then add slowly under stirring 20 cm^3 of ethanol. From the automatic dispensers, add 9.6 g (0.08 mol = 9.5 cm^3) of acetophenone and 8.5 g (0.08 mol = 8.5 cm^3) 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 cm^3 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 irrigating chalcone!!!

Questions:

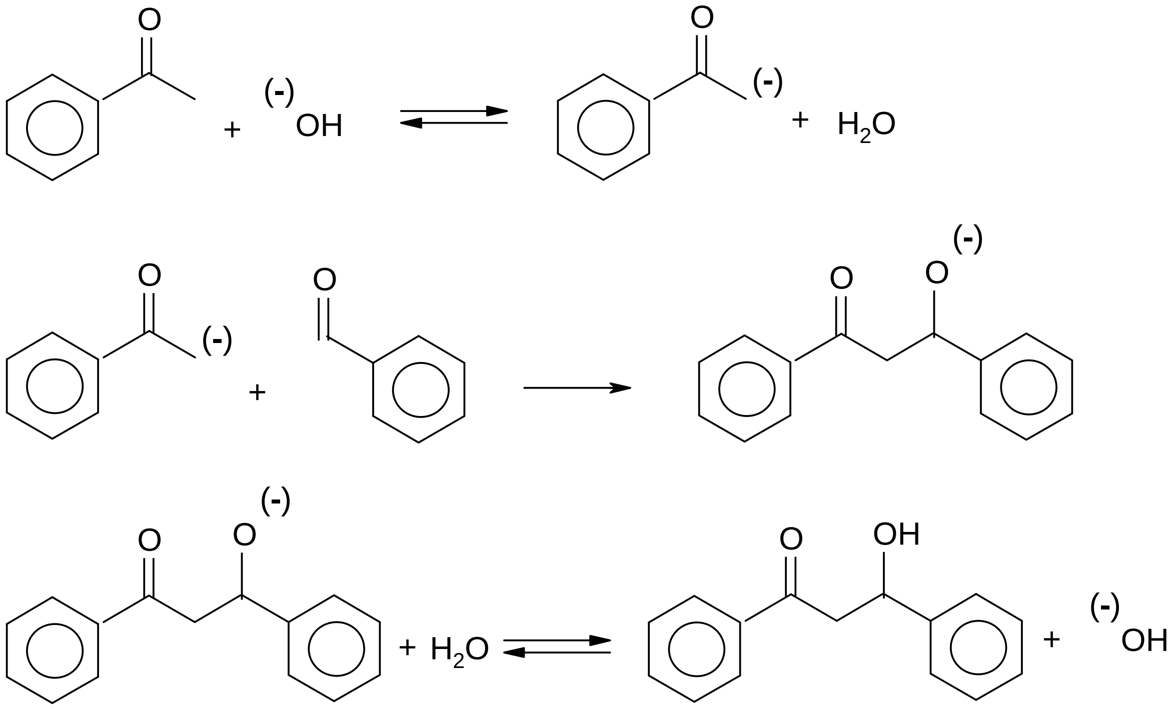
1.1 Write the mechanism for this reaction.

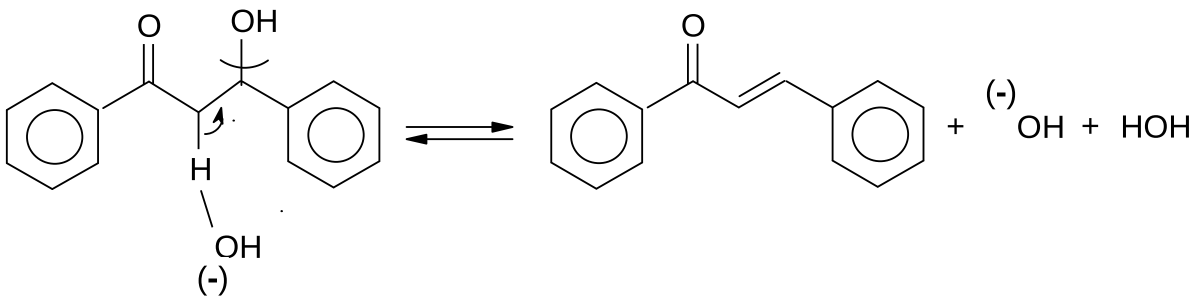
1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.

1.3 Calculate the yield of recrystallized product based on starting material and calculate the efficiency of the recrystallization process.

SOLUTION

1.1




O
OH
H
OH
(-)
O
+
(-)
OH
+
HOH

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

- $Al^{3+} + HCl \rightarrow$ no reaction
- $Al^{3+} + 3\ NH_3 + 3\ H_2O \rightarrow Al(OH)_3\downarrow + 3\ NH_4^+$
- $Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3\downarrow$

- $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$ (aq)

calcium(II) nitrate

- $Ca^{2+} + HCl \rightarrow$ no reaction
- $Ca^{2+} + 2\ OH^- \rightarrow Ca(OH)_2 \downarrow$

lead(II) nitrate

- $Pb^{2+} + 2\ Cl^- \rightarrow PbCl_2 \downarrow$ (in cold solutions)
- $Pb^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Pb(OH)_2 \downarrow + 2\ NH_4^+$
- $Pb^{2+} + 2\ OH^- \rightarrow Pb(OH)_2 \downarrow$

  $Pb(OH)_2 + 2\ OH^- \rightarrow [Pb(OH)_4]^{2-}$ (aq)

silver(I) nitrate

- $Ag^+ + Cl^- \rightarrow AgCl \downarrow$
- $Ag^+ + NH_3 + H_2O \rightarrow AgOH \downarrow + NH_4^+$ (or Ag_2O)

  $AgOH + 2\ NH_3 \rightarrow [Ag(NH_3)_2]^+$ (aq) $+ OH^-$
- $Ag^+ + OH^- \rightarrow AgOH \downarrow$

  $2\ AgOH \rightarrow Ag_2O + H_2O$

zinc(II) nitrate

- $Zn^{2+} + HCl \rightarrow$ no reaction
- $Zn^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Zn(OH)_2 \downarrow + 2\ NH_4^+$

  $Zn(OH)_2 + 4\ NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$(aq) $+ 2\ OH^-$
- $Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \downarrow$

  $Zn(OH)_2 + 2\ OH^- \rightarrow [Zn(OH)_4]^-$ (aq)

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 $Mn(OH)_3$ 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
Mn^{3+} / Mn^{2+}	1.51	
$Mn(OH)_3$ / $Mn(OH)_2$		0.13
O_2 / H_2O	1.23	0.39
I_2 / I^-	0.62	0.62
$S_4O_6^{2-}$ / $S_2O_3^{2-}$	0.09	0.09

Solubility products: $K_{sp}(Mn(OH)_2) = 1\times10^{-13}$

$K_{sp}(Mn(OH)_3) = 1\times10^{-36}$

Gas constant: $R = 8.315$ J $K^{-1}mol^{-1}$

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 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 cm^3 of thiosulphate added at the endpoint. Determine that concentration for the water tested.

Deduce the volume of oxygen (in cm^3), 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 $E^0(O_2/H_2O) > E^0(Mn(III)/Mn(II))$ at $pH = 14$

3.2 $O_2 + 4\ e^- + 2\ H_2O \rightarrow 4\ OH^-$

$Mn(OH)_2 + HO^- \rightarrow Mn(OH)_3 + e^-$

$O_2 + 4\ Mn(OH)_2 + 2\ H_2O \rightarrow 4\ Mn(OH)_3$

$2\ I^- \rightarrow I_2 + 2\ e^-$

$Mn^{3+} + e^- \rightarrow Mn^{2+}$

$2\ I^- + 2\ Mn^{3+} \rightarrow I_2 + 2\ Mn^{2+}$

$I_2 + 2\ e^- \rightarrow 2\ I^-$

$2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ e^-$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

3.4 1 mol $O_2 \triangleq$ 4 mol Mn(II) $\triangleq$ 4 mol Mn(III)

4 mol Mn(III) $\triangleq$ 4 mol I^- $\triangleq$ 2 mol I_2

2 mol $I_2 \triangleq$ 4 mol $S_2O_3^{2-}$

$c(S_2O_3^{2-}) \times V(S_2O_3^{2-}) = 4 \times c(O2) \times 50$

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:

tert-BuCl + H_2O = *tert*-BuOH + HCl

The rate of the reaction is given by

$$\frac{d\,[\text{HCl}]}{d\,t} = k_1\,[\textit{tert}\ \text{BuCl}]$$

The aim of this experiment is to determine the rate constant k_1 at ambient temperature.

Procedure:

1. Using a pipette transfer 2.0 cm^3 of *tert*-butyl chloride (flask 4.1 on the general-use bench) into a clean and dry 250 cm^3 ground neck Erlenmeyer (conical) flask.
2. As soon as possible add 148 cm^3 (measure with the graduated cylinder) of the aqueous ethanol solution standing on the general-use bench (flask 4.2).
3. Stopper the Erlenmeyer flask and stir vigorously using the magnetic stirrer. Start your timer. Note carefully the temperature, T(0), of the solution.
4. After approximately 5, 15, 25, 35, 45, 55 min (determined accurately), transfer 10.0 cm^3 samples using a pipette into 20 cm^3 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:

$$\ln \frac{[\text{tertBuCl}]_0}{[\text{tertBuCl}]_t} = k_1 . t$$

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 $t(8)$.

$t_\infty = t(8)$; $V_\infty = V(8)$

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:

$$t(\text{min}),\ V(\text{cm}^3),\ V_\infty,\ V,\ \frac{V_\infty}{V_\infty - V},\ \ln\frac{V_\infty}{V_\infty - V}$$

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

4.1 $\text{t-BuCl} + H_2O \rightarrow \text{t-BuOH} + \text{HCl}$

$t = 0$	$(\text{t-BuCl})_0$	
t	(t-BuCl)	$(\text{t-BuCl})_0 - (\text{t-BuCl})$
$t(8)$		$(\text{t-BuCl})_0$

$$\frac{d(\text{HCl})}{d\,t} = -\frac{(t-\text{BuCl})}{d\,t} = k_1\,(t-\text{BuCl})$$

$$\ln\frac{(t-BuCl)_0}{(t-BuCl)} = k_1\,t$$

t:

$$c(\text{HCl}) = c_0(\text{t-BuCl}) - c(\text{t-BuCl}) = \frac{V(\text{NaOH}) \times c(\text{NaOH})}{V(\text{HCl})} = \frac{V \times \text{Y} \times 10^{-2}}{10}$$

$t(8)$

$$c(\text{HCl}) = c_0(\text{t-BuCl}) = \frac{a\,Y}{10}$$

$$c(\text{t-BuCl}) = \frac{(a - V)\,\text{Y}}{10}$$

$$\ln\frac{c_0(\text{t-BuCl})}{c(\text{t-BuCl})} = \ln\frac{a}{a - V} = k_1\, t$$

4.2 $n_0(\text{t-BuCl}) = \dfrac{1.70}{92.5}$ $M(\text{t-BuCl}) = 92.5\ \text{g mol}^{-1}$

$$\text{Y} \times \text{a} \times 10^{-3} = \frac{10}{150} \times n_0(\text{t-BuCl})$$

$$\text{a}_{(\text{ml})} = \frac{170}{\text{Y} \times 10^{-3} \times 15 \times 92.5}$$

23rd

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 Tl_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.

$E^0(S/S^{2-}) = -0.48$ V $\quad E^0(NO_3^- / NO_{(aq)}) = 0.96$ V

$pK_a(H_2S) = 7$ $\quad pK_a(HS^-) = 13$

$K_{sp}(Tl_2S) = 1\times10^{-20}$ $\quad K_{sp}(CuS) = 1\times10^{-35}$

Solubility of NO in water (298 K): 2.53×10^{-2} mol dm^{-3}

Solubility of H_2S in water (298 K): 0.1 mol dm^{-3}

$R = 8.314$ J K^{-1} mol^{-1} $\quad F = 96\,487$ C mol^{-1}

SOLUTION

1.1 Solubility condition: $[Tl^+]^2\,[S^{2-}] \le 1\times10^{-20}$

$[Tl^+] = c(Tl^+) = 0.2$ mol dm^{-3}

$$c(S^{2-}) = [S^{2-}] + [HS^-] + [H_2S] = [S^{2-}]\left(1+\frac{[H^+]}{K_2}+\frac{[H^+]^2}{K_1K_2}\right) = 0.1 \text{ mol dm}^{-3}$$

$$[S^{2-}] = \frac{0.1}{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}} \quad \Rightarrow$$

For a strong monoprotic acid (1 mol dm^{-3}) and $[H^+] \approx 1$.

Then

$1 + 10^{13}\,[H^+] \ll 10^{20}\,[H^+]^2$ and $[S^{2-}] \approx \frac{0.1}{1\times10^{20}}$

$[Tl^+]^2\,[S^{2-}] = \frac{(0.2)^2 \times 0.1}{1\times10^{20}} = 4\times10^{-23} < K_s(Tl_2S)$

Thus, 0.1 mol of Tl_2S 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 mol dm^{-3}

  $[Cu^{2+}] = 0.1$

  $c(S^{2-})$ = 0.1 mol dm^{-3}

  Similarly as in part (1.1):

  $$[S^{2-}] = \frac{0.1}{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}}$$

  $$[S^{2-}] \approx \frac{0.1}{1\times10^{20}}$$

  $[Cu^{2+}]\,[S^{2-}] = \frac{(0.1)^2 \times 0.1}{1\times10^{20}} \approx 1\times10^{-23} > K_s(CuS)$

  Conclusion: 0.1 mol CuS does not dissolve in 1 M solution HCl.

- When dissolving 0.1 mol CuS in 1 M HNO_3 an additional redox process occurs: the oxidation of S^{2-} to S.

  $2\,NO_3^- + 8\,H^+ + 3\,S^{2-} \rightarrow 3\,S + 2\,NO + 4\,H_2O$

  The emf of this reaction is $\Delta E = E_1^0 - E_2^0$ = (0.96 + 0.48) = $\underline{1.44\ V}$

  $\log K = \frac{\Delta G}{RT} = \frac{n\,F}{R\,T}\,\Delta E = \frac{n_1 n_2 (E_1^0 - E_2^0)}{0.0591} \cong 144$ $K = 1\times10^{144}$

The equilibrium constant of this process can also be written in the form:

$$K = \frac{[\mathrm{NO}]^2}{[\mathrm{NO}_3^-]^2\,[\mathrm{H}^+]^8\,[\mathrm{S}^{2-}]^3}$$

From the above equilibrium follows that $[\mathrm{S}^{2-}] = \sqrt[3]{\frac{K\,[\mathrm{NO}_3^-]^2\,[\mathrm{H}^+]^8}{[\mathrm{NO}]^2}}$

Since $[\mathrm{NO}_3^-] = [\mathrm{H}^+] = 1$

$$[\mathrm{S}^{2-}] = \sqrt[3]{\frac{K}{[\mathrm{NO}]^2}}$$

$c_{\mathrm{CuS}} = [\mathrm{S}] + [\mathrm{H_2S}] + [\mathrm{HS}^-] + [\mathrm{S}^{2-}]$

$$[\mathrm{S}^{2-}] = \frac{c_{\mathrm{CuS}}}{1 + \frac{[\mathrm{H}^+]}{K_1} + \frac{[\mathrm{H}^+]^2}{K_1\,K_2} + \sqrt[3]{\frac{K}{[\mathrm{NO}]^2}}}$$

However

$$1 + \frac{[\mathrm{H}^+]}{K_1} + \frac{[\mathrm{H}^+]^2}{K_1\,K_2} \ll \sqrt[3]{\frac{K}{[\mathrm{NO}]^2}} = \sqrt[3]{\frac{1\times 10^{144}}{(0.0253)^2}} = 1.16\times 10^{49}$$

$$[\mathrm{S}^{2-}] = \frac{0.1}{1.16\times 10^{49}} = 8.62\times 10^{-51}$$

$[\mathrm{Cu}^{2+}]\,[\mathrm{S}^{2-}] = 0.1 \times 8.62\times 10^{-51} = 8.62\times 10^{-52} \ll K_{sp}(\mathrm{CuS})\ (= 1\times 10^{-35})$

Conclusion: CuS dissolves in 1 M solution of $\mathrm{HNO_3}$.

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** ($C_8H_{14}O_4$).

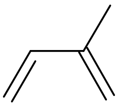
2.6 Sketch the structures of **C**, **D**, **E**, **F** and **Z.**

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**.

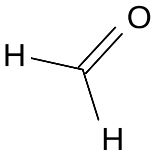
SOLUTION

2.1 **Y** = Isoprene, C_5H_8 , M = 68 g mol^{-1}

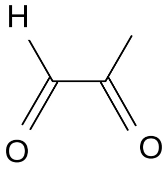
2.2



Y

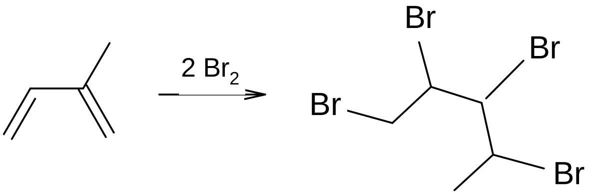


A



B

2.3

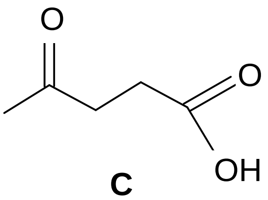


2.4 **Z** = $C_5H_8O_2$

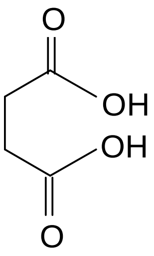
There is one double bond per monomer unit.

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.

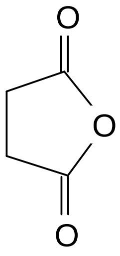
2.6



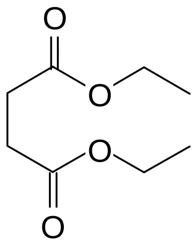
C



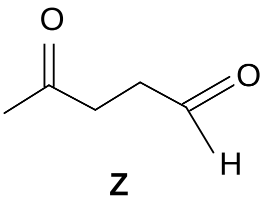
D



E

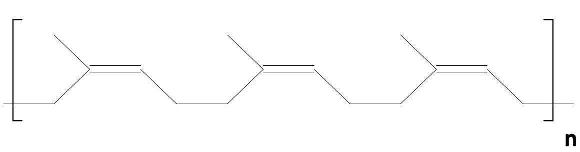


F

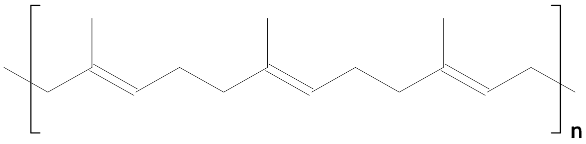


Z

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, Hg_2Cl_2/Cl^-) are examples of such electrodes. The standard emf of a cell built of those electrodes (–) Ag,AgCl/Cl^- || Hg_2Cl_2/Hg (+) is $E^0 = 0.0455$ V at $T = 298$ K. The temperature coefficient for this cell is $dE^0/dT = 3.38\times10^{-4}$ 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 $E^0 = 0.799$ V and the solubility product of AgCl $K_{sp} = 1.73\times10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between E^0(Ag/Ag^+) and E^0(Ag, AgCl/Cl^-).

3.5 Calculate the solubility product of Hg_2Cl_2 knowing that the standard potential of the calomel electrode is $E^0 = 0.798$ V.

$F = 96487$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}, $T = 298$ K

SOLUTION

3.1 Reduction (calomel electrode (+)): $1/2\ Hg_2Cl_2 + e^- \rightarrow Hg + Cl^-$

Oxidation (silver/silver chloride electrode (-)) $Ag + Cl^- \rightarrow AgCl + e^-$

Summary reaction: $Ag + 1/2\ Hg_2Cl_2 \rightarrow Hg + AgCl$

3.2 $\Delta G^o = -n\,F\,E^0 = -\,96497\ C\ mol^{-1} \times 0.0455\ V = -\,4.39\ kJ\ mol^{-1}$;

Since ΔG^o is negative, the reaction is spontaneous.

3.3 The change of enthalpy is related to the Gibbs-Helmholtz equation:

$$\Delta H = \Delta G + T\Delta S = -n\,F\,E + T\,n\,F\left(\frac{\Delta E^0}{\Delta t}\right) = -n\,F\left(E - T\left(\frac{\Delta E^0}{\Delta t}\right)\right) =$$

$$= -96487 \text{ C mol}^{-1} (0.0455 \text{ V} - 298 \text{ K} \times 3.38\times10^{-4} \text{ V K}^{-1}) = 5.36 \text{ kJ mol}^{-1}$$

3.4 For the Ag│ Ag^+ electrode: $E = E^o + 0.0591 \log[Ag^+]$

For the Ag,AgCl│ Cl^- electrode $[Ag^+]$ is determined by the solubility product:

$$[Ag^+] = \frac{K_{sp}}{\left[Cl^-\right]}$$

$$E^o(\text{Ag, AgCl}\,|\,\text{Cl}^-) = E^o(\text{Ag}\,|\,\text{Ag}^+) + 0.0591 \log K_{sp} = 0.799 - 0.577 = 0.222 \text{ V}$$

3.5 $E^o(\text{Hg, Hg}_2\text{Cl}_2\,|\,\text{Cl}^-) = E^o(\text{Hg}\,|\,\text{Hg}^{2+}) + \dfrac{0.0591}{2} \log K_{sp}(\text{Hg}_2\text{Cl}_2)$

The standard potential of the calomel electrode is equal to 0.0455 + 0.222 = = 0.2675 V.

Thus, $\log K_{sp}(Hg_2Cl_2)$ can be calculated as:

$$\log K_{sp}(\text{Hg}_2\text{Cl}_2) = \frac{2(0.2675 - 0.798)}{0.0591} = -17.99$$

$K_{sp} = 1.03\times10^{-18}$

PROBLEM 4

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18\times10^{-18}/n^2$ [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:

a) another hydrogen atom in its ground state?

b) a copper atom in the Cu crystal?

The electron work function of Cu is $\Phi_{Cu} = 7.44\times10^{-19}$ 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.

$h = 6.6256\times10^{-34}$ J s; $m_e = 9.1091\times10^{-31}$ kg; $c = 2.99792\times10^{8}$ m s^{-1}

SOLUTION

4.1 $\Delta E_{n\to1} = E_n - E_1 = 2.18\times10^{-18}\,(1 - n^2)$

$\Delta E_{2\to1} = 1.635\times10^{-18}$ J

$\Delta E_{7\to1} = 2.135\times10^{-18}$ J

4.2 The Lyman series is due to $\Delta E_{n\to1}$ varying from 1.635×10^{-18} J (n = 1) to 2.135×10^{-18} J ($n \to \infty$), 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 $\Delta E_{\infty\to1} = 2.18\times10^{-18}$ J. Both $\Delta E_{2\to1}$ and $\Delta E_{7\to1}$ are smaller than $\Delta E_{\infty\to1}$ 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:

$h\nu = \Phi_{Cu} + E_{kin} = \Phi_{Cu} + \frac{1}{2}\, m_e v^2$

Because $\Delta E_{2\to1} > \Phi_{Cu}$ and $\Delta E_{7\to1} > \Phi_{Cu}$ both photons are indeed able to ionize a Cu-atom in the crystal.

The kinetic energy of the emitted electrons is:

ΔE_{kin} (2→1) = $\Delta E_{2\rightarrow1} - \Phi_{\mathrm{Cu}} = 8.91\times10^{-19}$ J

ΔE_{kin} (7→1) = $\Delta E_{7\rightarrow1} - \Phi_{\mathrm{Cu}} = 13.91\times10^{-19}$ J

4.4 The wavelength of an electron is:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2\,E_{\mathrm{kin}}\,m_e}}$$

($p = m_e v_e$ and $E_{\mathrm{kin}} = \dfrac{p^2}{2\,m_e}$)

$\Delta E_{2\rightarrow1}$: $\lambda_1 = 4.16\times10^{-10}$ m = 4.16 Å

$\Delta E_{7\rightarrow1}$: $\lambda_2 = 5.20\times10^{-10}$ m = 5.20 Å

PROBLEM 5

Halogen 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 dm^3 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}F = 100 %;
  ^{35}Cl = 75.53 %; ^{37}Cl = 24.47 %;
  ^{79}Br = 50.54 %; ^{81}Br = 49.46 %;
  ^{127}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 $\Phi = 0$, $\pi/2$, π, 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**.

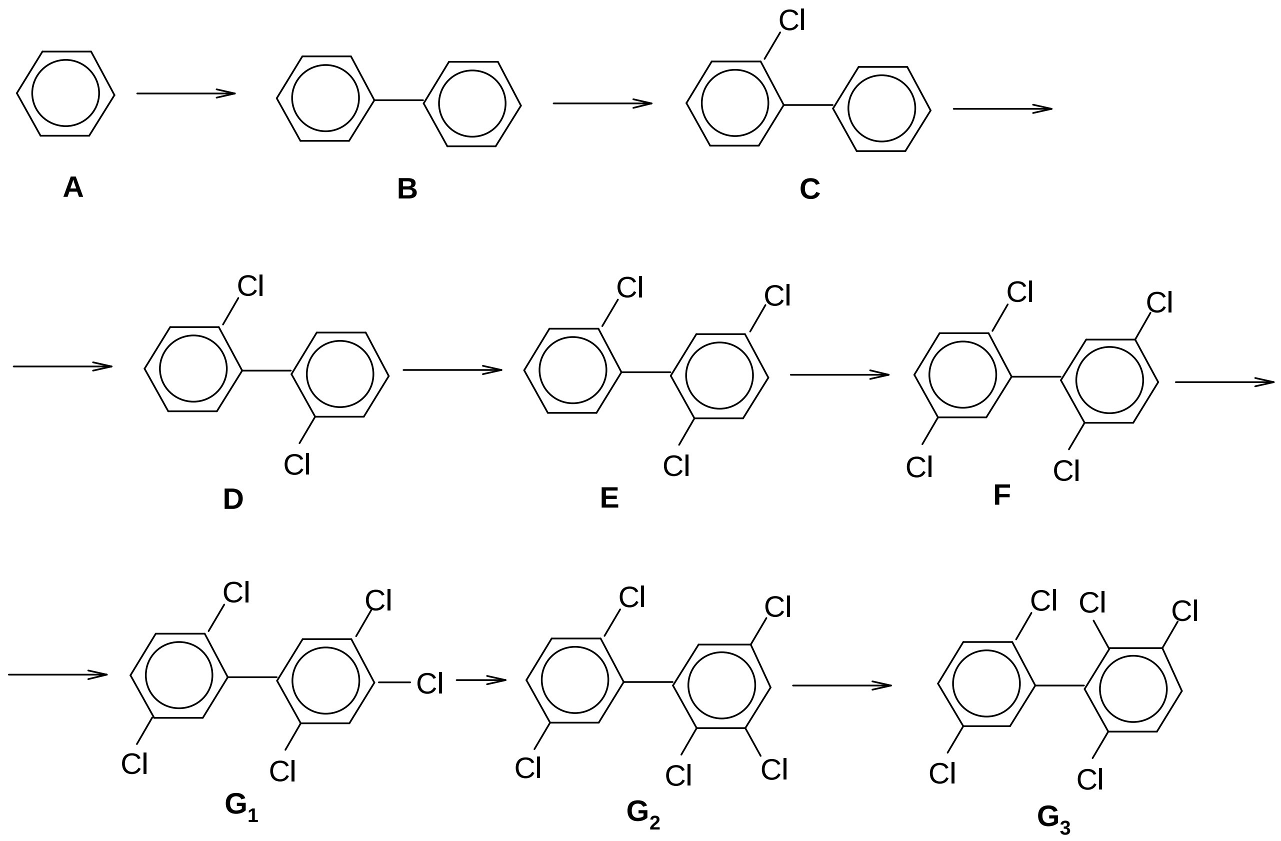
5.5 Give a sequence of **G$_1$**, **G$_2$**, **G$_3$** according to their increasing difficulty of racemization. Explain your answer.

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



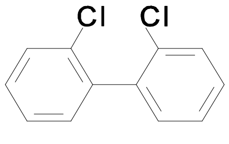
5.2 For the determination of the halogen of **E** we consider the ratio of the isotopic peaks in the mass spectrum.

For **E** (n = 3) we have: $(x + y)^3 = x^3 + 3\,x^2y + 3\,xy^2 + y^3$.

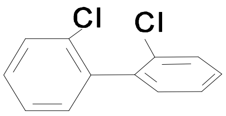
Therefore, with Br we would obtain: $x : y = 50.54 : 49.46 \cong 1 : 1$ hence $(x + y)^3 = 1 + 3 + 3 + 1$ and the ratio would be 1 : 3 : 3 : 1 which is not in agreement with the text.

For chlorine the isotopic ratio is 75.53 : 24.47 ≅ 1 : 3 and therefore $(x + y)^3 = 3^3 + (3\times3^2\times1) + (3\times3\times1^2)$, which yields to a ratio of 1 : 1 : 0.33 : 0.04. So, the X-atom is chlorine.

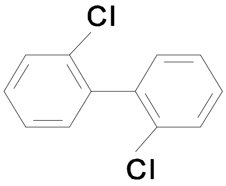
5.3



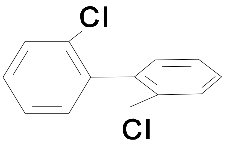
Φ =0 π



Φ =1/2 π

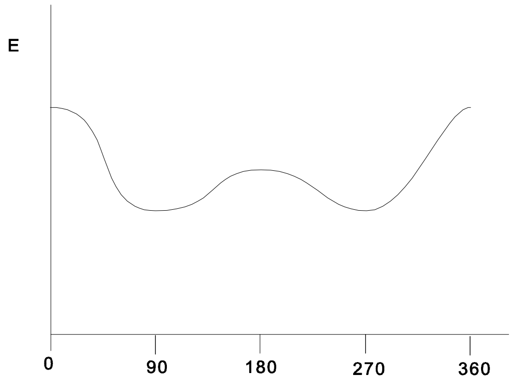


Φ = π

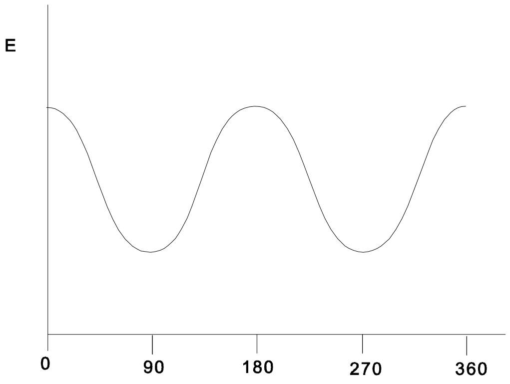


Φ =3/2 π

5.4



Compound C

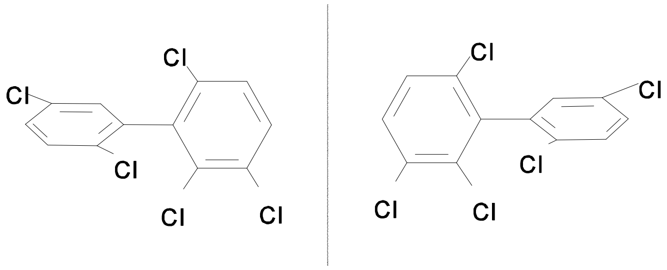


Compound D

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

1.1 $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{(a)}$$

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:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad \text{(b)}$$

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 a 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 $[Cu(NH_3)_4]^{2+}$ and $[Zn(NH_3)_4]^{2+}$

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 cm^3 of $CuSO_4$ and 20 cm^3 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)

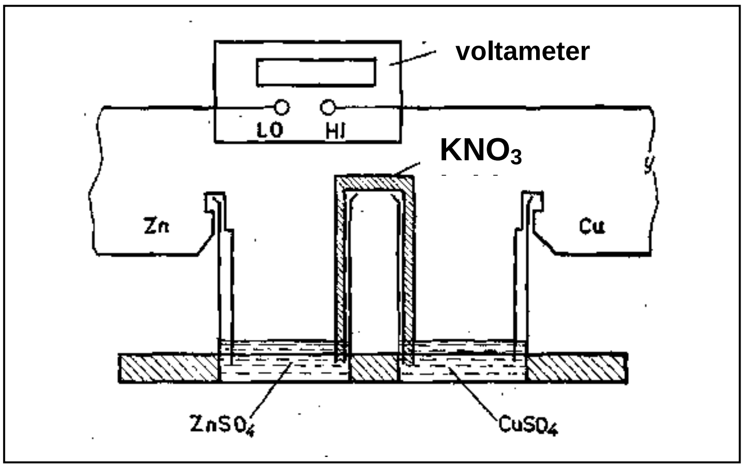


Fig. 1

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:

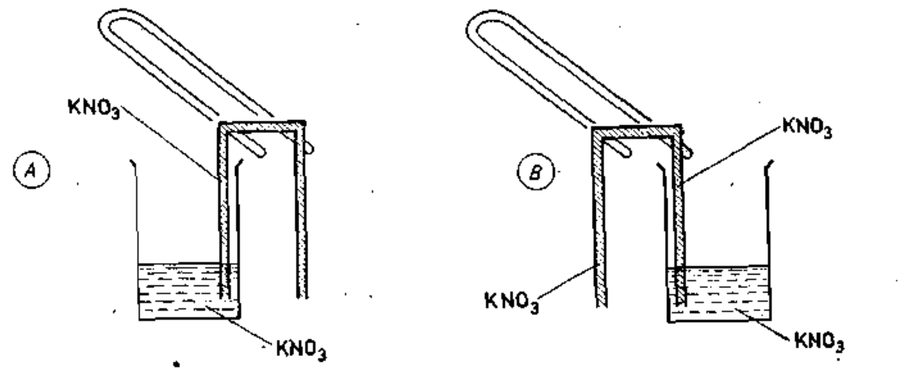


Fig. 2

Pipette 20 cm^3 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).

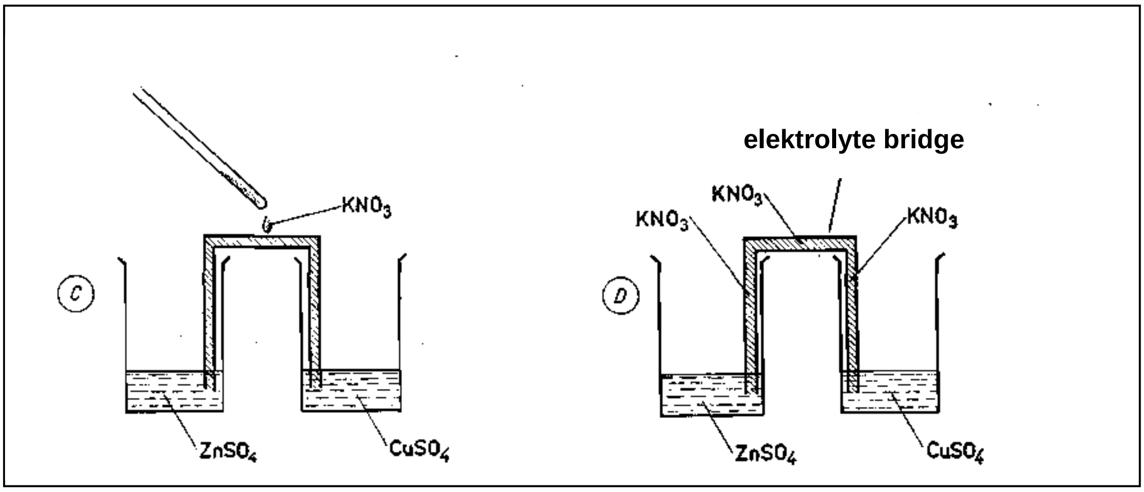


Fig. 3

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 $Cu/[Cu(NH_3)_4]^{2+}$ 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 J K^{-1} mol^{-1}
Faraday constant F = 96 487 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:

$CuSO_4$: $d_1 = 1.0923$ (kg dm^{-3}) **–** 0.0002700 (kg $dm^{-3}K^{-1}$) T
$ZnSO_4$: $d_2 = 1.0993$ (kg dm^{-3}) **–** 0.0002900 (kg $dm^{-3}K^{-1}$) T
NH_3 : $d_3 = 1.0740$ (kg dm^{-3}) **–** 0.0002800 (kg $dm^{-3}K^{-1}$) 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 $a_i = f_i * c_i$. 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 Cu^{2+}_{aq}, Zn^{2+}_{aq}, $[Cu(NH_3)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$ 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^o of your Daniell cell using the Nernst equation.

2.3 Calculate the concentrations of $[Cu(NH_3)_4]^{2+}$ 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 $[Cu(NH_3)_4]^{2+}$ ions.

2.5 Calculate the concentrations of $[Zn(NH_3)_4]^{2+}$ 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 $[Zn(NH_3)_4]^{2+}$ 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 $$E=\left(E^0(\text{Cu}^{2+}/\text{Cu})+\frac{RT}{2F}\ln([\text{Cu}^{2+}]\times f_{Cu^{2+}})\right)-\left(E^0(\text{Zn}^{2+}/\text{Zn})+\frac{RT}{2F}\ln([\text{Zn}^{2+}]\times f_{Zn^{2+}})\right)-E_{dif}$$

For E_{dif} = 0 :

$$E_A=E^0(\text{Cu}^{2+}/\text{Cu})-E^0(\text{Zn}^{2+}/\text{Zn})+\frac{RT}{2F}\ln\frac{[\text{Cu}^{2+}]\times f_{Cu^{2+}}}{[\text{Zn}^{2+}]\times f_{Zn^{2+}}}$$

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:

$$[\text{Cu(NH}_3)_4^{2+}]=\frac{c(\text{Cu}^{2+})\times V}{V+V_1}$$

$$[\text{NH}_3]=\frac{(c(\text{NH}_3)\times V_1)-(4\,c(\text{Cu}^{2+})\times V)}{V+V_1}$$

2.4 After the addition of NH_3 the following complex equilibrium is established:

$$\text{Cu}^{2+} + 4\ \text{NH}_3 \rightleftharpoons \text{Cu(NH}_3)_4^{2+}$$

$$\beta_4=\frac{[\text{Cu(NH}_3)_4^{2+}]\times f_{\text{Cu(NH}_3)_4^{2+}}}{[\text{Cu}^{2+}]\times f_{\text{Cu}^{2+}}\times[\text{NH}_3]^4}$$

Then the Nernst equation has the form:

$$E_1^{'} = E^0(\mathrm{Cu}^{2+}/\mathrm{Cu}) = \frac{RT}{2F}\ln\frac{[\mathrm{Cu(NH_3)_4^{2+}}]\times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{\beta_4\times[\mathrm{NH_3}]^4}$$

$$E_B = E'_1 - E_2 = E^0(\mathrm{Cu}^{2+}/\mathrm{Cu}) - E^0(\mathrm{Zn}^{2+}/\mathrm{Zn}) + \frac{RT}{2F}\ln\frac{[\mathrm{Cu(NH_3)_4^{2+}}]\times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{[\mathrm{Zn}^{2+}]\times f_{Zn^{2+}}\times\beta_4\times[\mathrm{NH_3}]^4}$$

From the above equation β_4 or lnβ_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 lnβ_4 for complex $\mathrm{Zn(NH_3)_4^{2+}}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\mathrm{Cu(NH_3)_4^{2+}}$.

24th

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:

$6\ CO_2 + 6\ H_2O + \text{solar energy} \rightarrow C_6H_{12}O_6 + 6\ O_2$

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 ($C_6H_{12}O_6$), 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).

i) 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?

ii) 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 1.37×10^{18} m^3.

1.3 Three percent of the mass of a 9.1×10^4 kg adult whale is nitrogen. When a 9.1×10^4 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 9.1×10^4 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.

$CaSiO_3(s) + 2\ CO_2(g) + 3\ H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ HCO_3^-(aq) + H_4SiO_4(aq)$

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 $5 \times 365 \times 75 \times 10 = 1.4\times10^6$ kg krill which themselves need 1.4×10^7 kg of carbohydrates coming from diatoms.

For 180 g $C_6H_{12}O_6$, 6×44 g CO_2 are necessary, and thus

for 1.4×10^7 kg carbohydrates $1.4\times10^7 \times (264/180) = 2.00\times10^7$ kg of CO_2 are needed, i. e. 1.0×10^{10} dm^3 CO_2

1.2 i) The amount of water is 4×10^{13} dm^3.

ii) 3×10^{-5} of the total ocean volume (0.03 ‰).

1.3 The mass of nitrogen from a whale is $0.03 \times 9.1\times10^4$ kg $= 2.7\times10^6$ g.

$$n(N) = n(NH_4^+) = \frac{2.7\times10^6\ g}{14\ g\,mol^{-1}} = 1.9\times10^5\ mol$$

$$m(NH_4^+) = 1.9\times10^5\ mol \times 18\ g\ mol^{-1} = 3\times10^6\ g\ NH_4^+ = 3\times10^3\ kg\ NH_4^+$$

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: $n(CaSiO_3) = 6.5\times10^5$ mol

$$m(CaSiO_3) = 6.5\times10^5\ mol \times 116\ g\ mol^{-1} = 7.5\times10^7\ g\ CaSiO_3$$

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.

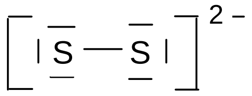
2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, FeO(OH).

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



2.2 $FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

2.3 $Fe^{2+} + 1/4\ O_2 + 3/2\ H_2O \rightarrow FeOOH + 2\ H^+$

2.4 $[H^+] = 1\times10^{-3}$

$n[H^+] = 1\times10^{-3}$ mol

From both equations: $n(FeS_2) = 2.5\times10^{-4}$ mol

2.5 Total flow into pond in 2 years =

2 yr × 365 days yr^{-1} × 24 h day^{-1} × 60 min h^{-1} × 20.0 dm^3 min^{-1} =

= 2.10×10^7 dm^3 of water

$n(Fe^{2+})$ into pond = 2.10×10^7 dm^3 × $8{,}35\times10^{-3}$ mol dm^{-3} = 1.76×10^5 mol

$n(Fe^{3+})$ produced = $0.75 \times 1.76\times10^5$ mol = 1.32×10^5 mol

mass of deposited Fe_2O_3:

$m(Fe_2O_3) = 0.5 \times 1.32\times10^5$ mol × 159.7 g mol^{-1} = 1.05×10^7 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.

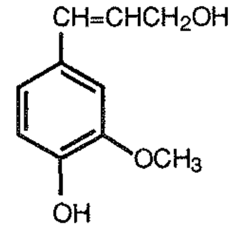
Coniferyl alcohol reacts with cold HBr to form **D** ($C_{10}H_{11}O_2Br$). Hot HI converts ArOR to ArOH and RI. Coniferyl alcohol reacts with excess hot HI to give **E** ($C_9H_9O_2I$) and CH_3I. CH_3I in aqueous base reacts with coniferyl alcohol to form **F** ($C_{11}H_{14}O_3$), which is not soluble 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.

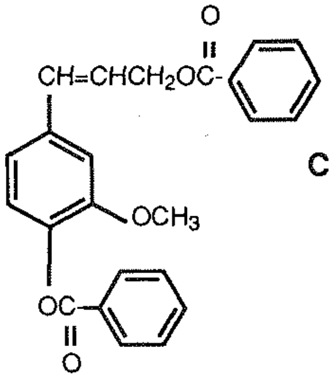
SOLUTION

3.1

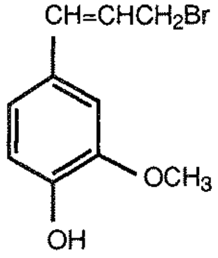


coniferyl alcohol

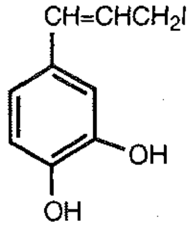
$O=CHCH_2OH$ **B**



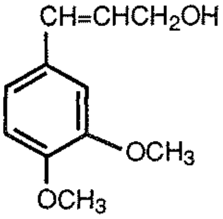
C



D



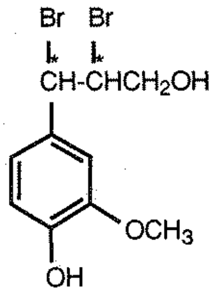
E

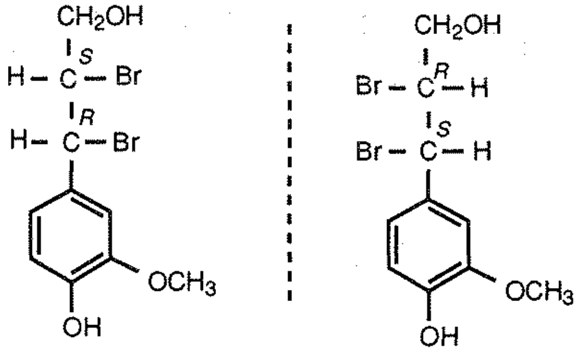


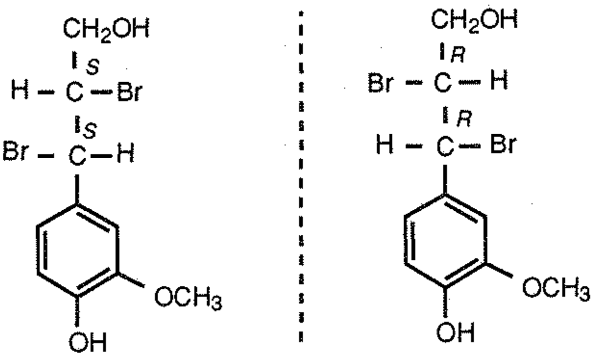
F

I

3.2 There are no geometric isomers of compound **A**, but there are 4 diastereomers (2 pairs of enantiomers).



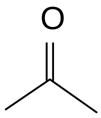


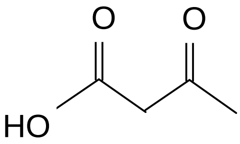


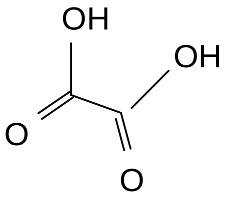
PROBLEM 4

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.**

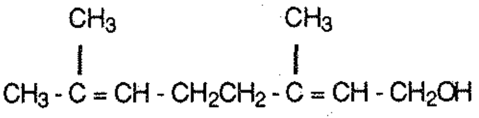
4.2 Give the structure of compound **B.**

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

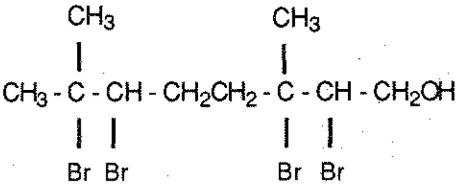
4.1



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2OH$$

geraniol **A**

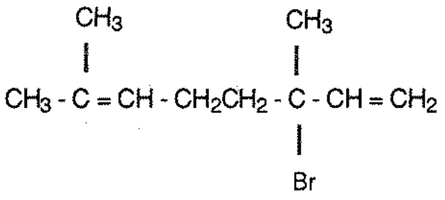
4.2



$$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_2CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_2OH$$

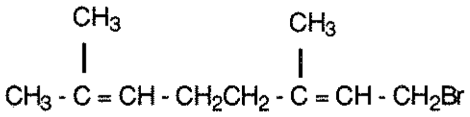
B

4.3



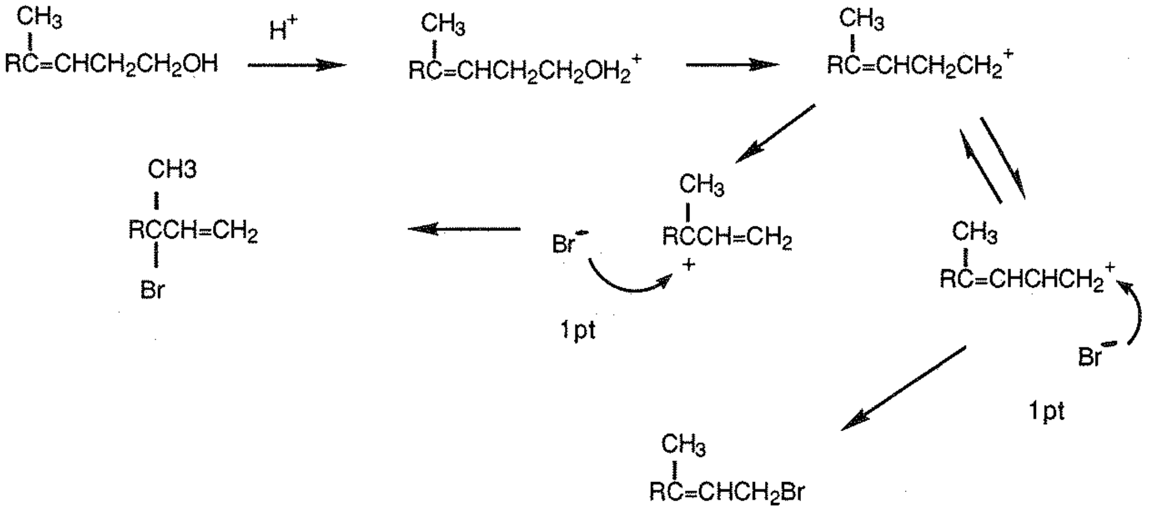
$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2CH_2-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH=CH_2$

or



$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2Br$

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):

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

5.1 With a diagram, show the bonds present in NO_2(g) using the concept of resonance if necessary. Nitrogen dioxide, NO_2, is paramagnetic.

5.2 Show, with bonding diagrams, how two molecules of NO_2(g) combine to give a molecule of N_2O_4 (g) which is not paramagnetic.

5.3 At 298 K, the ΔG^o of formation for N_2O_4(g) is 98.28 kJ, whereas for NO_2(g) is 51.84 kJ. Starting with one mole of N_2O_4(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.

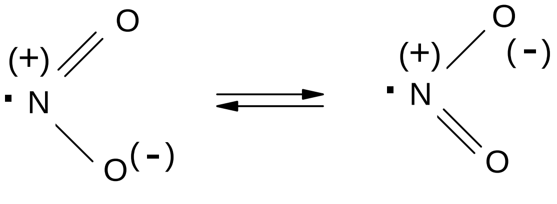
5.4 If ΔH^o for the reaction $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?

5.5 The dissociation of N_2O_4(g) to give NO_2(g) is a first order process with a specific rate constant of 5.3×10^4 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?

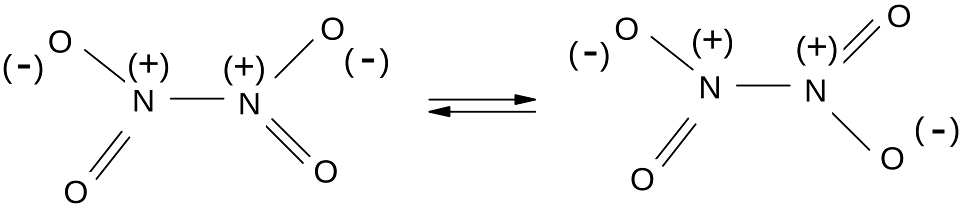
5.6 The association of NO_2(g) to give N_2O_4(g) is a second-order process with a specific rate constant of 9.8×10^6 $dm^3mol^{-1}s^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c, at 298 K for the reaction $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$

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: O=N—ONO_2 , nitrosyl nitrate)

5.3 $N_2(g) + 2\ O_2(g) \rightarrow N_2O_4(g)$ $\Delta G^o = 98.28$ kJ

$N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$ $\Delta G^o = 2 \times (51.84) = 103.68$ kJ

$N_2O_4\ (g) \rightarrow 2\ NO_2\ (g)$ $\Delta G^o = 5.4$ kJ

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:

$\Delta G^0 = -RT \ln K$; $K = e^{(-\,5.4\ \text{kJ}/\ 8.314\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1})}$

$$K_p = 0.113 = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(P_T X_{NO_2})^2}{P_T X_{N_2O_4}} = \frac{\left(\dfrac{2x}{1+x}\right)^2}{\left(\dfrac{1-x}{1+x}\right)} = \frac{4\,x^2}{1-x^2}$$

wherefrom <u>x = 0.166</u>

5.4 If $2 \times 0.166 = 0.332$ mol N_2O_4 decomposes, 0.664 mol NO_2 are formed, thus

$$K_p = \frac{\left(\dfrac{0.664}{1.332}\right)^2}{\dfrac{1-0.332}{1.332}} = 0.496$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{0.496}{0.113}\right) = -\frac{58.03\ \text{Jmol}^{-1}}{8.314\ \text{Jmol}^{-1}\text{K}^{-1}}\left(\frac{1}{T_2} - \frac{1}{298\ \text{K}}\right)$$

$T_2 = 318$ K

5.5 $\ln\dfrac{[N_2O_4]_t}{[N_2O_4]_0} = -k\,t$

$$\ln 0.80 = -(5.3\times10^{4}\ s^{-1})\ t$$

$$t = 4.2 \times 10^{-6}\ \text{s}$$

5.6 $K = \dfrac{k_{\text{forward}}}{k_{\text{reverse}}} = \dfrac{9.8\times10^{6}}{5.3\times10^{4}} = 1.8\times10^{2}$

PROBLEM 6

The concentration of carbon dioxide in the atmosphere has increased substantially during this century and is predicted to continue to increase. The [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 $dm^3\ mol^{-1}\ atm^{-1}$

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 $[CO_2\ (aq)] = K_H\, p_{CO2} = 0.0343\ \text{M atm}^{-1} \times 440\times10^{-6}\ \text{atm} = \underline{1.51\times10^{-5}\ \text{M}}$

6.2 $CO_2(aq) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq)$ $\quad \Delta G^o = 36.3\ \text{kJ mol}^{-1}$

$K = e^{-\Delta G / RT} = 4.37\times10^{-7}$

Since $x = [H^+] = [HCO_3^-]$,

$$K = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[CO_2\right]} = \frac{x^2}{\left[CO_2\right]}$$

Solving for x yields $[H^+] = 2.57\times10^{-6}$; $\quad \underline{pH = 5.59}$

6.3 $\Delta H^o = \Delta H^o_f\,(HCO_3^-) - \Delta H^o_f\,(CO_2) - \Delta H^o_f\,(H_2O) =$

$= -691.2 - (-412.9) - (-285.8) = \underline{7.5\ \text{kJ mol}^{-1}}$

6.4 Since the reaction is endothermic, the equilibrium constant will increase with temperature. Therefore, $[H^+]$ 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 cm^3 of a stock solution buffered at a pH of 7.2.

7.9 The chloride concentration in another 50.00 cm^3 sample of bay water was determined by the Volhard method. In this method an excess of $AgNO_3$ 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 $FeSCN^{2+}$ complex that forms when Ag^+ is depleted. If the excess Ag^+ from the addition of 50.00 cm^3 of 0.00129 M $AgNO_3$ to the water sample required 27.46 cm^3 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:

$$AgCl(s) \rightarrow Ag(s) + ½ Cl_2(g).$$

Furthermore, if this photodecomposition occurs in the presence of excess Ag^+, the following additional reaction occurs:

$$3 Cl_2 (g) + 3 H_2O + 5 Ag^+ \rightarrow 5 AgCl + ClO_3^- + 6 H^+$$

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: $K_{sp}(AgCl) = 1.78 \times 10^{-10}$

$K_{sp}(Ag_2CrO_4) = 1.00 \times 10^{-12}$

SOLUTION

7.1 $n(Ag^+) = n(Cl^-)$

$$c(Cl^-) = \frac{0.01616\ dm^3 \times 0.00164\ mol\ dm^{-3}}{0.050\ dm^3} = 5.30\times10^{-4}\ mol\ dm^{-3}$$

7.2 Concentration in mg dm^{-3} = 5.30×10^{-4} mol dm^{-3} × 35.5 g mol^{-1} = 0.0188 g dm^{-3} = = 18.8 mg dm^{-3}

Thus the chloride concentration is sufficiently high for normal oyster growth.

7.3 $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl \downarrow(s)$

7.4 $2\ Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4 \downarrow(s)$ (brick-red colour)

7.5 $K_{sp}(Ag_2CrO_4) = [Ag^+]^2[CrO_4^{2-}] = 4\ x^3$ if $x = [Ag^+]$ $\Rightarrow$

$[Ag^+] = 7.07 \times 10^{-6}$; $[CrO_4^{2-}] = 2 \times10^{-2}$

$$[Cl^-] = \frac{K_{sp}(AgCl)}{\left[Ag^+\right]} = \frac{178 \times 10^{-10}}{7.07 \times 10^{-6}} = 2.5 \times 10^{-5}$$

7.6 $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

either/or

$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- + H_2O$

7.7 A buffer system has its maximum buffer capacity when $pH = pK_a$. So, the system 3 would be best since $pK_a = 7.2$

7.8 $m(NaH_2PO_4) = 0.10\ mol\ dm^{-3} \times 0.500\ dm^3 \times 119.98\ g\ mol^{-1} = 6.0\ g$

$m(Na_2HPO_4) = 0.10\ mol\ dm^{-3} \times 0.500\ dm^3 \times 141.96\ g\ mol^{-1} = 7.1\ g$

7.9 mol Ag^+ added: $n(Ag^+)_{ad} = 0.05\ dm^3 \times 0.00129\ mol\ dm^{-3} = 6.45\times10^{-5}\ mol$

mol Ag^+ left over: $n(Ag^+)_{left} = 0.02746\ dm^3 \times 0.0141\ mol\ dm^{-3} = 3.87\times10^{-5}\ mol$

mol Cl^- in sample:

$n(Cl^-) = n(Ag^+)_{ad} - n(Ag^+)_{left} = (6.45\times10^{-5}\ mol) - (3.87\times10^{-5}\ mol) = 2.58\times10^{-5}\ mol$

$$\Rightarrow \quad [Cl^-] = \frac{2.58\times10^{-5}}{0.050} = 5.16\times10^{-4}\ mol\ dm^{-3}$$

7.10 n(AgCl) lost: $\frac{0.010 \text{ g AgCl}}{143.35 \text{ gmol-1}} = 6.98 \times 10^{-5}$ mol

$n(Cl_2)$ produced: ½ (6.98×10^{-5} mol) = 3.49×10^{-5} mol

n(AgCl) new prod.: 5/3 (3.49×10^{-5} mol) = 5.82×10^{-5} mol ≡ 8.34 mg

The amount of Ag formed is equal to the amount of AgCl lost, thus

$[Ag]_{formed} = 6.98\times10^{-5}$ mol × 107.9 g mol^{-1} = 7.53×10^{-3} g

The mass of the sample is equal to 3.0 g – 0.010 g + 0.00834 g + 0.00753 g =

= 3.006 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

i) in O_2-rich lakes of pH ≈ 6,

ii) in highly O_2-depleted lakes that are strongly contaminated with acid rain (pH ≈ 3),

8.2 Which species of manganese is predominant

i) in O_2-rich lakes of pH ≈ 6,

ii) in highly O_2-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.

i) Write the chemical formula of the black solid?

ii) 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 Mn^{2+}(aq).

i) Write the formulas of these two nitrogen species.

ii) Which of the two species of nitrogen does not oxidize Mn(s) (in practice) at room temperature ?

8.5 According to the Poubaix diagrams, some of the chemical forms of manganese should oxidize NH_3(aq) or NH_4^+(aq) to N_2(g).

Choose in the following list the forms of Mn that should do it:

Mn, $Mn(OH)_2$, Mn^{2+}, Mn_3O_4, Mn_2O_3, MnO_2, MnO_4^{2-} , MnO_4^-

8.6 Ammonium permanganate, NH_4MnO_4, is a well-known salt, but ammonium manganate, $(NH_4)_2MnO_4$, is a rarely known salt.

i) Is NH_4MnO_4 expected to be thermodynamically stable? (YES or NO)

ii) Is $(NH_4)_2MnO_4$ expected to be thermodynamically stable? (YES or NO)

iii) Write and balance an equation for the decomposition of NH_4MnO_4 to give MnO_2 a N_2.

iv) Write and balance an equation for the decomposition of $(NH_4)_2MnO_4$ to give Mn a N_2.

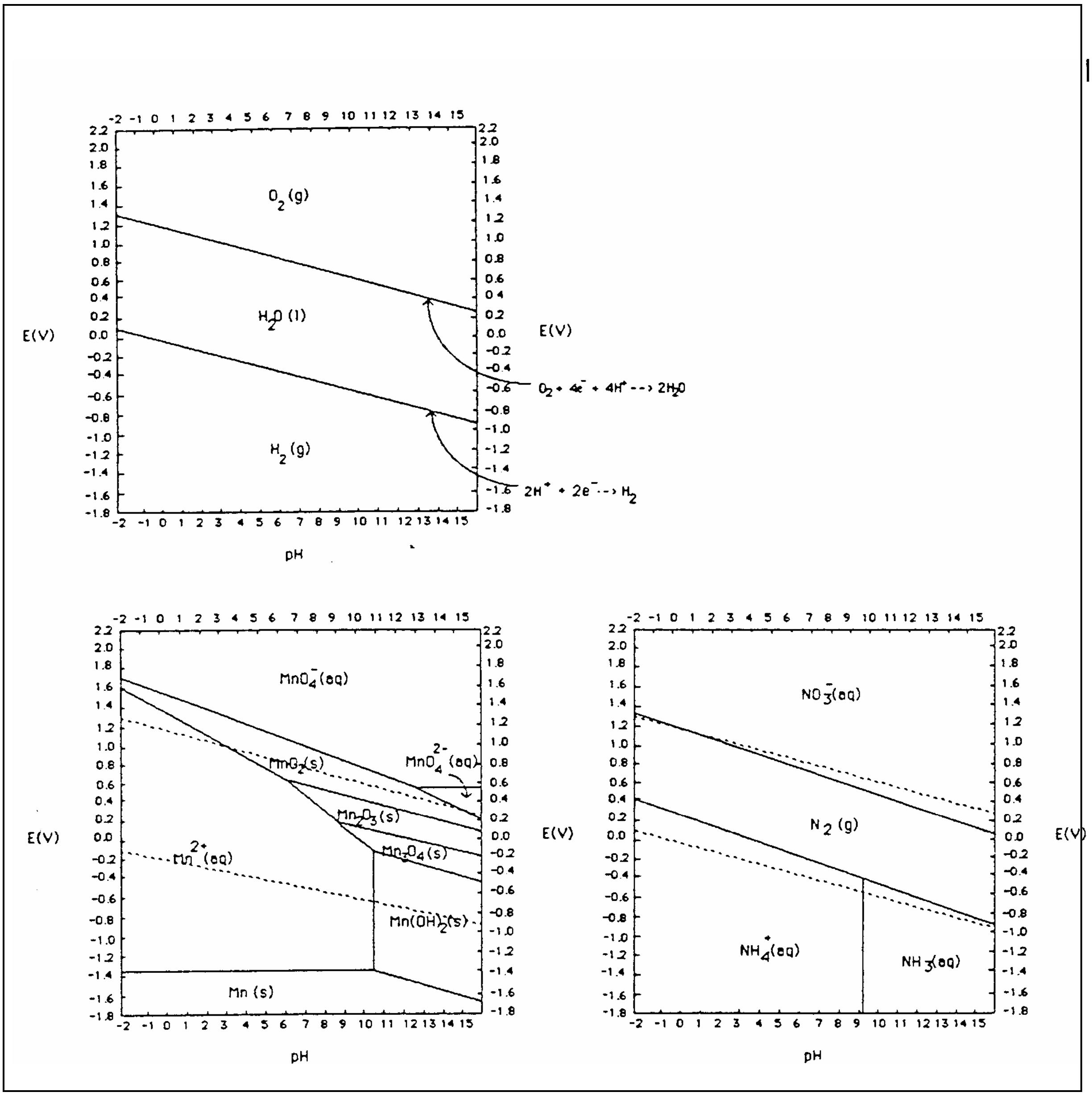
8.7 According to the Pourbaix diagrams, is it dangerous to grind together in a mortar and pestle

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 pH = 4.0.

Figure 1



SOLUTION

8.1 i) N_2 ii) NO_3^-

8.2 i) MnO_2 ii) $Mn(OH)_2$

8.3 i) MnO_2, ii) Mn^{2+}

8.4 NO_3^- and N_2. In practice only NO_3^- would oxidize Mn, since the activation energy for N_2 in order to break the triple bonds is very high.

8.5 Mn_3O_4, Mn_2O_3, MnO_2, MnO_4^{2-}, MnO_4^-

8.6 i) NH_4MnO_4: YES

ii) $(NH_4)_2MnO_4$: NO

iii) $2\ NH_4MnO_4 \rightarrow 4\ H_2O + 2\ MnO_2 + N_2$

iv) $(NH_4)_2MnO_4 \rightarrow 4\ H_2O + Mn + N_2$

8.7 According to the diagrams, KNO_3 is easily reduced by Mn whereas the potential of MnO_2 is more positive than the potential of NO_3^-. So a mixture of KNO_3 and Mn could be explosive.

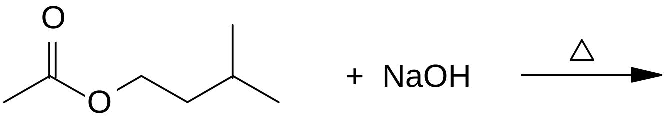
8.8
$$E = E^o + \frac{0.0591}{3}\log[MnO_4^-] + \frac{0.0591}{3}\log[H^+]^4) =$$

$$= 1.692 + 0.0197 \log 0.001 - 0.0788\ pH = 1.633 - 0.0788\ pH = \underline{1.34\ V}$$

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.

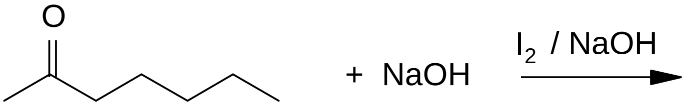
9.1



isoamyl acetate,
bee alarm pheromene

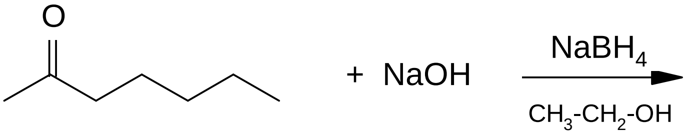
9.2

i)

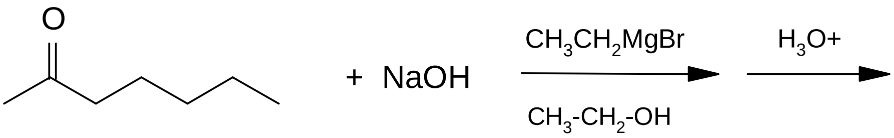


2-heptanone
ant alarm pheromone

ii)

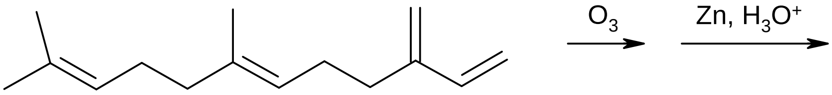


iii)



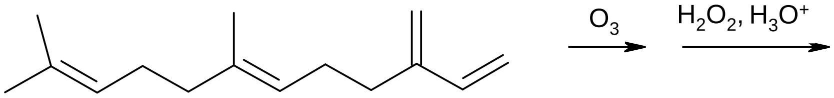
9.3

i)



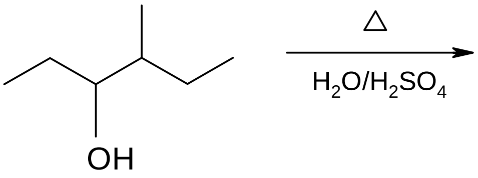
green peach -
aphid pheromone

ii)

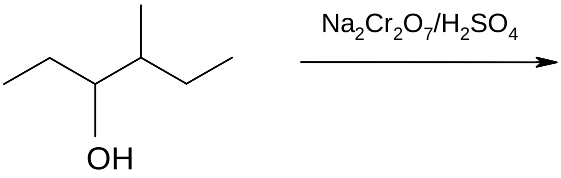


9.4

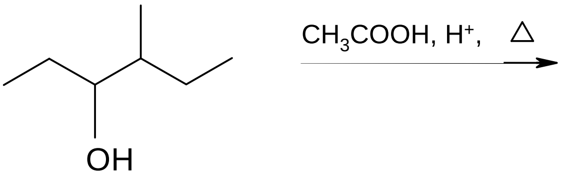
(i)



(ii)

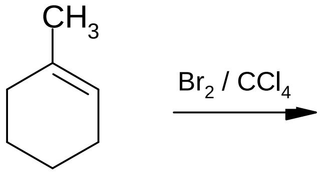


(iii)

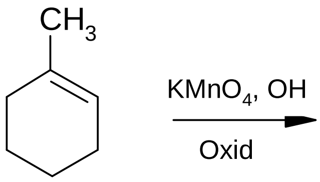


9.5

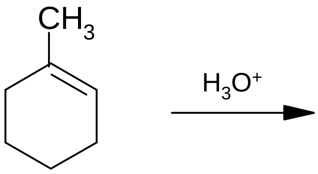
i)



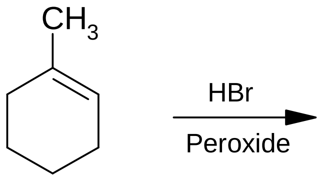
ii)



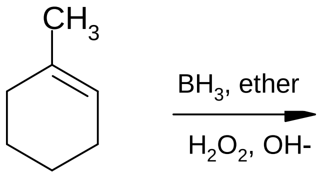
iii)



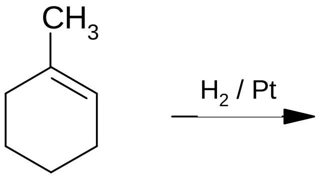
iv)



v)

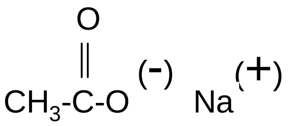


vi)



SOLUTION

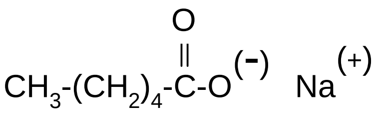
9.1



$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^{(-)}\ Na^{(+)}$ and $HOCH_2CH_2CH(CH_3)_2$

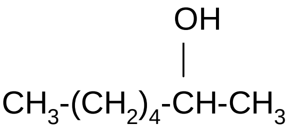
9.2 i)

CHI_3 and



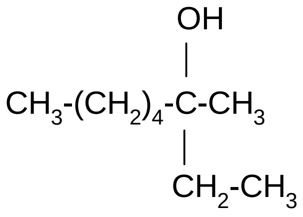
$CH_3\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^{(-)}\ Na^{(+)}$

ii)



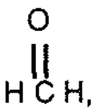
$CH_3\text{-}(CH_2)_4\text{-}\overset{\overset{OH}{|}}{CH}\text{-}CH_3$

iii)

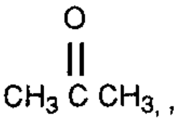


$CH_3\text{-}(CH_2)_4\text{-}\underset{\underset{CH_2\text{-}CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_3$

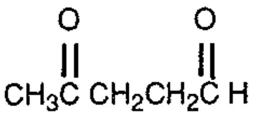
9.3 i)



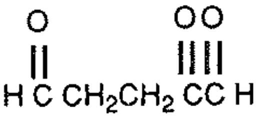
$H\overset{O}{\overset{\|}{C}}H$,



$CH_3\overset{O}{\overset{\|}{C}}CH_3$, ,

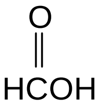


$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}H$,

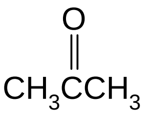


$H\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}H$

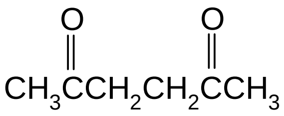
ii)



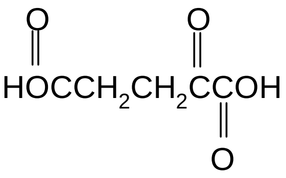
$H\overset{O}{\overset{\|}{C}}OH$



$CH_3\overset{O}{\overset{\|}{C}}CH_3$

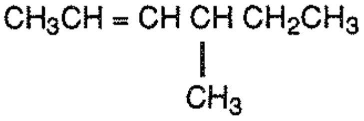


$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

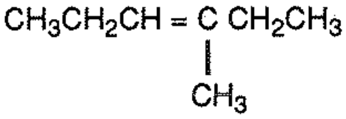


$HO\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{O}{\underset{\|}{C}}OH$

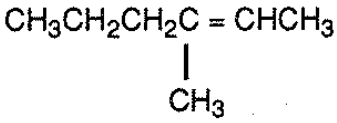
9.4 i)



$CH_3CH=CH\underset{CH_3}{\underset{|}{CH}}CH_2CH_3$

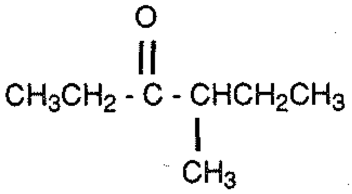


$CH_3CH_2CH=\underset{CH_3}{\underset{|}{C}}CH_2CH_3$



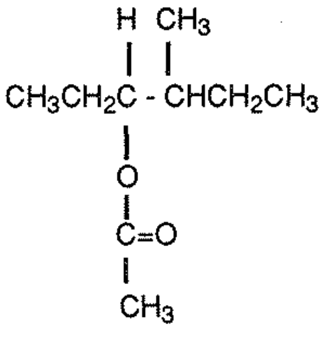
$CH_3CH_2CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_3$

(ii)



$CH_3CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$

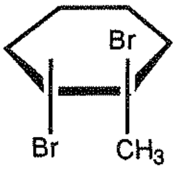
(iii)



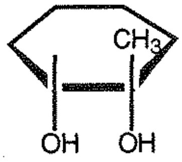
$CH_3CH_2\overset{H}{\overset{|}{\underset{\begin{array}{c}|\\O\\|\\C=O\\|\\CH_3\end{array}}{C}}}-\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

9.5

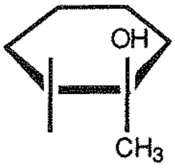
(i)



(ii)



(iii)



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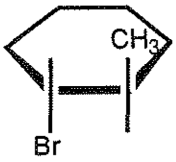
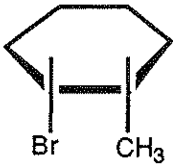


and



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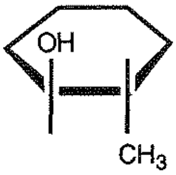

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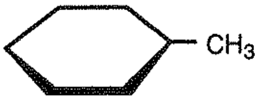


PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Effects of CO_2 on Solubility

Calcium carbonate is a partially soluble material commonly known as limestone, marble, chalk, or calcite. In the presence of CO_2-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 aqueuos solution saturated with carbon dioxide and in solution free of carbon dioxide. The [Ca^{2+}] will be determined by complexometric titration with EDTA (ethylenediamine-tetraacetic acid).

a) Procedure for the determination of [Ca^{2+}]

1. Calibrate your *pH* meter.
2. Measure and record the *pH* of the sample equilibrated with solid $CaCO_3$ and CO_2 gas.
3. Filter all your sample into a second 250 cm^3 plastic bottle to remove any suspended $CaCO_3$. 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 cm^3 aliquots of this sample to three Erlenmeyer flasks. Recap the sample bottle after removing each 25 cm^3 aliquot.
6. Add 15 drops of 6 M HCl to each of the three flasks with stirring. Any $CaCO_3$ that may have formed should dissolve. Before proceeding with the next step, make sure there is no solid $CaCO_3$ 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 cm^3 of a pH 10 NH_3 buffer. Proceed immediately with steps 8 - 10.
8. Add 20 drops of 0.001 M $Mg^{2+}/EDTA^{4-}$ 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 ^{o}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 CO_2 being evolved and some $CaCO_3$ 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 $CaCO_3$.
16. Transfer three 25 cm^3 aliquots of this filtered solution to three Erlenmeyer flasks. Add about 25 cm^3 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 $CaCO_3$, (molar mass 100.09 g mol^{-1}) which will be found in the weighing bottle in the desiccator. Note: $CaCO_3$ is hygroscopic.
2. Add 25 cm^3 of deionized water to the $CaCO_3$, then carefully add 5 cm^3 of 6 M HCl. Quickly cover with a watch glass.
3. When the $CaCO_3$ has dissolved, quantitatively transfer the solution to a 250 cm^3 volumetric flask and dilute to the mark.
4. Transfer three 25 cm^3 aliquots of the standard Ca^{2+} 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 $CaCO_3$ and CO_2 and in solution free of CO_2.

1.2 List all the ionic species that increase in concentration as a result of the dissolving of $CaCO_3$ in water.

1.3 Given below are brief descriptions of two solutions. Circle the one in which the concentration of CO_3^{2-} would be highest:

a) a solution produced by dissolving $CaCO_3$(s) in CO_2 -saturated water

b) a solution produced by dissolving $CaCO_3$(s) in CO_2 -free water

1.4 Will the solubility of $CaCO_3$ increase or decrease in a solution from which the CO_2 has been removed?

SOLUTION

1.1 The results of the titration (volumes of titrants, mass of $CaCO_3$) 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 $CaCO_3$ in its saturated solutions containing CO_2 and in those without CO_2.

The other tasks to be solved:

1.2 The ionic species mentioned above are as follows: Ca^{2+}, HCO_3^-, OH^-.

1.3 Correct answer: (b) A solution produced by dissolving $CaCO_3$(s) in CO_2-free water.

1.4 The solubility of $CaCO_3$ will decrease.

25th

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 9.93×10^{-7} 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} μc , 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

1.1 $^{131}\text{I} = {}^{131}\text{Xe} + \text{e}$

1.2 Decay reactions are first order reactions. Then:

$$k = \frac{\ln 2}{t_{1/2}} \qquad t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{0.693}{9.93\times10^{-7}\times 86400\,\text{s}\,\text{d}^{-1}} = 8.08\,\text{d}$$

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:

$$\ln\frac{100}{30} = 9.93\times10^{-7}\times t$$

$$t = \frac{1.212\times10^{6}}{8.64\times10^{4}} = 14.03\ \text{d}$$

1.4 1 Curie (c) is the amount of a radioisotope that produces 3.7×10^{10} disintegrations s^{-1}

1 mc = 3.7×10^{7} dis s^{-1}

1 μc = 3.7×10^{4} dis s^{-1}

Then:

$$10^{-4}\ \mu\text{c}\times3.7\times10^{4}\ \text{dis s}^{-1} = 3.7\ \text{dis s}^{-1} = -\frac{dN}{dt}$$

$t_{1/2}$ of ^{131}I expressed in seconds is = 8.08 d × 86400 s d^{-1} = 6.98×10^{5} s

$$m = -\frac{dN}{dt}\times\frac{t_{1/2}\times A_r(\text{I})}{\ln 2\times N_A} = \frac{3.7\times6.98\times10^{5}\times131}{0.693\times6.02\times10^{23}} = 8.11\times10^{-16}\ \text{g}$$

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 μmoles 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 *t* (s)	Column B *t* (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:

$$R = \frac{\sqrt{N}}{4} \times \frac{\alpha - 1}{\alpha} \frac{K'}{K' + 1} \qquad (1)$$

$$\alpha = \frac{t_2'}{t_1'} = \frac{t_2 - t_0}{t_1 - t_0} \qquad (2)$$

$$K' = K_2' = \frac{t_2'}{t_0} = \frac{t_2 - t_0}{t_0} \qquad (3)$$

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 ≥ 1.5 for each pair of peaks (GCA/CA, i.s./GCA). N can be calculated from N m^{-1} value taking into account that the column length is 25 cm:

$N = 2.56\times10^4 \times (25/100) = 64\times10^2$

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 cm^3) 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:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ (I)

$CH_4(g) + 3/2\ O_2(g) \rightarrow CO(g) + 2\ H_2O(g)$ (II)

Compound	CH_4	O_2	CO_2	CO	H_2O
ΔH^0_f (kJ mol^{-1})	–74.9	0	–393.5	–110.5	–241.8
S^0 (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^o and ΔS^o 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 $CH_4 : O_2$ is 1 : 2.

Assume the following volume composition of air: 80 % N_2 and 20 % O_2.

Make the approximation that $n(CH_4) \cong 0$ 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 CO_2 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 O_2 : 1 mol CH_4).

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.

3.1 $\Delta_I H^0 = 74.9 - 393.5 - (2 \times 241.8) = -802.2 \text{ kJ mol}^{-1}$

$\Delta_I S^0 = -186.2 - (2 \times 205.0) + 213.6 + (2 \times 188.7) = -5.2 \text{ J K}^{-1} \text{ mol}^{-1}$

$$K_I = \exp -\frac{\Delta_I H^0 - T\Delta_I S^0}{R\,T} = \exp \frac{802.2 - 1.5 \times 5.2}{8.314 \times 1.5} = 4.62 \times 10^{27}$$

$\Delta_{II} H^0 = 74.9 - 110.5 - (2 \times 241.8) = -519.2 \text{ kJ mol}^{-1}$

$\Delta_{II} S^0 = -186.2 - (1.5 \times 205.0) + 197.6 + (2 \times 188.7) = 81.3 \text{ J K}^{-1} \text{ mol}^{-1}$

$$K_{II} = \exp \frac{519.2 - 1.5 \times 81.3}{8.314 \times 1.5} = 2.13 \times 10^{22}$$

3.2 Since K_I and K_{II} are very large, both equilibria are completely shifted to the right so that $n_{CH_4} = 0$.

At equilibrium: $n_{CH_4} = 0$; $n_{H_2O} = 2$; $n_{N_2} = 8$; $n_{CO_2} + n_{CO} = 1$;

$$n_{O_2} = 2 - (2\,n_{CO_2} + 1.5\,n_{CO}) = 0.5\,n_{CO}$$

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 N_2), but this change affects the total number of moles only negligibly since $K_{II} << K_I$.

Before reaction: $n_{tot} = n_{CH_4} + n_{O_2} + n_{N_2} = 1 + 2 + 8 = 11$

$$\frac{K_{II}}{K_I} = \frac{p_{CO}\ p_{O_2}^{1/2}}{p_{CO_2}} = \frac{x_{CO}\ (x_{O_2}\ p)^{1/2}}{x_{CO_2}}$$

$x_{CO_2} = \dfrac{n_{CO_2}}{n_{tot}} = \dfrac{1 - n_{CO}}{n_{tot}} = \dfrac{1}{11}$ since $n_{CO} \ll n_{CO_2}$ as a consequence of $K_{II} \ll K_I$

$$x_{CO}^{3/2} = \frac{K_{II}}{K_I}\ \frac{(2/p)^{1/2}}{11} = \frac{2.13\times10^{22}\times1.414}{4.62\times10^{27}\times11} = 5.93\times10^{-7}$$

$x_{CO} = 7.06 \cdot 10^{-5}$

3.4 $n_{tot} = n_{CH_4} + n_{O_2} + n_{N_2} = 1 + 4 + 16 = 21$

At equilibrium: $n_{O_2} = 4 - (2\ n_{CO_2} + 1.5\ n_{CO}) = 2 + 0.5\ n_{CO} = 2$

$n_{CO_2} = 1 - n_{CO}$

$$\frac{K_{II}}{K_I} = \frac{x_{CO}\ (x_{O_2}\ p)^{1/2}}{x_{CO_2}} = x_{CO}\ (2/21)^{1/2}\times21 = (42)^{1/2}\ x_{CO}$$

$$x_{CO} = 42^{-1/2}\ \frac{K_{II}}{K_I} = 42^{-1/2}\times\frac{2.13\times10^{22}}{4.62\times10^{27}} = 7.11\times10^{-7}$$

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:

$x_{CO} = 7.06\times10^{-5}\times\dfrac{11}{9} = 8.63\times10^{-5}$ and to:

$x_{CO} = 7.11\times10^{-7}\times\dfrac{21}{19} = 7.86\times10^{-7}$ 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 $NaHCO_3$ (gas evolution is observed) as well as with cold aq $KMnO_4$ which turns to a brown colour.

iii) The compound **B** is then converted by $LiAlH_4$ into a new compound **C** ($C_6H_{12}O$).

iv) Treatment of **C** with p-toluenesulfonyl chloride in pyridine and then sodium cyanide in dimethylsulfoxide, affords **D** ($C_7H_{11}N$).

v) The subsequent reaction of **D** with methylmagnesium iodide, followed by hydrolysis, yield **E** ($C_8H_{14}O$). **E** shows IR absorption at ca 1700 cm^{-1}.

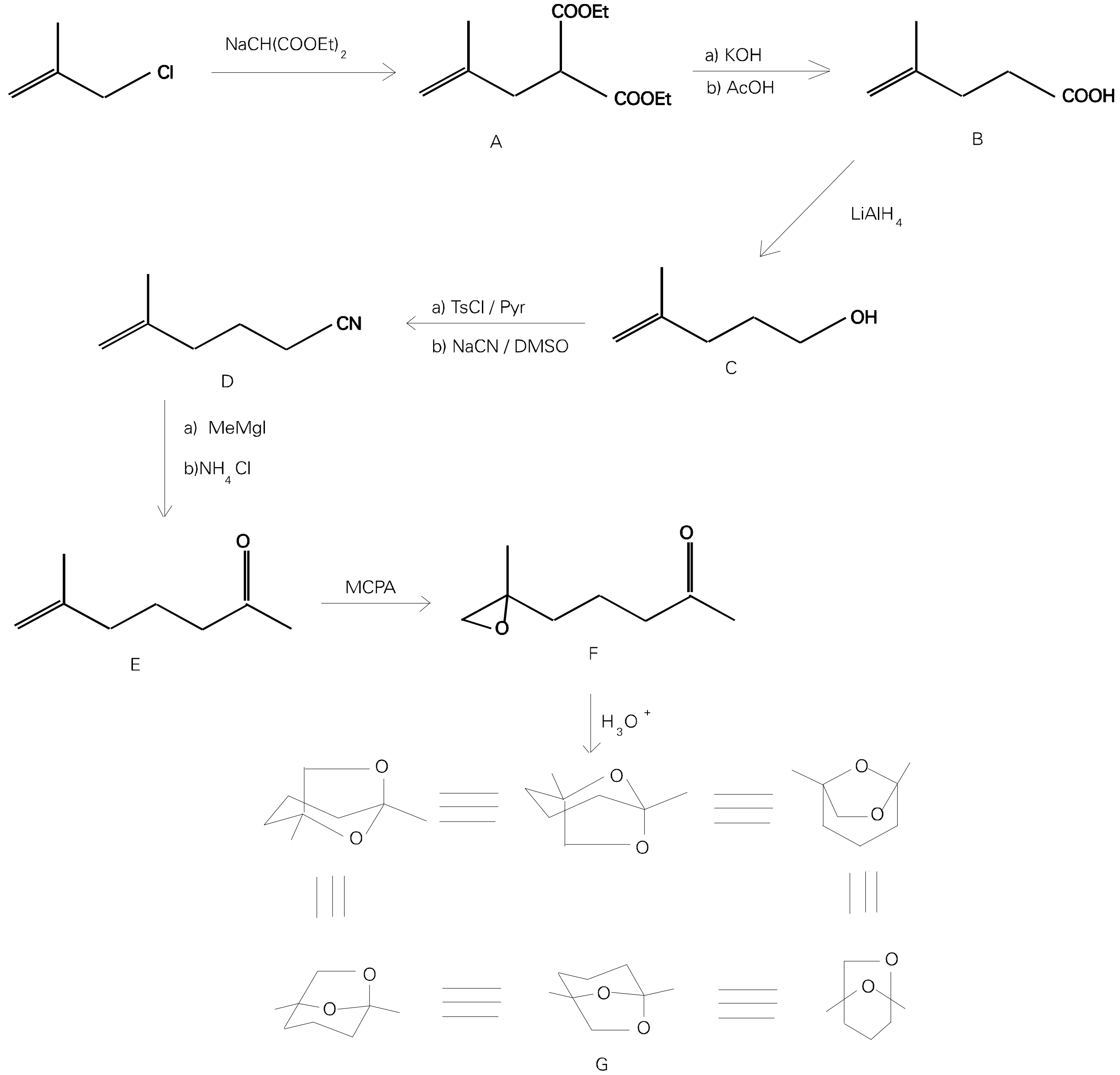
vi) The epoxidation of **E** with metachloroperbenzoic acid then affords **F** ($C_8H_{14}O_2$) which, by treatment with diluted acids is converted to frontalin acetal **G**.

Questions:

4.1 Draw the structures of compounds **A** - **G**.

SOLUTION

4.1


Cl
NaCH(COOEt)$_2$
COOEt
COOEt
A
a) KOH
b) AcOH
COOH
B
LiAlH$_4$
OH
C
a) TsCl / Pyr
b) NaCN / DMSO
CN
D
a) MeMgI
b)NH$_4$Cl
O
E
MCPA
O
O
F
H$_3$O$^+$
O
O
G

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:

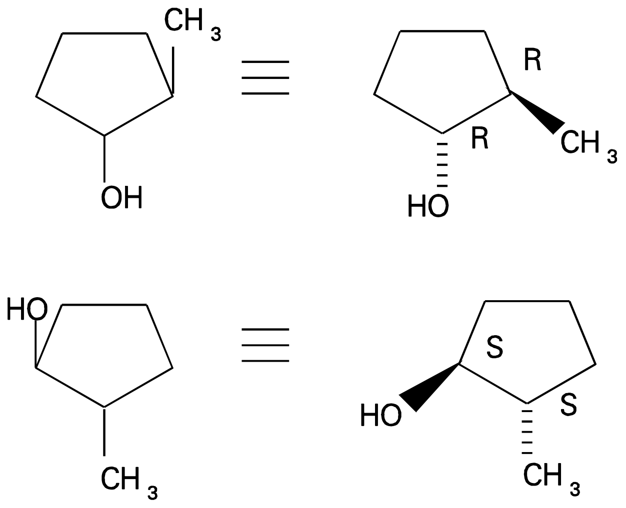
5.1 Write the structures of the alcohols.

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 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

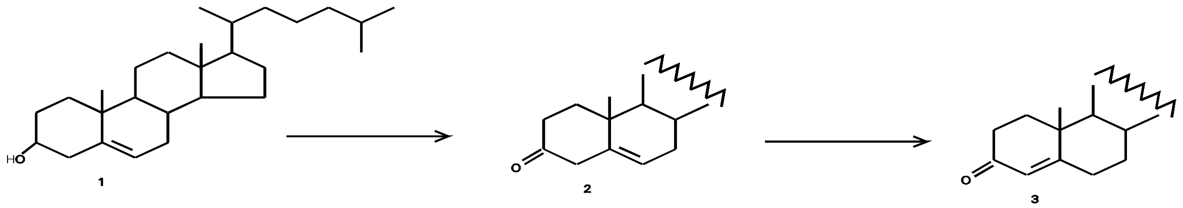
PROBLEM 1 (Practical)

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^5-3β-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:

a) Dissolve your pre-weighed sample of cholesterol (386 mg, 1 mmol) contained in a 50 cm^3 flask A with acetone (20 cm^3) 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.

b) Add dropwise 0.40 cm^3 of Jones' reagent to the solution, gently swirling the flask in a bath of cold water. The formation of a green precipitate [$Cr_2(SO_4)_3$] is observed during the addition of Jones' reagent.

c) Remove the green precipitate by filtration with paper filter.

d) Add slowly water (10 cm^3) to the clean filtrate. The ketone (2) begins to precipitate.

e) Filter the precipitate over the Büchner funnel under reduced pressure, washing the crystals with small portions of a 2 : 1 acetone/water mixture.

f) Dissolve the ketone (2) in methanol (15 cm^3). 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 cm^3) 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.

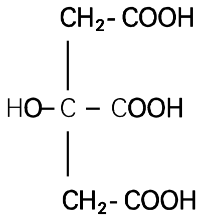
Some additional points were given for melting point measurements.

PROBLEM 2 (Practical)

Analysis

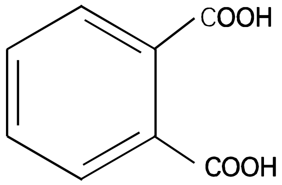
Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is widely distributed in plants and in animal tissues. Lemon juice contains from 5 to 8% of this acid. It is produced by mycological fermentation on an industrial scale using crude sugar solutions, such as molasses, and stains of *Aspergillus niger*.

It is utilized as an acidulant and antioxidant in several beverages.



$$\begin{array}{c} CH_2-COOH \\ | \\ HO-C-COOH \\ | \\ CH_2-COOH \end{array}$$

MM = 192.12 g/mol



MM = 204.23 g/mol

$pK_1 = 3.06$; $pK_2 = 4.74$; $pK_3 = 5.40$

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 cm^3 volumetric flask B. Dilute this sample with water to the mark. Phenolphthalein indicator (2 - 3 drops) is added to an aliquot of 25.0 cm^3 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 cm^3 volumetric flask C. Dilute the sample with water to the mark. Transfer 25.0 cm^3 of the resulting solution into a 250 cm^3 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

International Chemistry Olympiad

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 $K_{HL} = 1.4\times10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{a1} = 4.5\times10^{-7}$ and $K_{a2} = 4.7\times10^{-11}$. 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 $[HCO_3^-]$ = 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 $CaCO_3$(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, $[HCO_3^-]$ = 0.022) given in 1.4.

SOLUTION

1.1 $HL + H_2O \rightarrow H_3O^+ + L^-$: $K_{HL} = 1.4\times10^{-4}$

c_0 - x x x

$$K_a = \frac{x^2}{c_0 - x} = 1.4\times10^{-4} \qquad c_0 = 3.00\times10^{-3}$$

Assumption $c_0 >> x$ gives $x = 6.5 \cdot 10^{-4}$, not valid

Quadratic formula: $x = 5.8\times10^{-4}$, $[H_3O^+] = 5.8\times10^{-4}$, $pH = 3.24$

1.2 1: $HL + HCO_3^- \rightleftharpoons H_2CO_3 + L^-$: K_1

2: $HL + H_2O \rightleftharpoons H_3O^+ + L^-$: $K_2 = K_{HL}$

3: $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$: $K_3 = \frac{1}{K_{a1}}$

Reaction 1 = 2 + 3, $K_1 = K_2 \cdot K_3 = 311$ (3.1×10^2)

Alternative: $K_1 = \frac{[H_2CO_3]\,[L^-]}{[HL]\,[HCO_3^-]} \times \frac{[H_3O^+]}{[H_3O^+]} = \frac{[H_3O^+][L^-]}{[HL]} \times \frac{[H_2CO_3]}{[HCO_3^-][H_3O^+]}$

1.3 i) HCO_3^- is amphoteric, $pH \approx \frac{1}{2}(pK_{a1} + pK_{a2}) = \underline{8.34}$

ii) $HL + HCO_3^- \rightleftharpoons H_2CO_3 + L^-$, "reaction goes to completion"

	HL	HCO_3^-	H_2CO_3	L^-
Before:	0.0030	0.024	0	0
After :	0	0.021	0.0030	0.0030

Buffer: $pH \approx pK_{a1} + \log\frac{0.021}{0.0030} = 6.35 + 0.85 = 7.20$

(Control: $\frac{K_{HL}}{[H_3O^+]} = \frac{[L^-]}{[HL]} = 2.2\times10^3$, assumption is valid)

1.4 A: $pH = 7.40$; $[H_3O^+] = 4.0\times10^{-8}$; $[HCO_3^-]_A = 0.022$.

From K_{a1}: $[H_2CO_3]_A = 0.0019$;

(1) $[HCO_3^-]_B + [H_2CO_3]_B = 0.0239$ (0.024)

B: $pH = 7.00$; $\frac{[HCO_3^-]}{[H_2CO_3]} = 4.5$;

(2) $[HCO_3^-]_B = 4.5\ [H_2CO_3]_B$

From (1) and (2): $[HCO_3^-]_B = 0.0196$

$[H_2CO_3]_B = 0.0043$

$n(HL) = \Delta n(H_2CO_3) = \Delta c(H_2CO_3) \times 1.00\ dm^3 = 2.4\times10^{-3}$ mol

1.5 $[OH^-] = 8.9\times10^{-5}$ $[H_2CO_3]$ of no importance

Reactions: A: $CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$

c_0 c_0

B: $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ $K = K_b = 2.1\times10^{-4}$

c_0 - x x x

From B: $[HCO_3^-] = [OH^-] = 8.9\times10^{-5}$

$$[CO_3^{2-}] = \frac{[HCO_3^-][OH^-]}{K_b} = 3.8\times10^{-5}$$

$[Ca^{2+}] = [HCO_3^-] + [CO_3^{2-}] = 1.3\times10^{-4}$

$c_0(Ca^{2+}) = 1.3\times10^{-4}\ mol\ dm^{-3}$ = solubility

1.6 $K_{sp} = [Ca^{2+}]\,[CO_3^{2-}] = 1.3\times10^{-4} \times 3.8\times10^{-5} = 4.9\times10^{-9} = \mathbf{5\times10^{-9}}$

From K_{a2} : $$[CO_3^{2-}] = \frac{K_{a_2}\ [HCO_3^-]}{[H_3O^+]} = 2.6\times10^{-5}$$

$Q = [Ca^{2+}]\,[CO_3^{2-}]$; Precipitation when $Q > K_{sp} = 5\times10^{-9}$

No precipitation when $Q < K_{sp}$

Max. concentration of "free" Ca^{2+} ions:

$$[Ca^{2+}]_{max} = \frac{K_{sp}}{[CO_3^{2-}]} = 1.9\times10^{-4}$$

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 cm^3 of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 cm^3 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 cm^3, 9.65 cm^3, 19.30 cm^3 and 28.95 cm^3 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 cm^3 of 0.1010 M hydrochloric acid. A titration volume of 17.50 cm^3 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

2.1 $$[(50.00 \times 0.1010) - (19.30 \times 0.1050)]\, \frac{14.01}{1000} \times \frac{100}{0.2515} = 16.84\ \%\ \mathrm{N}$$

2.2 0 cm^3 added: $$[\mathrm{H}^+] = \frac{19.30 \cdot 0.1050}{50} = 0.04053$$

$$pH = 1.39$$

9.65 cm^3 added: $[H^+] = \quad = 0.01699$

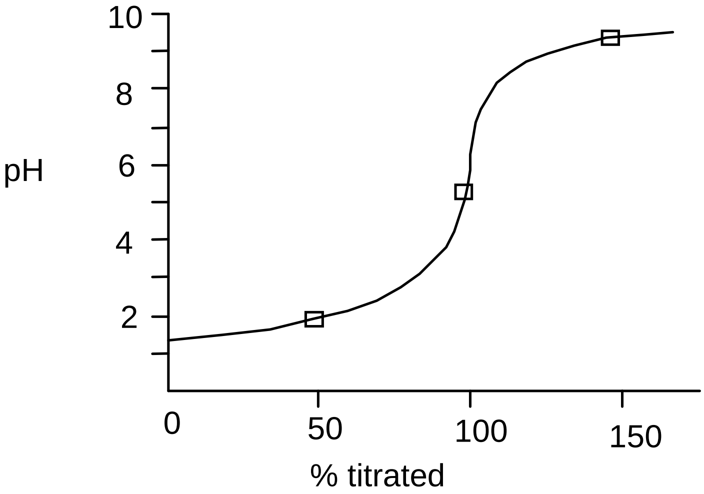
$pH = 1.77$

19.30 cm^3 added: $[H^+] = \sqrt{5.7 \cdot 10^{-10} \times \dfrac{50.00 \cdot 0 \times 101019 \times 30 \cdot 0 \times 1050}{50 + 19.30}}$

$pH = 5.30$

28.95 cm^3 added: $\boldsymbol{pH} = pK_a + \log \dfrac{[NH_3]}{[NH_4^+]} = 9.24 + \log \dfrac{1.01}{2.01} = 8.94$

2.3



2.4 Indicator *pH* transition range: *pH* 5.3 ± 1

2.5 $[(50.00 \times 0.1010) - (17.50 \times 0.1050)] \dfrac{14.01}{1000} \times \dfrac{100}{0.2345} = 19.19\ \%\ N$

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 $Ba(NO_3)_2$.

iii) Adjustment to $pH = 7$ with NH_3 and addition of $Ca(NO_3)_2$.

Write the equations for the possible reactions in the tests:

iv) Addition of $KMnO_4$ followed by $Ba(NO_3)_2$ to an acid solution of the substance.

v) Addition of $Cu(NO_3)_2$.

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 $Ba(NO_3)_2$.

v) No precipitate.

Write the formulas of the possible compounds, taking the results of these tests into account.

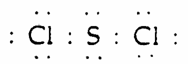
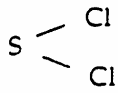
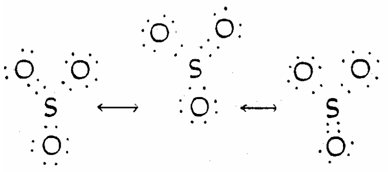
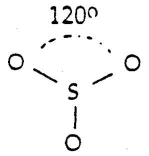
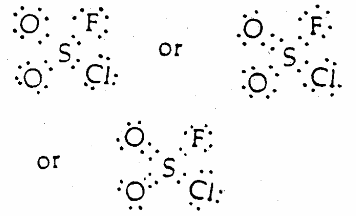
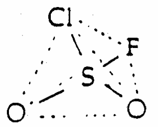
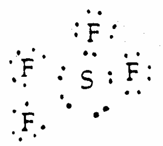
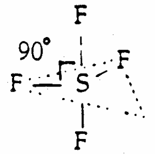
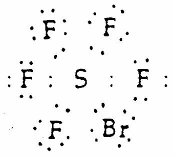
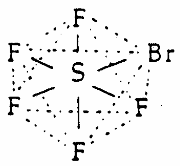
3.5 Finally, a simple quantitative analysis was undertaken:

7.190 g of the substance was weighed out and dissolved in water to give 250.0 cm^3 of a solution. To 25.00 cm^3 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		Bent 
SO_3		Trigonal planar 
SO_2ClF		Tetrahedral 
SF_4		Trigonal bipyramidal ÷ 1 corner 
$SBrF_5$		Octahedral 

3.3 i) Cl^-, Br^-, I^-

ii) SO_4^{2-}

iii) F^-

iv) $2\ MnO_4^- + 5\ HSO_3^- + H^+ \rightarrow 5\ SO_4^{2-} + 2\ Mn^{2+} + 3\ H_2O$

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\,(s)$

v) $2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI(s) + I_2$

3.4 SOClBr and $SOBr_2$

3.5 SOClBr

[SOClBr: 1.456g, and $SOBr_2$: 1.299g]

3.6 $SOClBr + 2\ H_2O \rightarrow HSO_3^- + Cl^- + Br^- + 3\ H^+$

$SOClF + 2\ H_2O \rightarrow HSO_3^- + Cl^- + HF + 2\ H^+$

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 (= 1.01325×10^5 Pa) and 650 ℃.

4.1 This suggests that the conditions on the Earth, when the minerals we know were formed, were:

[1] $p(O_2)$ = 1 atm, t = 650 ℃;

[2] $p(O_2)$ < 1 atm, t < 650 ℃;

[3] $p(O_2)$ > 1 atm, t < 650 ℃;

[4] $p(O_2)$ < 1 atm, t > 650 ℃;

[5] $p(O_2)$ > 1 atm, t > 650 ℃

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 ℃?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process $PtO_2 \cdot n\ H_2O$ 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.

$PtO_2 \cdot 4\ H_2O$ or $Pt(OH)_4 \cdot 2\ H_2O$ 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 $PtO_2 \cdot 4\ H_2O$ 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 $Pt(NH_3)_2Cl_2$ which occurs in *cis* (ΔH_f^0 = – 467.4 kJ mol^{-1}, ΔG_f^0 = – 228.7 kJ mol^{-1}) and *trans* (ΔH_f^0 = – 480.3 kJ mol^{-1}, ΔG_f^0 = – 222.8 kJ mol^{-1}) form.

4.7 The occurrence of the isomers shows that $Pt(NH_3)_2Cl_2$ hasgeometry:

[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 (ΔH_f^0 = –110.5 kJ mol^{-1}, ΔG_f^0 = –137.3 kJ mol^{-1}) reacts with oxygen to carbon dioxide (ΔH_f^0 = –393.5 kJ mol^{-1}, ΔG_f^0 = –394.4 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 $\Delta S°$ for the reaction.

Establish whether the entropy of the reaction system

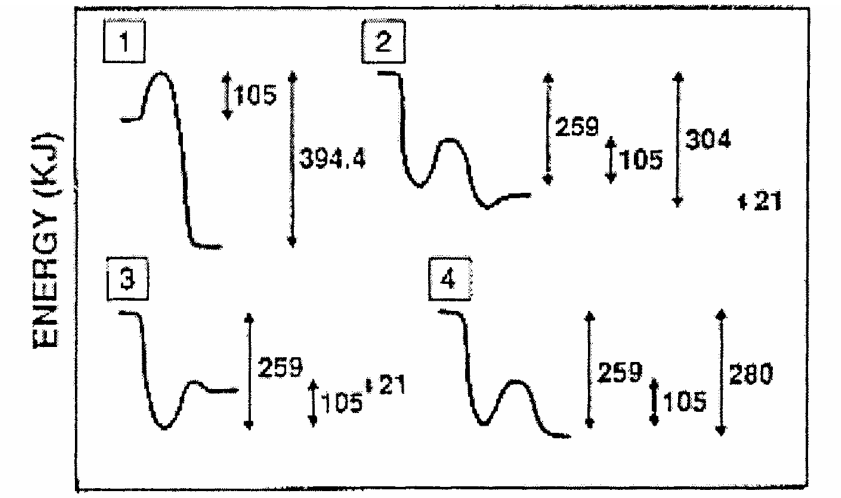
[5] increases, or

[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 O_2 (ΔH = –259 kJ per mol CO + O), (ii) their activation (105 kJ per mol CO + O) and (iii) the reaction and the desorption of CO_2 (ΔH = 21 kJ per mol CO_2).

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 ΔG = 0 kJ and K_p = 1 according to the chemical equation

$Pt(s) + O_2(g) \rightarrow PtO_2(s)$

4.3 $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq)$

$PtCl_6^{2-}(aq) + 4\ OH^{-}(aq) + 2\ H_2O(l) \rightarrow Pt(OH)_4 \cdot 2\ H_2O(s) + 6\ Cl^{-}(aq)$

Alternative I: $PtO_2 \cdot 4\ H_2O(s) + 6\ Cl^{-}(aq)$

Alternative II: $(n-2)\ H_2O \rightarrow PtO_2 \cdot n\ H_2O(s) + 6\ Cl^{-}(aq)$

$PtO_2 .\ 4\ H_2O(s) \rightarrow PtO_2(s) + 4\ H_2O(g)$

$[PtO_2 \cdot 4\ H_2O(s) \rightarrow Pt(OH)_4 \cdot 2\ H_2O(s)]$

4.4 In hydrochloric acid:

$PtO_2 \cdot 4\ H_2O(s) + 4\ H^{+}(aq) + 6\ Cl^{-}(aq) \rightarrow PtCl_6^{2-}(aq) + 6\ H_2O$

In sodium hydroxide:

$PtO_2 \cdot 4\ H_2O(s) + 2\ OH^{-}(aq) \rightarrow Pt(OH)_6^{2-}(aq) + 2\ H_2O$

4.5 $3\ HCl(sol) + HNO_3(sol) \rightarrow NOCl(sol) + 2\ Cl(sol) + 2\ H_2O(sol)$

$Pt(s) + 4\ Cl(sol) + 2\ HCl(sol) \rightarrow PtCl_6^{2-}(sol) + 2\ H^{+}(sol)$

4.6 $(NH_4)_2PtCl_6(s) \rightarrow Pt(s) + 2\ NH_3(g) + 2\ HCl(g) + 2\ Cl_2(g)$

4.7 Correct is No 2.

4.8 The cis form is thermodynamically more stable.

4.9 [1] Yes. ($\Delta G° = -257.1$ kJ for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$)

[4] The reaction is exothermic.

($\Delta H° = -283.0$ kJ for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$)

[6] is correct.

$\Delta S° = -0.0869$ kJ K^{-1} for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$;

As seen from the sign for $\Delta S°$ as well as for the reaction enthalpy the entropy of the system decreases.

4.10 $\ln K_p = 34037 / T - 10.45$ for $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$

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?

$(CH_3)_2CHCH(CH_2CH_3)(CH_2CH_2CH_3)$

☐ 1 3-Isopropylhexane

☐ 2 2-Methyl-3-propylpentane

☐ 3 Ethyl isopropyl propyl methane

☐ 4 3-Hexylpropane

☐ 5 3-Ethyl-2-methylhexane

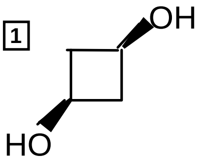
5.2 How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for C_5H_{10}?

☐ 1 4 isomers ☐ 2 5 isomers ☐ 3 6 isomers

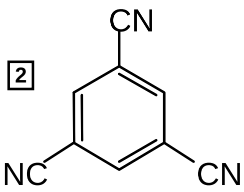
☐ 4 7 isomers ☐ 5 8 isomers

5.3 Which one of the following compounds has a dipole moment significantly different from zero?

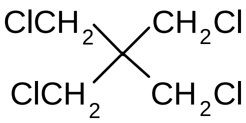
1



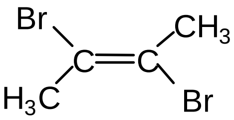
2



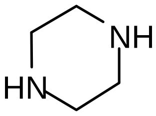
3



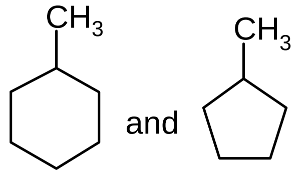
4

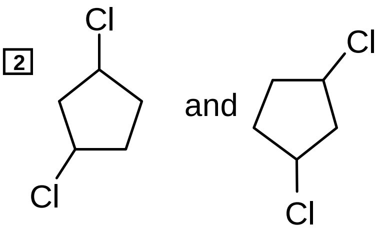


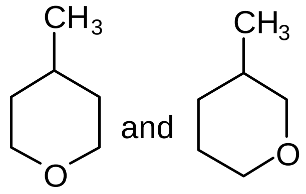
5

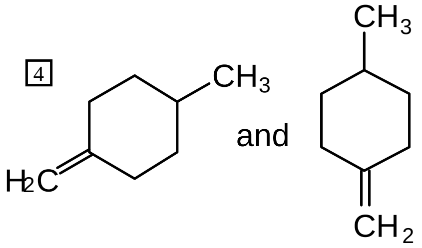


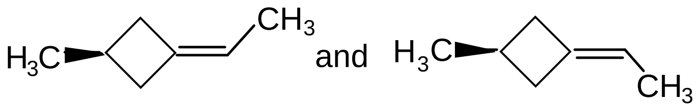
5.4 Which of the following is a pair of structural isomers?

1


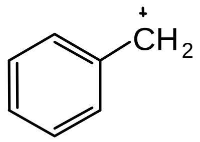
2


3


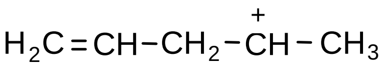
4


5


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)?

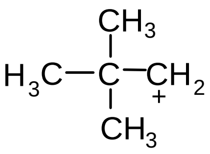


a



$H_2C=CH-CH_2-\overset{+}{C}H-CH_3$

b

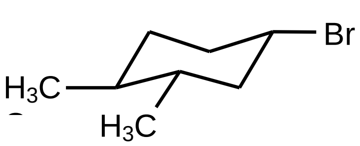


$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\overset{}{\underset{+}{C}H_2}$

c

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?

☐ 1 $(CH_3)_3N\text{-}B(CH_3)_3$ ☐ 2 $(CH_3)_2N\text{-}O\text{-}CH_3$ ☐ 3 $CH_2{=}N{=}N$

☐ 4 $(CH_3)_3N\text{-}O$ ☐ 5 $F_3B\text{-}O(CH_3)_2$

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 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}.

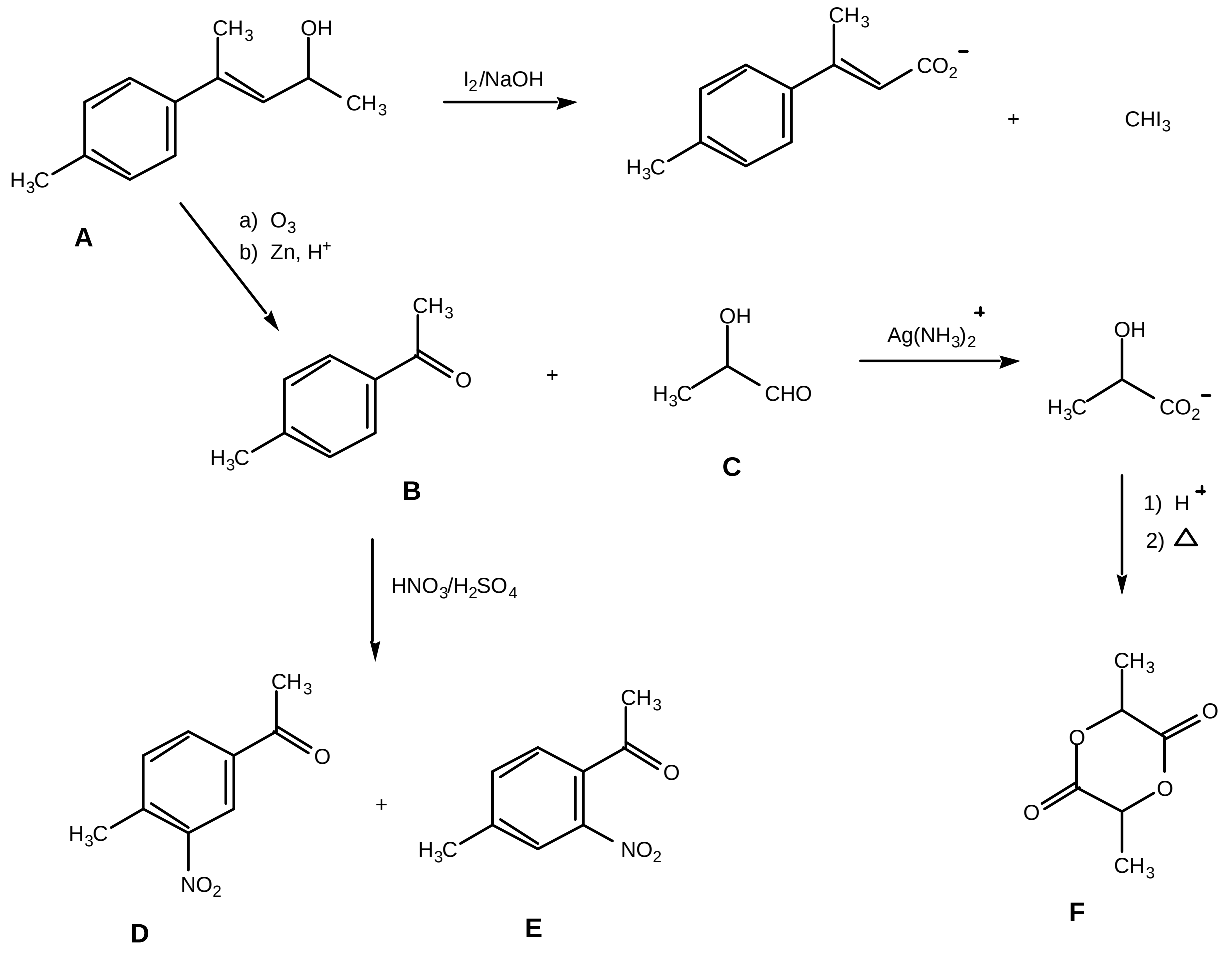
6.1 Based on the above information draw the structure formula(e) for the compounds **A** – **F** and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.

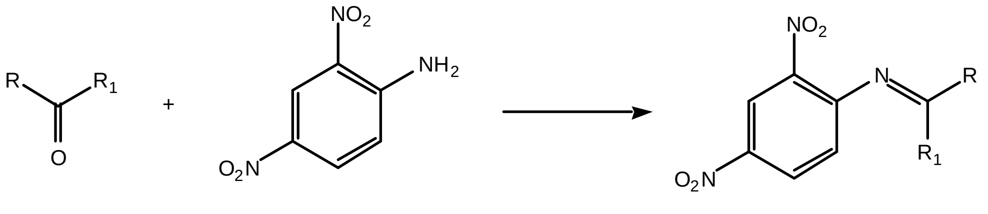
6.2 Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a **D** or L configuration.

SOLUTION

(See the next page.)

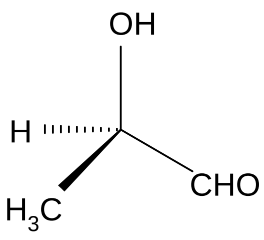
6.1



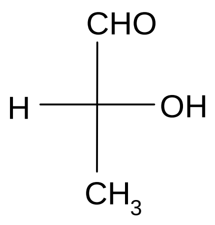


B and **C**

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 <u>on</u> the system <u>by</u> 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 dm^3 to V_2 = 20.0 dm^3 at the temperature T = 300.0 K.

Given: The gas constant R = 8.314 J K^{-1} 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.

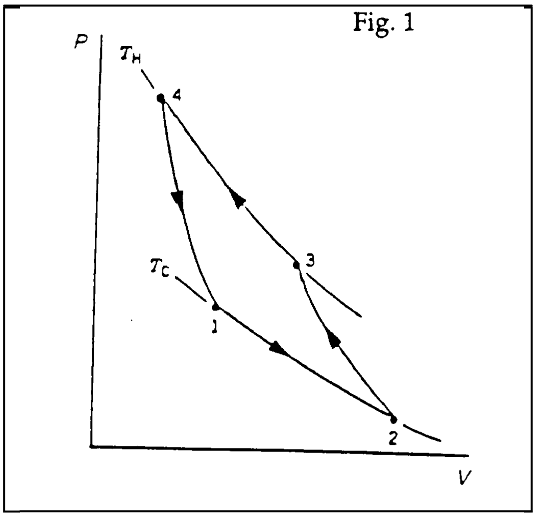


Fig. 1

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 $\underline{q} = -w = 7.47$ kJ mol^{-1}.

7.3 (3) No heat is supplied to the gas.

7.4

isotherm	[✓ 1-2]	2-3	[✓ 3-4]	4-1
adiabat	1-2	[✓ 2-3]	3-4	[✓ 4-1]

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 ß$^-$-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:

$^{235}\text{U} + \text{n} \rightarrow {}^{137}\text{Te} + \text{X} + 2\,\text{n}$

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:

$^{97}\text{Ru} \rightarrow {}^{97}\text{Tc} \rightarrow {}^{97}\text{Mo}$ (stable).

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 ß$^-$'s (only α's gives ^{206}Os, to come from Os to Pb requires 6 ß$^-$'s).

ii) ^{234}U, all other answers are incorrect.

8.2 ^{97}Zr

8.3 i) $D = \lambda N$, i.e. $D_1 / D_2 = \lambda_1 N_1 / \lambda_2 N_2$ = abund.(1)$T_{1/2}$·(2) / abund.(2)$T_{1/2}$(1)

$= (99.28 \times 7.0\times10^8) / (0.72 \times 4.5\times10^9) = 21.4$ (0.047 is also of course correct)

ii) $N = (m/\text{AW(U)}) \times \text{abundance(238)} \times N_A = (500 / 238.01) \times 0.9928 \times 6.022\times10^{23}$

$= 1.26\times10^{24}$

$D = N \ln 2 / T_{1/2} = 1.26\times10^{24} \times \ln 2 / (4.5\times10^9 \text{ (y)} \times 3.16\times10^7 \text{ (s/y)}) = 6.1\cdot10^6$ Bq

8.4 i) $\lambda = \ln 2 / 2.7\text{(d)} = 0.26 \text{ d}^{-1}$

$D = D_0 \, e^{-\lambda t} = 1.0\times10^9 \times e^{-(0.26 \times 6.0)} = 2.1\times10^8$ Bq

ii) Number of ^{97}Ru atoms in the source:

$N = D \, T_{1/2}(^{97}\text{Ru}) / \ln 2 = 1.0\times10^9 \text{ (Bq)} \times 2.7 \text{ (d)} \times 24 \text{ (h/d)} \times 3600 \text{ (s/h)} / 0.6931 =$

$= 3.4\times10^{14}$ atoms

When all ^{97}Ru has disintegrated, these atoms have all become ^{97}Tc, and the disintegration rate of this nuclide is

$D = N \ln 2 / T_{1/2}(^{97}\text{Tc}) = (3.4\times10^{14} \times 0.6931) / (2.6\cdot10^6 \text{ y} \times 3.16\times10^7 \text{ s y}^{-1}) =$

$= 2.9$ 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 cm^3 of this solution contain a total of 1.00 g acid plus ester). By titration the acid number$^{1)}$, the saponification number$^{2)}$ and the iodine number$^{3)}$ 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 cm^3). 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(I) = 126.90 A_r(O) = 16.00
A_r(K) = 39.10 A_r(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 cm^3), Erlenmeyer flasks (3 x 250 cm^3), measuring cylinder (100 cm^3), graduated pipette (2 cm^3), funnel.

Procedure:

Pipette out aliquots (2.00 cm^3) from the unknown mixture into Erlenmeyer flasks (250 cm^3). Add first ca. 100 cm^3 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 cm^3), round bottom flask (250 cm^3), Liebig condenser, burette (50 cm^3), Erlenmeyer flasks (3 x 250 cm^3), volumetric pipette (25 cm^3), volumetric pipette (10 cm^3), graduated pipette (2 cm^3), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

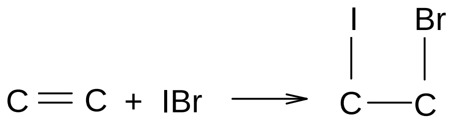
Procedure

Pipette out a 2.00 cm^3 aliquot of the unknown sample into a round bottom flask (250 cm^3) and add 25.0 cm^3 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 cm^3 volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm^3 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.



$$C{=}C + IBr \longrightarrow \overset{I}{C}{-}\overset{Br}{C}$$

The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I_2, ($IBr + I^- \rightarrow I_2 + Br^-$) 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 cm^3), buret (50 cm^3), graduated pipette (2 cm^3), measuring cylinders (10 and 100 cm^3), volumetric pipette (25 cm^3), aluminium foil.

Procedure

Pipette out aliquots (1.00 cm^3) of the unknown mixture into Erlenmeyer flasks (500 cm^3) and add 10 cm^3 of dichloromethane. With a pipette add 25.0 cm^3 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 cm^3 of the 15 % KI solution, shake thoroughly and add 100 cm^3 of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm^3) 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 cm^3 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.

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s) \qquad \text{(faint yellow-green)}$$

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:

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s) \qquad \text{(white)}$$

Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:

$$Fe^{3+}(aq) + SCN^-(aq) \rightarrow FeSCN^{2+}(aq) \qquad \text{(red)}$$

a) ***Procedures***

Every candidate has got a 0.5 dm^3 brown bottle with screw cap, containing the potassium thiocyanate solution (about 0.08 M) and also a 0.25 dm^3 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 cm^3 volumetric flask containing the bromide sample solution to the mark with water. Transfer three 25.00 cm^3 portions (pipette) of the sample solution to three Erlenmeyer flasks. Add about 5 cm^3 of 6 M nitric acid (measuring cylinder) to each flask. Transfer 25.00 cm^3 (pipette) of the accurately known silver solution and about 1 cm^3 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 cm^3 (pipette) of the silver nitrate solution to an Erlenmeyer flask, add about 5 cm^3 of 6 M nitric acid and about 1 cm^3 of the iron(III) indicator solution and about 25 cm^3 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(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:

$$K_{sp}(AgBr) = 5.00\times10^{-13} \qquad K_{sp}(AgSCN) = 1.00\times10^{-12}$$

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 examplifications of how the calculations are carried out.

27th

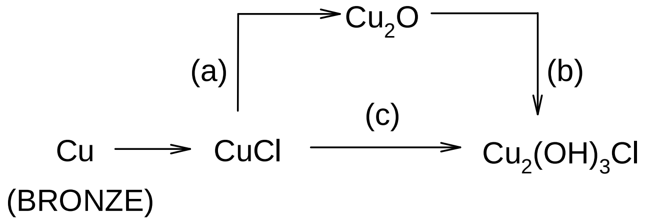
6 theoretical problems
3 practical problems

THE TWENTY-SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–20 JULY 1995, BEIJING, CHINA

THEORETICAL PROBLEMS

PROBLEM 1

1.1 Excavated Chinese ancient bronze musical instrument, carillon, was covered entirely by rust. Chemical analysis showed that the rust contains CuCl, Cu_2O and $Cu_2(OH)_3Cl$. Simulation experiments showed that CuCl was formed first under the action of both air and Cl containing aqueous solution and then $Cu_2(OH)_3Cl$ produced through the following two different ways:



Using the molar standard formation Gibbs free energies of the species concerned answer the following questions:

Species	Cu_2O(s)	CuO(s)	CuCl(s)	**$Cu_2(OH)_3Cl$(s)**	Cl(aq)	OH(aq)	H_2O(l)
Δ_fG^0(298 K) (kJ mol^{-1})	-146	-130	-120	-1338	-131	-157	-237

i) Write balanced equations for reactions (a), (b) and (c).

ii) Calculate the molar standard Gibbs free energy Δ_fG^0(298 K) for reactions (a), (b) and (c).

iii) Decide the spontaneous direction of reaction (a) in air through calculation, when T = 298K, c(HCl) = 1.0×10^{-4} mol dm^{-3}.

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 ℃	25	40
k_c / mol dm^{-3} s^{-1}	1.29×10^{-4}	2.50×10^{-4}

i) Write the equation for calculating the activation energy of reaction (c) and fínd the value.

ii) Assign the overall reaction order of reaction (c).

iii) Knowing that the rate determining step of reaction (c) is the monolayer adsorption of O_2 (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 O_2 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.

i) An galvanic cell with Cu(1) and Cu**(2)** was designed as Cu(1)l$CuSO_4$(aq)ICu**(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

ii) 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 (Cu) = 63.5, A_r (Zn) = 65.4.

SOLUTION

1.1 i)

a) $2\ CuCl(s) + H_2O(l) \rightarrow Cu_2O(s) + 2\ H^+(aq) + 2\ Cl^-(aq)$

b) $Cu_2O(s) + \frac{1}{2}\ O_2(g) + H_2O(l) + H^+(aq) + Cl^-(aq) \rightarrow Cu_2(OH)_3Cl(s)$

c) $2\ CuCl(s) + \frac{1}{2}\ O_2\ (g) + 2\ H_2O(l) \rightarrow Cu_2(OH)_3Cl\ (s) + H^+(aq) + Cl^-(aq)$

ii) a) $\Delta G^0 = 69$ kJ mol^{-1}

b) $\Delta G^0 = -\ 824$ kJ mol^{-1}

c) $\Delta G^0 = -\ 755$ kJ mol^{-1}

iii) Calculation (dilute HCl solution can be considered as an ideal solution)

$\Delta_r G = \Delta_r G^0 + 2\ RT \ln [H^+]\ [Cl^-] = -\ 22.3$ kJ mol^{-1} < 0

Spontaneous: to the right

1.2 i) Formula: $\ln \frac{k_c(T_2)}{k_c(T_1)} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$E_a = 34.2$ kJ mol^{-1}

ii) overall reaction order = 0

when $b\ p(O_2) \gg 1$

$$r = k_c\ \theta = \frac{k_c\ b\, p(O_2)}{1 + b\, p(O_2)};\quad r = k_c \quad \textit{zero order}$$

1.3 i) (C) $E > 0$

ii) Net cell reaction: Cu(1) = Cu(2)

Thermodynamic reason for choosing 3 (C) is $\Delta_r G < 0$, $\Delta_r G = -\ nFE$ and $E > 0$

1.4 $r = 1.30\times10^{-10}$

formula: $a = 2\sqrt{2r}$

$$d = \frac{4\left(63.5 \times 0.75\ +\ 65.4\ \times\ 0.25\right)\times10^{-3}}{a^3\, N_A} = 8.51\times10^{-3}\ \text{kg m}^{-3}$$

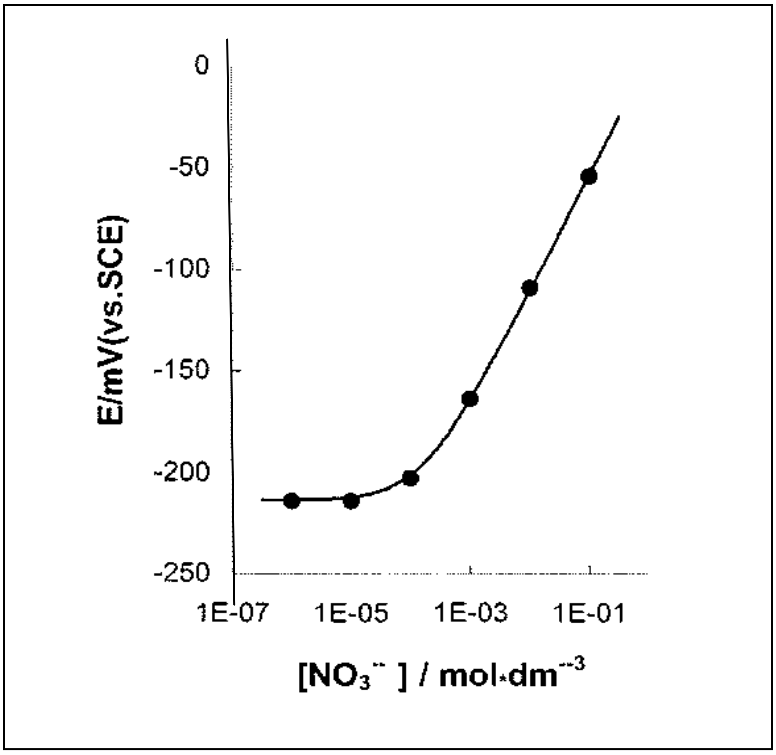
$r^3 = 2.209\times10^{-30}$ m^3

r = 1.30×10^{-10} 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 mol dm^{-3} K_2SO_4, 1.0×10^{-3} mol dm^{-3} H_2SO_4 and 2.6×10^{-3} mol dm^{-3} 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

$$K_{NO_3^-,Cl^-} = \frac{c_{NO_3^-}}{c_{Cl^-}} = 4.9\times10^{-2} \quad K_{NO_3^-,SO_4^{2-}} = \frac{c_{NO_3^-}}{c_{SO_4^{2-}}^{1/2}} = 4.1\times10^{-3}$$

$$K_{NO_3^-,ClO_4^-} = \frac{c_{NO_3^-}}{c_{ClO_4^-}} = 1.0\times10^{-3}$$

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 1.40×10^{-3} mol dm^{-3} NO_3^- and 1.60×10^{-2} mol dm^{-3} 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 1.00×10^{-3} mol dm^{-3} NO_3^- standard solution to the above solution, ***E*** changes to –130 mV. Find the pNO_3 of the serum.

2.4 The selective coefficient of CH_3COO^- versus NO_3^- $K(NO_3^-/CH_3COO^-) = 2.7\times10^{-3}$. 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_{sp}(AgCl) = 3.2\times10^{-10}$$K_{sp}(Ag_2SO_4) = 8.0\times10^{-5}$

$K_{sp}(AgCH_3COO) = 8.0\times10^{-3}$ $K_a(CH_3COOH) = 2.2\times10^{-5}$

$A_r(N) = 14.00$

SOLUTION

2.1 Yes

2.2 B

$(1.4\times10^{-3} \times 0.01) / [Cl^-] = 4.9\times10^{-4}$ mol dm^{-3}

$[Cl^-] = 2.9\times10^{-4}$ mol dm^{-3}

Excess $[Cl^-] = 1.6\times10^{-2} - 2.9\times10^{-3} \cong 1.6\times10^{-2}$ mol dm^{-3}

To reduce the interference of Cl^- at least 1.6×10^{-2} mol Ag^+ ion or 8.0×10^{-3} mol Ag_2SO_4 has to be added to 1 dm^3 sample solution.

2.3 $\Delta E = E_2 - E_1 = 0.059 \log \{(c_X V_X + c_S V_S)(c_X [V_x + V_S])\}$

$0.03 = 0.059 \log [(25.00\ V_x + 0.10) / (26.00 \times c_x)]$

$c_x = 1.7\times10^{-3}$ mol dm^{-3}

$p\mathrm{NO_3} = 2.77$

2.4 $pH = 4.4$

$(1.4\times10^{-3} \times x) \div 1.6\times10^{-2} = 2.7\times10^{-3}$

$x = 3.1\ \% > 1\ \%$

$(1.4\times10^{-3} \times 0.01) \div [\mathrm{CH_3COO^-}] = 2.7\times10^{-3}$

$[\mathrm{CH_3COO^-}] = 5.2\times10^{-3}$ mol dm^{-3}

$1.6\times10^{-2} - 5.2\times10^{-3} = 1.08\times10^{-2}$ mol dm^{-3}

$\{[\mathrm{H^+}] \times 5.2\times10^{-3}\} \div (1.08\times10^{-2}) = 2.2\times10^{-5}$

$[\mathrm{H^+}] = 4.3\times10^{-5}$ 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 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.

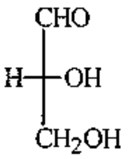
3.3 Write the structural formula for the dimer.

3.4 Using Haworth projection formula represent the possible stereoisomers which fit the dipole moment data.

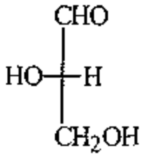
3.5 Denote each chiral carbon atom in the above formulae with *R* or *S*.

SOLUTION

3.1

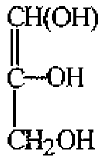


D(+)

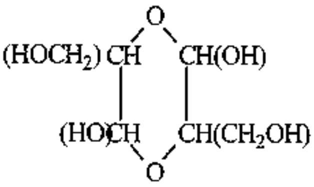


L(-)

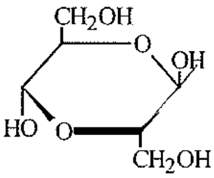
3.2



3.3


O
(HOCH2) CH
CH(OH)
(HO)CH
CH(CH2OH)
O

3.4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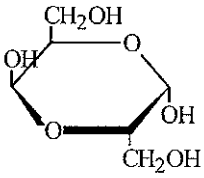
OH
HO
O
CH2OH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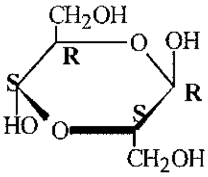
OH
O
OH
CH2OH

3.5


CH2OH
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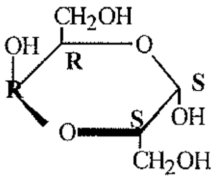
OH
R
S
R
S
HO
O
CH2OH


CH2OH
OH
O
R
R
S
O
S
OH
CH2OH

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.

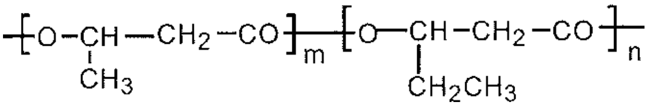
4.1 PHB, Poly(3-hydroxybutanoic acid), produced by bacteria contains only (R)-HB repeating units, while that synthesized by polymer chemists may contain only (R)-HB or only (S)-HB or both (R)-and (S)-HB in an alternating manner or both but in random distributions. Sketch chain structures of the atactic 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:



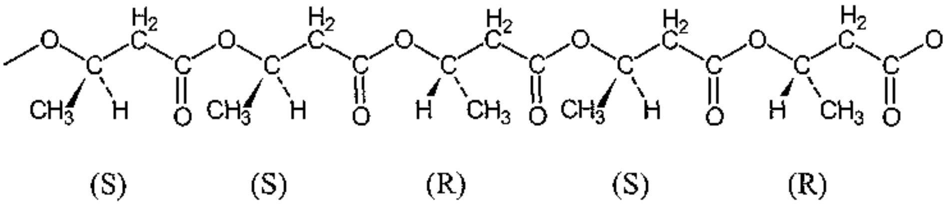
$$-\!\left[O-\underset{CH_3}{CH}-CH_2-CO \right]_m\!-\!\left[O-\underset{CH_2CH_3}{CH}-CH_2-CO \right]_n\!-$$

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

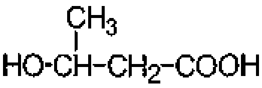


Other arrangements with (*R*) and (*S*) randomly distributed along the chain are correct, e.g. *RSRRS*, *SRSSR*, *RRSRS*, etc.

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*.

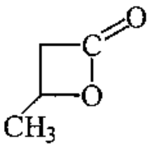
4.2 Monomer 1:



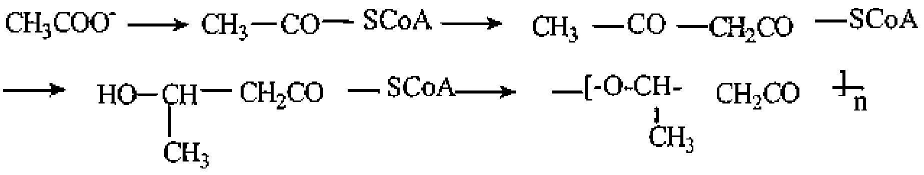
$HO\text{-}CH(CH_3)\text{-}CH_2\text{-}COOH$

3-hydroxybutanoic acid

Monomer 2:

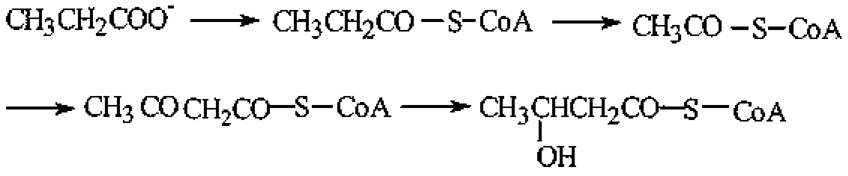


4.3



$$\mathrm{CH_3COO^- \longrightarrow CH_3-CO-SCoA \longrightarrow CH_3-CO-CH_2CO-SCoA \longrightarrow HO-\underset{\underset{CH_3}{|}}{CH}-CH_2CO-SCoA \longrightarrow -[-O-\underset{\underset{CH_3}{|}}{CH}-CH_2CO]_n}$$

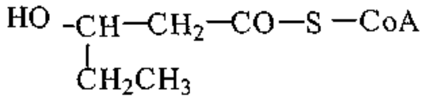
4.4



$$\mathrm{CH_3CH_2COO^- \longrightarrow CH_3CH_2CO-S-CoA \longrightarrow CH_3CO-S-CoA \longrightarrow CH_3COCH_2CO-S-CoA \longrightarrow CH_3\underset{\underset{OH}{|}}{C}HCH_2CO-S-CoA}$$

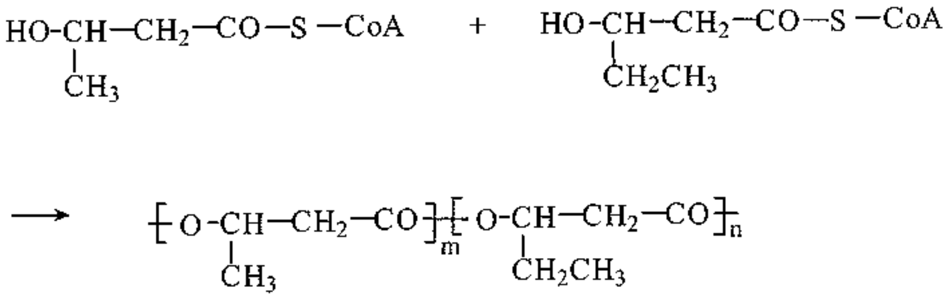
(Coenzyme A activated monomer 3-hydroxypentanoic acid)

This monomer may also be written in the following way:



$$\mathrm{HO-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CO-S-CoA}$$

Polymerization of these two monomers will result in the desired copolymer:



$$\mathrm{HO-\underset{\underset{CH_3}{|}}{CH}-CH_2-CO-S-CoA + HO-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CO-S-CoA}$$

$$\mathrm{\longrightarrow \left[O-\underset{\underset{CH_3}{|}}{CH}-CH_2-CO\right]_m\left[O-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CO\right]_n}$$

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 ↑ and/or ↓.

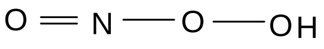
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species really exists in the iron complex?

a) NO b) NO^+ c) NO^-

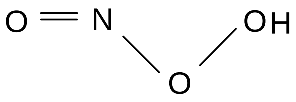
5.3 The cell damage is caused by free radical OH, which is one of the product of reaction between O_2^- and NO:

O_2^- + NO + H^+ → HOONO → $\bullet NO_2$ + $\bullet OH$

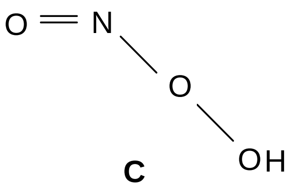
in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.



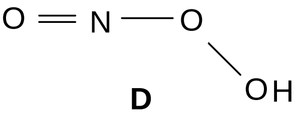
A



B

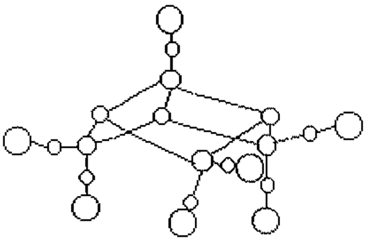


C



D

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 $[Fe_4S_3(NO)_7]^-$. 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 $[Fe_4S_3(NO)_7]^-$ anion can be reduced and a new complex $[Fe_2S_2(NO)_4]^{2-}$ is formed which contains a cyclic structure unit of Fe_2S_2.

i) Write the structural formula for the anion $[Fe_2S_2(NO)_4]^{2-}$.

ii) Give the oxidation state of each iron atom with Arabic numerals.

iii) $[Fe_2S_2(NO)_4]^{2-}$ can be converted into $[Fe_2(SCH_3)_2(NO)_4]^n$, a carcinogen. Which of the following three species is added to $[Fe_2S_2(NO)_4]^{2-}$: CH_3^+, $\bullet CH_3$ or CH_3^-? Assign the value of n.

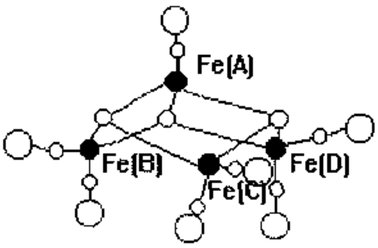
SOLUTION

5.1 The HOMO of NO molecule is π*, its electron arrangement ↑;
The LUMO of NO molecule is π*.

5.2 (b)

5.3 B

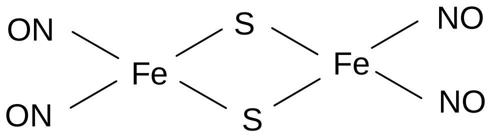
5.4



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.

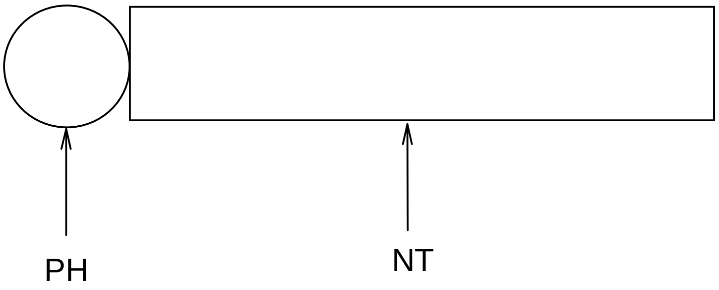


Fig. 1

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)×10^4	Isoelectronic 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.

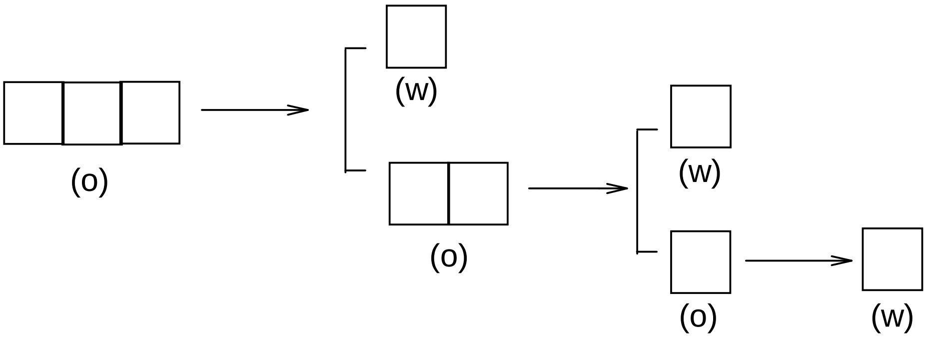


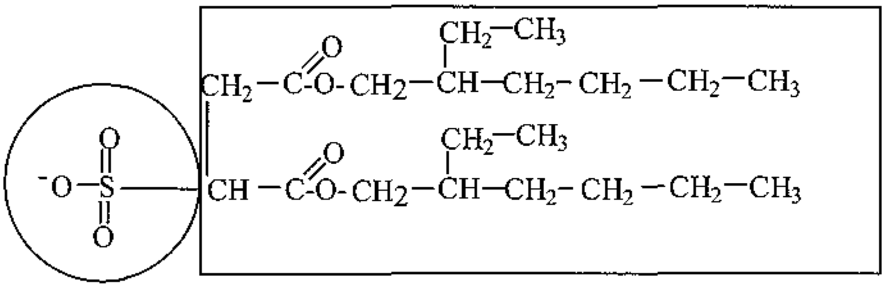
Fig. 2

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.

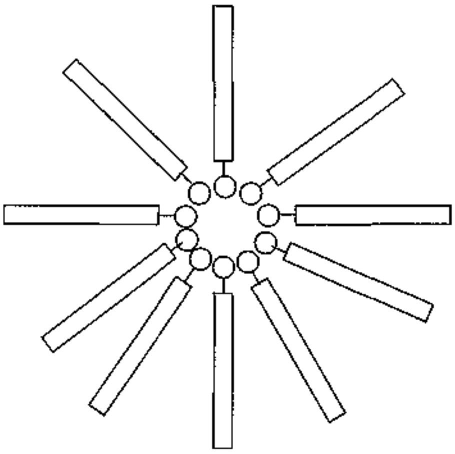
SOLUTION

6.1 i)



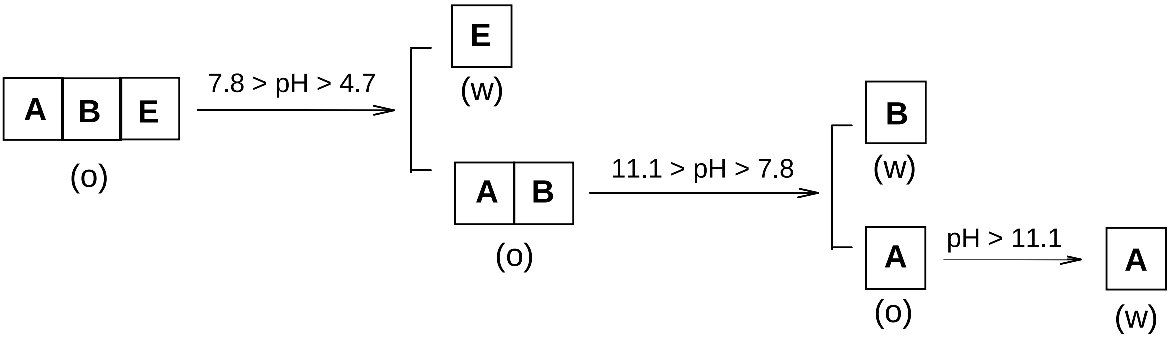
ii) (b)

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:

NH_4Cl $(NH_4)_2SO_4$ $NaNO_3$ $MgCl_2$ Na_2SO_4

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})
$Ba(OH)_2$ (satd.)	NaOH (6 mol dm^{-3})
$BaCl_2$ (0.5 mol dm^{-3})	$Ba(NO_3)_2$ (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 [$Cu(gly)_2 \bullet xH_2O$]

Copper(II) amino acidate coordination compounds are monometric 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 ℃.

Reagents:
$CuSO_4 \cdot 5 H_2O(s)$
NH_3 (aq) (3 mol dm^{-3})
glycine(s)
95% ethanol,
acetone
NaOH (2 mol dm^{-3})
$BaCl_2$ (0.5 mol dm^{-3})

1. *Preparation of $Cu(OH)_2$*

Procedure:

(1) Dissolve your pre-weighted sample of $CuSO_4 \cdot 5 H_2O$ (6.0 g) in 40 cm^3 of water with a 250 cm^3 beaker as a container.

(2) Add slowly 3 mol dm^{-3} ammonia solution to the $CuSO_4$ 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 SO_4^{2-} ion is detected in the filtrate.

(5) Collect $Cu(OH)_2$ for the preparation of $Cu(gly)_2 . x H_2O$.

Write the equations for the main chemical reactions having taken place in the above procedure.

2. <u>Preparation of cis-Copper-bis-Glycinate Hydrate</u>

Procedure:

(1) Dissolve a pre-weighted sample of glycine (3.6 g) in 130 cm^3 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 cm^3 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 cm^3 of ethanol-water mixing solvent and then twice with 10 cm^3 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:

1. $Cu^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Cu(OH)_2 + 2\ NH_4^+$

$Cu(OH)_2 + 4\ NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2\ OH^-$

2. $Cu(OH)_2 + 2\ NH_2CH_2COOH \rightarrow Cu(NH_2CH_2COO^-)_2 + 2\ H_2O$

PROBLEM 3 (Practical)

Determination of Copper(II) Content in Cu(gly)$_2$. x H_2O

The Cu(II) content in Cu(gly)$_2$. *x* H_2O 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 Cu(gly)$_2$. *x* H_2O.

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 %)

$Na_2S_2O_3$ (to be standardized)

1. *Standardization of $Na_2S_2O_3$ 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 $Na_2S_2O_3$ 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 Cu(gly)$_2$.xH_2O*

(1) Weigh 1.0 – 1.2 g (precision of ±0.0002 g) of Cu(gly)$_2$. *x* H_2O 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 cm^3 of the Cu(II) solution to an Erlenmeyer flask, add 50 cm^3 of water and 10 cm^3 of KI solution to the flask.

(5) Titrate immediately with standardized $Na_2S_2O_3$ solution.

(6) Add 2 cm^3 of starch solution and 3 cm^3 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 $Na_2S_2O_3$ solution
- Calculation of the concentration of $Na_2S_2O_3$ solution.

Part 2

- Mass of the product.
- Volumes of $Na_2S_2O_3$ solution
- Mass % of Cu(II) in $Cu(gly^-)_2 \cdot x\,H_2O$. 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 $Na_2S_2O_3$ solution.
2. Write the equation for the reaction between Cu^{2+} and I^-.

Solutions of the tasks:

1. $IO_3^- + 5\,I^- + 6\,H_3O^+ \rightarrow I_2 + 9\,H_2O$

   $I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$

2. $2\,Cu^{2+} + 4\,I^- \rightarrow 2\,CuI + I_2$

28^{th}

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 = ($TeCl_4$ + 4 $AlCl_3$). The second component B was considered as an analog of Te(IV) chloroaluminate $Te[AlCl_4]_4$ 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 ± 43 g mol^{-1} and 867 ± 48 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 Te(cryst.) + 2 $TeCl_4$ + 8 $AlCl_3$ and the minimum atomic ratio for the composition from which the excess of $TeCl_4$ is not substracted 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. Substracting one mole of $TeCl_4$ from the obtained ratio and dividing by 2 we obtain 4 Te + 4 Al + 14 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 Te(cryst.) + $TeCl_4$ + 4 $AlCl_3$ = 8 Te + 4 Al + 16 Cl and the ratio is Te : Al : Cl = 2 : 1 : 4. 91.7 % of Te(cryst.) corresponds to 11 Te(cryst.) + $TeCl_4$ + 4 $AlCl_3$ = 12 Te + 4 Al + 16 Cl and the ratio is Te : Al : Cl = 3 : 1 : 4.

1.2 The molecular formulae of compounds **I** and **II**:

Compound **I**: $Te_4Al_4Cl_{14}$

Compound **II**: $Te_4Al_2Cl_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to double simplest formula.

For compound I: 2 ($Te_2Al_2Cl_7$) 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**: $[Te_4]^{2+}$ $[Al_2Cl_7]^-$

Compound **II**: $[Te_4]^{2+}$ $[AlCl_4]^-$

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 $[Te_4]^{2+}[AlCl_4]_2^-$. As according to similar colouration the cations are likely to be the same in both cases, the structure of **I** should contain $[Te_4]^{2+}$ cations and $[Al_2Cl_7]^-$ 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:

$[Te_4]^{2+}$ 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:

$Te_4[Al_2Cl_7]_2 = Te_4[AlCl_4]_2 + 2\ AlCl_3$

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 $[C_9H_6(OH)NH][BiI_4]$ ($M_r = 862.7$).

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 (≈ 2 cm^3) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($K_3[Cr(SCN)_6]$) 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 $(BiO)_2CO_3$ 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 cm^3 of 2 M H_2SO_4 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 cm^3 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 IO_3^-.

Step 6: To eliminate an excess of molecular bromine 3 cm^3 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 $Na_2S_2O_3$ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

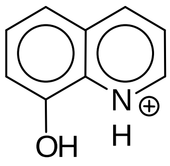
2.10 a) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

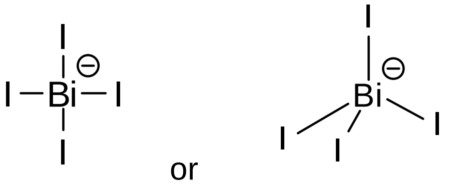
b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm^3 of standard 0.00200 M $Na_2S_2O_3$ solution)?

2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

SOLUTION

2.1 a)





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.

2.3 $Bi^{3+} + [Cr(SCN)_6]^{3-} \longrightarrow Bi[Cr(SCN)_6]$.

2.4 $2\ Bi[Cr(SCN)_6] + 6\ HCO_3^- \longrightarrow (BiO)_2CO_3 + 2\ [Cr(SCN)_6]^{3-} + 3\ H_2O + 5\ CO_2$

or

$2Bi[Cr(SCN)_6] + HCO_3^- + 5\ OH^- \longrightarrow (BiO)_2CO_3 + 2\ [Cr(SCN)_6]^{3-} + 3\ H_2O$ etc.

(variations are possible)

2.5 $[Cr(SCN)_6]^{3-} + 24\ I_2 + 24\ H_2O \longrightarrow Cr^{3+} + 6\ SO_4^{2-} + 6\ ICN + 42\ I^- + 48\ H^+$

2.6 $ICN + I^- + H^+ \longrightarrow I_2 + HCN$

2.7 a)

$3\ Br_2 + I^- + 3\ H_2O \longrightarrow IO_3^- + 6\ Br^- + 6\ H^+$

b)

$Br_2 + HCN \longrightarrow BrCN + Br^- + H^+$

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.

2.8 $Br_2 + HCOOH \longrightarrow 2\ Br^- + CO_2 + 2\ H^+$

2.9 a)

$IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$

b)

$BrCN + 2I^- + H^+ \longrightarrow I_2 + HCN + Br^-$

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:

$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$.

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 × 3 = 108 moles of I_2, which take 108 × 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 $Na_2S_2O_3$, which corresponds to $209.0 \times 2.00 \times 10^{-6} / 228 = 1.83 \times 10^{-6}$ g $= 1.83 \times 10^{-3}$ mg = = 1.83 μg**.**

2.11 $\dfrac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplicated method}} = 6600$

The multiplicative method is more sensitive than the gravimetric method by 12.1 mg / 1.83×10^{-3} 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 $^{226}_{88}$Ra) and found that 1.00 g of radium emits $x = 3.42\times10^{10}$ 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_{He} = 6.58 mm^3 corrected to 0^o 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).

$$\text{Ra} \xrightarrow[\alpha]{>1500\text{ years}} \text{Rn} \xrightarrow[\alpha]{3.83\text{ days}} \text{RaA} \xrightarrow[\alpha]{3.05\text{ min}} \text{RaB} \xrightarrow[\beta]{26.8\text{ min}} \text{RaC} \xrightarrow[\beta]{19.7\text{ min}}$$

$$\longrightarrow \text{RaC'} \xrightarrow[\alpha]{1.63\times10^{-4}\text{s}} \text{RaD} \xrightarrow[\beta]{27.1\text{ years}} \text{RaE} \xrightarrow[\beta]{5\text{ days}} \text{Po} \xrightarrow[\alpha]{138\text{ days}} \text{Pb (stable)}$$

(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?

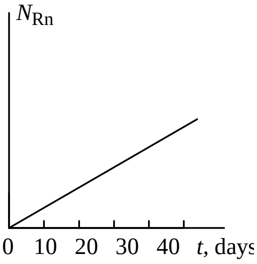
b) How many helium atoms were formed in total during the experiment?

3.3 Calculate an approximate value of Avogadro's number from the above data.

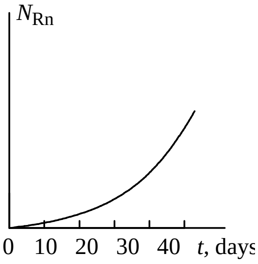
For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}$(Rn) = 3.83 days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

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.

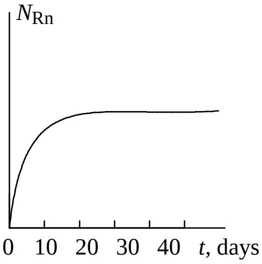
A



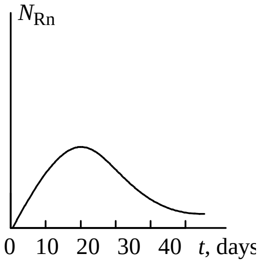
B



C

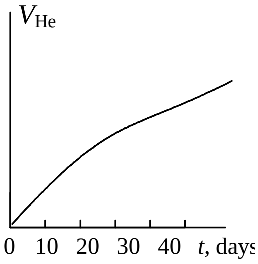


D

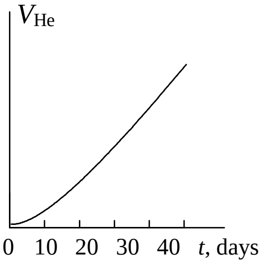


3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.

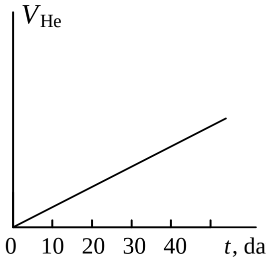
E



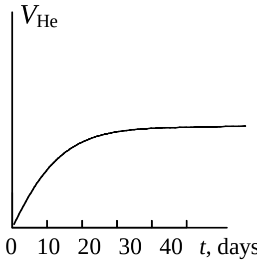
F



G



H



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

$$\text{Ra} \xrightarrow{k_1} \text{Rn} \xrightarrow{k_2} \text{RaA}$$

(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 ($x = 3.42\times10^{10}$ 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:

a) the number of helium atoms formed;

b) the Avogadro's number.

SOLUTION

3.1 $^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$

$^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$

$^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb} + {}^{4}_{2}\text{He}$

$^{214}_{82}\text{Pb} \rightarrow {}^{214}_{83}\text{Bi} + \text{e}$

$^{214}_{83}\text{Bi} \rightarrow {}^{214}_{84}\text{Po} + \text{e}$

$^{214}_{84}\text{Po} \rightarrow {}^{210}_{82}\text{Pb} + {}^{4}_{2}\text{He}$

3.2 a) The correct answer: 4

b) Number of helium atoms (rough 1.9×10^{17} estimate)

$N_{\text{He}} = 4\,x\,m\,t = 1.9\times10^{17}$

3.3 The first estimate of Avogadro's number: 6.4×10^{23} 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

$$N_A = \frac{4\,x\,m\,t}{\nu_{\text{He}}} = \frac{4\times3.42\times10^{10}\times0.192\times(83\times24\times3600)}{\dfrac{6.58\times10^{-6}}{22.4}} = 6.4\times10^{23}\ \text{mol}^{-1}.$$

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:

$k = 1 / T_{1/2}$	$\underline{k = \ln 2 / T_{1/2}}$	$k = \ln 2 \cdot T_{1/2}$	$k = \pi / T_{1/2}$

3.7 a) Underline the correct answer:

$\underline{N'_{Rn} = k_1 \cdot N_{ra} / k_2}$	$N'_{Rn} = k_2 \cdot N_{Ra} / k_1$	$N'_{Rn} = k_1 \cdot N_{Ra} / 2k_2$	$N'_{Rn} = k_1 \cdot N_{Ra} / 3k_2$

The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay $k_2 N'_{Rn} = k_1 N_{Ra}$, whence $N'_{Rn} = k_1 \cdot N_{Ra} / k_2$

b) $N'_{Rn} = 3.14 \times 10^{15}$

The rate of radium decay is $k_1 N_{Ra} = xm$, whence

$$N'_{Rn} = \frac{xm}{\dfrac{\ln 2}{T_{1/2(Rn)}}} = \frac{3.42 \times 10^{10} \times 0.192}{\dfrac{0.693}{3.83 \times 24 \times 3600}} = 3.14 \times 10^{15}$$

3.8 Underline the correct answer:

$4N'_{Rn}$	$2N'_{Rn}$	$5N'_{Rn}$	N'_{Rn}	$\underline{3N'_{Rn}}$

3.9 a) A more accurate estimate of the number of helium atoms: 1.79×10^{17}

$$N_{He} = 4\,xmt - 3N'_{Rn} = 1.9 \times 10^{17} - 3 \times 3.14 \times 10^{15} = 1.79 \times 10^{17}$$

b) A more accurate estimate of Avogadro's number (mol^{-1}): 6.09×10^{23}

$$N_{\text{À}} = \frac{N_{He}}{n(\text{He})} = \frac{1.79 \times 10^{17}}{\dfrac{6.58 \times 10^{-6}}{22.4}} = 6.09 \times 10^{23}$$

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).

$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-}$ log K_1 = -6.50

$2\,HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$ log K_2 = 1.36

4.1 Calculate the equilibrium constants

a) $CrO_4^{2-} + H_2O \rightleftarrows HCrO_4^- + OH^-$

b) $Cr_2O_7^{2-} + 2\,OH^- \rightleftarrows 2\,CrO_4^{2-} + H_2O$

The ionic product of water $K_W = 1.0\times10^{-14}$.

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?

a) KOH

b) HCl

c) $BaCl_2$

d) H_2O

The solubility product of $BaCrO_4$ is 1.2×10^{-10}. $BaCr_2O_7$ is well soluble in water.

4.3 Calculate the pH value of the following solutions

a) 0.010 M K_2CrO_4

b) 0.010 M $K_2Cr_2O_7$

c) 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH

Dissociation constant of acetic acid $K_a = 1.8\times10^{-5}$.

4.4 Calculate the equilibrium concentrations of the following ions in the solution of 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH

a) CrO_4^{2-}

b) $Cr_2O_7^{2-}$

Pb^{2+} and Ag^+ form poorly soluble compounds with chromate and dichromate ions. The solubility products of these compounds are indicated below.

$PbCrO_4$	$K_{s1} = 1.2\times10^{-14}$
Ag_2CrO_4	$K_{s2} = 1.3\times10^{-12}$
$Ag_2Cr_2O_7$	$K_{s3} = 1.1\times10^{-10}$

To the aqueous solution of the mixture of 1.0×10^{-3} M $Pb(NO_3)_2$ and 2.0×10^{-4} M $AgNO_3$ an equal volume of 0.020 M solution of $K_2Cr_2O_7$ 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}

$$\frac{[HCrO_4^-]\,[OH^-]}{[CrO_4^{2-}]} = \frac{[HCrO_4^-]\,[OH^-]\,[H^+]}{[CrO_4^{2-}]\,[H^+]} = \frac{K_w}{K_1}$$

$$\frac{1.0\times10^{-14}}{3.16\times10^{-7}} = 3.2\times10^{-8}$$

b) Equilibrium constant > 4.4×10^{13}

$$\frac{K_1^2}{K_2\,K_w^2} = \frac{\left(\dfrac{\left[CrO_4^{\,2-}\right]\left[H^+\right]}{\left[HCrO_4^{\,-}\right]}\right)^2}{\dfrac{\dfrac{\left[HCrO_4^{\,-}\right]^2}{\left[Cr_2O_7^{\,2-}\right]}}{\left(\left[H^+\right]\left[OH^-\right]\right)^2}} = \frac{10^{-2\times6.50}}{10^{1.36}\times10^{-2\times14.00}} = 10^{13.64} = 4.4\times10^{13}$$

4.2 Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a)		☑	
b)	☑		
c)		☑	
d)		☑	

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

$Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4$

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 $K_2Cr_2O_7$ the value of 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) $pH = 9.25$

b) $pH = 4.20$

c) $pH = 2.87$

Calculations:

a) $CrO_4^{2-} + H_2O = HCrO_4^- + OH^-$ $K = 3.16\times10^{-8}$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] \approx [CrO_4^{2-}]$,

$[HCrO_4^-] \approx [OH^-]$

$[OH^-]^2/c_{Cr} = K$, $[OH^-] = \sqrt{K\ c_{Cr}} = \sqrt{3.16\times10^{-8}\times0.01} = 1.78\times10^{-5}$

$[H^+] = 5.65\cdot10^{-10}$, $pH = 9.25$

b) $Cr_2O_7^{2-} + H_2O = 2\ HCrO_4^-$ $K = 1/K_2 = 4.37\times10^{-2}$

$HCrO_4^- = H^+ + CrO_4^{2-}$ $K = K_1 = 3.16\times10^{-7}$

$[H^+] \approx [CrO_4^{2-}] \Rightarrow [H^+] = \sqrt{K_1[HCrO_4^{2-}]}$

$[HCrO_4^-]$ = ?

$c_{Cr} = 2.0\cdot10^{-2}$ M (**) = $[CrO_4^{2-}] + [HCrO_4^-] + 2\ [Cr_2O_7^{2-}] \approx [HCrO_4^-] + 2\ [Cr_2O_7^{2-}]$

$[HCrO_4^-] = x$; $K_2 = [Cr_2O_7^{2--}]/ [HCrO_4^-]^2 = (c_{Cr} - x) / 2x^2$; $2\ K_2x^2 + x - c_{Cr} = 0$

hence $[H^+] = (3.16\times10^{-7} \times 1.27\times10^{-2})^{1/2} = 6.33\times10^{-5}$; pH = 4.20

c) In 0.10 M CH_3COOH $[H^+] = (K_a\ c)^{1/2/}$ (*) = $(1.8\times10^{-5} \times 0.10)^{1/2} = 1.34\times10^{-3}$

$pH = 2.87$

4.4 Equilibrium concentrations

a)	3.0×10^{-6}
b)	3.7×10^{-3}

Calculations:

The different methods can be used.

Method 1.

a)

$[HCrO_4^-] = 1.3\times10^{-2}$ (*)

$[CrO_4^{2-}] = K_1[HCrO_4^-] / [H^+] = 3.16\times10^{-7} \times 1.3\times10^{-2} / 1.34\times10^{-3} = 3.0\times10^{-6}$

b)

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2\ [Cr_2O_7^{2-}]$

$[Cr_2O_7^{2-}] = ½(c_{Cr} - [CrO_4^{2-}] - [HCrO_4^-]) = ½\ (2.0\times10^{-2} – 3.0\times10^{-6} – 1.3\times10^{-2}) = 3.7\times10^{-3}$

or otherwise

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-]^2 = 22.9 \times (1.3\times10^{-2})^2 = 3.9\times10^{-3}$

Method 2

a)

$[CrO_4^{2-}] = x$; $[HCrO_4^-] = x[H^+] / K_1$

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = x^2 K_2 [H^+]^2 / K_1^2$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] = 2K_2 [H^+]^2 / K_1^2 x^2 + (1 + [H^+] / K_1)x$

$K_1 = 3.16\times10^{-7}$; $K_2 = 22.9$; $[H^+] = 1.34\times10^{-3}$

$8.24\times10^8 x^2 + 4.24\times10^3 x - 2.0\times10^{-2} = 0$

$x = 3.0\times10^{-6}$

b)

$[Cr_2O_7^{2-}] = K_2[HCrO_4^-] = K_2 [H^+]^2 / K_1^2 [CrO_4^{2-}]^2 = 4.12\times10^8 \times (3.0\times10^{-6})^2 = 3.7\times10^{-3}$

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 $FeCl_2$ (aq)) and $FeCl_3$(aq), and solution **II** contains a mixture of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. The concentrations of iron-containing species satisfy the relations $[Fe^{2+}]_I = [Fe(CN)_6^{4-}]_{II}$ and $[Fe^{3+}]_I = [Fe(CN)_6^{3-}]_{II}$. 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 $Fe(CN)_6^{4-}$, $Fe(H_2O)_6^{3+}$, and $Fe(H_2O)_6^{2+}$ do not absorb light at 420 nm.

Molar absorption at this wavelength $\varepsilon([Fe(CN)_6^{3-}]) = 1100\ M^{-1}\,cm^{-1}$.

Standard redox potential for $Fe(H_2O)_6^{3+}$ / $Fe(H_2O)_6^{2+}$ 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

a) solution **I**,

b) 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 $\beta[Fe(CN)_6^{3-}]$ / $\beta[Fe(CN)_6^{4-}]$.

5.4 What is the absolute range of variation for the following physical values

a) transmittance *T*;

b) absorbance *A*.

5.5 Sketch the graphs of concentration dependences satisfying the Lambert-Beer law for

a) absorbance *A*;

b) transmittance *T*;

c) molar absorption ε.

5.6 Calculate the concentrations of

a) Fe^{2+} in solution **I**;

b) 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:

a) $E_I = E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log \dfrac{\left[Fe^{3+}\right]}{\left[Fe^{2+}\right]}$

b) $E_I = E°(Fe(CN)_6^{3-}/ Fe(CN)_6^{4-}) + 0.0590 \log \dfrac{\left[Fe(CN)_6^{3-}\right]}{\left[Fe(CN)_6^{4-}\right]}$

5.2 The units of pre-logarithm factor: V

5.3 The ratio of stability constants

$\beta\{Fe(CN)_6^{3-}\} / \beta\{Fe(CN)_6^{4-}\} = 8.90\times10^6$

Calculations:

$$E_{II} = E°(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) + 0.0590 \log[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] =$$

$$= E°(Fe^{3+}/Fe^{2+}) + 0.0590 \log(\beta_1/\beta_2) + 0.0590 \log([CN^-]^6/[CN^-]^6) +$$

$$+ 0.0590 \log[Fe(CN)_6^{3-}/Fe(CN)_6^{4-}] = 0.242$$

(where β_1 and β_2 are stability constants for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively.)

$[Fe(CN)_6^{3-}] / [Fe(CN)_6^{4-}] = [Fe^{3+}] / [Fe^{2+}]$, therefore

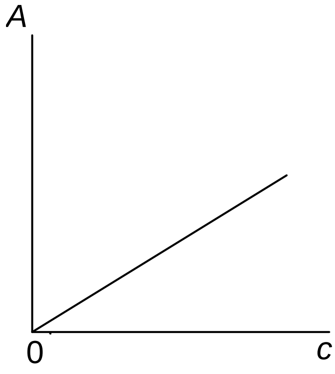
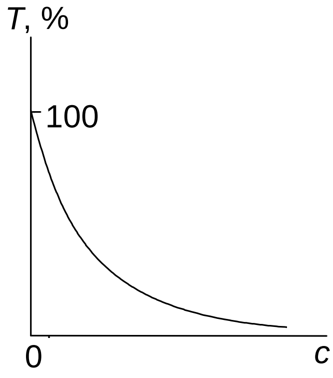
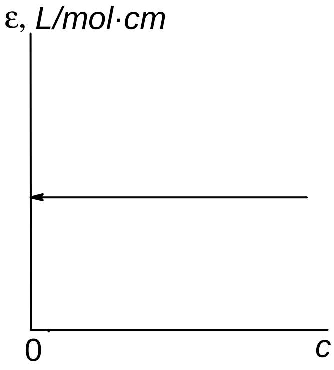
$\Delta E = E_{II} - E_I = 0.0590 \cdot \log(\beta_1/\beta_2)$, and $\beta_2/\beta_1 = 8.90\times10^6$.

5.4 The ranges of variation:

a) from 0 to 100

b) from 0 to ∞

5.5

a)	b)	c)
		

5.6 a) Using Bouger-Lambert-Beer law

$A = \varepsilon\, l\, c = \varepsilon\, l\, c[\text{Fe(CN)}_6^{3-}] = 0.971;$

$c[\text{Fe(CN)}_6^{3-}] = 0.971 / (1100 \times 0.502) = 1.76\times10^{-3}\ \text{M} = c[\text{Fe}^{3+}]$

b) using Nernst's equation

$E = E°(\text{Fe}^{3+} / \text{Fe}^{2+}) + 0.0590 \log[\text{Fe}^{3+}]_l / [\text{Fe}^{2+}]_l =$

$= 0.771 + 0.0590 \log [\text{Fe}^{3+}]_l / [\text{Fe}^{2+}]_l = 0.652\ V.$

hence,

$[\text{Fe}^{3+}]_l / [\text{Fe}^{2+}]_l = 9.62\times10^{-3};$

$[\text{Fe}^{2+}]_l = 1.76\times10^{-3} / 9.62\times10^{-3} = 0.183\ \text{M}.$

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 ℃, 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 peroxoacids 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 peroxoacetic 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**.

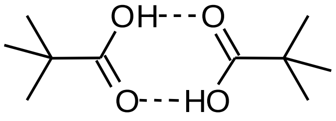
SOLUTION

6.1 The general formula: C_nH_{2n}

6.2 Compound **D**:

In aqueous solution: $(CH_3)_3CCOOH$

In vapours:

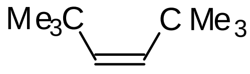


Dimeric structure in vapour phase is guessed using the value of vapour density.

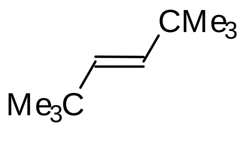
The relative molar weight in vapour phase is $9.1 \times 22.4 = 204$ which is close to double value of the molar weight of $(CH_3)_3CCOOH$. Possibly, as other simple fat acids, this acid is also dimerized in vapours.

6.3 Compound **C**: $(CH_3)_3CCHO$

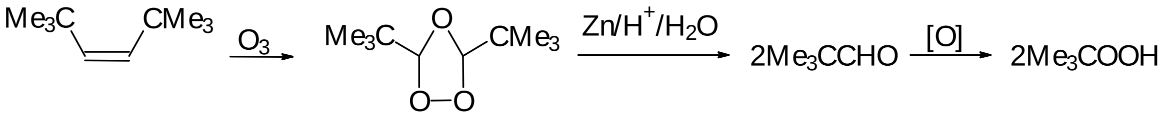
6.4 **A**:



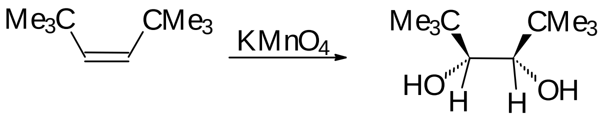
B:



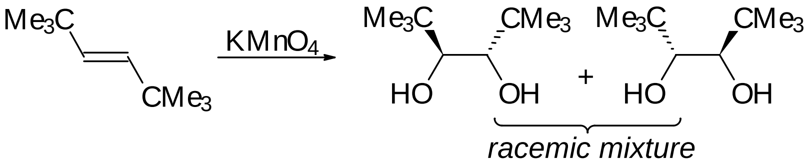
6.5 **A** ⟶ **C** ⟶ **D**



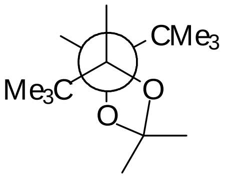
A ⟶ F



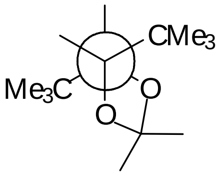
B ⟶ G1 + G2



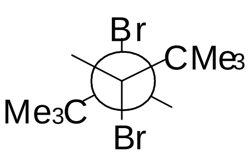
6.6 H1:



H2:



6.7 Non-polar bromination product (either of three types of structures may be given)



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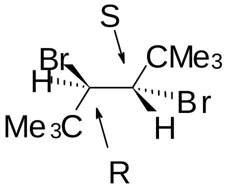

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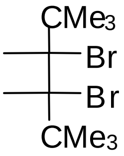
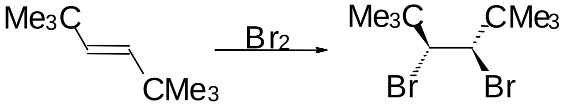
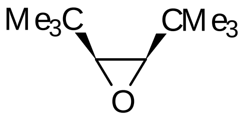


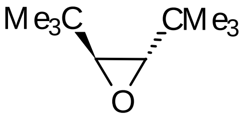


6.8 **K**:



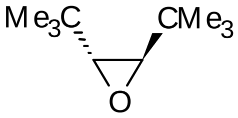
☑ NO; The molecule is not optically active.

L1:



☑ YES; The molecule is optically active.

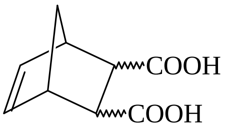
L2:



☑ 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**)



(no stereochemistry is shown)

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 **X_1** same to that is formed in the reaction of **X** with NaOH. The resulting solution of **X_1** is treated by I_2 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 **X_1** to **A**.

7.5 Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.

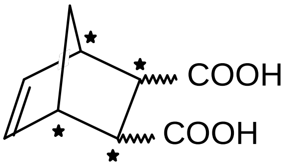
7.6 Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.

7.7 Write the reactions leading from **B** to **A**.

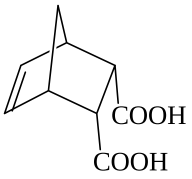
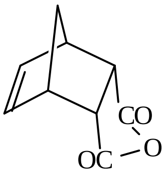
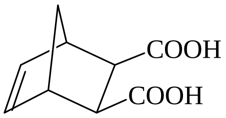
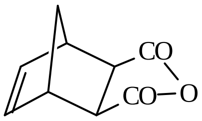
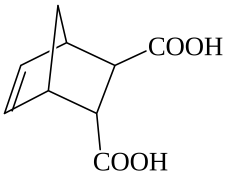
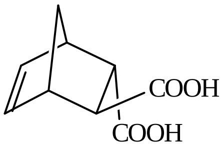
7.8 Are the compounds **A** and **B** diastereomers?

SOLUTION

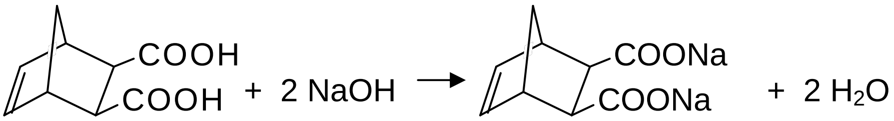
7.1



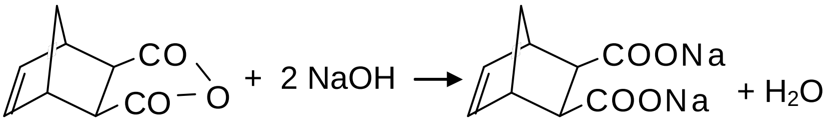
7.2 Fill in left column with the structures of stereoisomers of **X**, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus.

	
	
	—
	—

7.3 The reaction of a stereoisomer of **X** with NaOH:

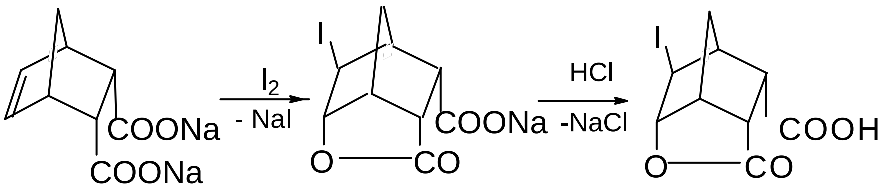


The reaction of a stereoisomer of **Y** with alkali:

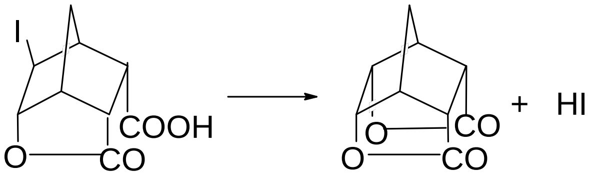


7.4 The molar mass of **A**: 308 g mol^{-1}

The reactions leading from **X_1** to **A**

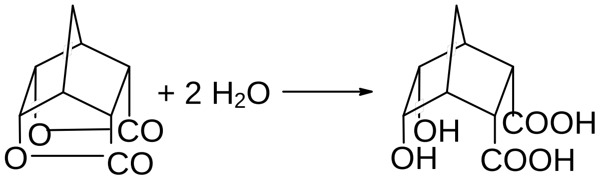


7.5 The transformation of **A** to **C**:

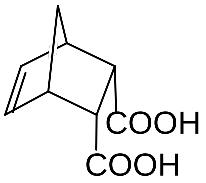


CO

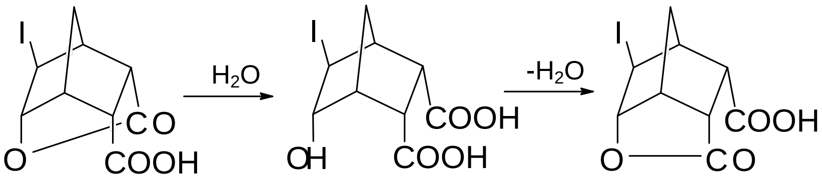
The reaction of **C** with water:



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

- $K_2Cr_2O_7$, 0.008333 M
- KI, 20 % by mass.
- HCl, 1 M
- H_2SO_4, 1 M
- $Na_4P_2O_7$, 5 % by mass.
- Starch, 1 % by mass.
- $Na_2S_2O_3$ (should be standardized)
- The solution to be analyzed in 100 cm^3 volumetric flask.

Procedure

1. Standardization of $Na_2S_2O_3$ solution

   (1) 10 cm^3 of 1 M solution of H_2SO_4 and 2 cm^3 of 20 % KI solution are placed into an Erlenmeyer flask (the solution remains colourless).

   (2) 10.00 cm^3 of $K_2Cr_2O_7$ 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 cm^3 of water is added to the flask.

   (5) The mixture is titrated immediately with $Na_2S_2O_3$ 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 $Na_2S_2O_3$ solution

1.2 Calculate the concentration of $Na_2S_2O_3$ solution, and write your calculations.

2. The determination of copper

(1) The solution to be analyzed in a 100 cm^3 volumetric flask is diluted with water to the mark and stirred

(2) A 10.00 cm^3 aliquot of the solution is placed into an Erlenmeyer flask.

(3) 20 cm^3 of 5 % solution of $Na_4P_2O_7$, 7 cm^3 of 1 M solution of HCl, and 10 cm^3 of 20 % solution of KI are added. A precipitate may form upon the addition of $Na_4P_2O_7$.

(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 $Na_2S_2O_3$ 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 Cu^{2+} 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 cm^3 aliquot of the solution prepared in the item 2(1) is placed into an Erlenmeyer flask.

(2) 2 cm^3 of 1 M HCl solution and 10 cm^3 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 $Na_2S_2O_3$ 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 Fe^{3+} ion.

1.6 Calculate the mass of iron in the solution under analysis, and write your calculations.

SOLUTION

1.1

Equations:

$Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ = 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

i

1.3

Equations:

$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$

$4\,Fe^{3+} + 3\,P_2O_7^{4-} = Fe_4(P_2O_7)_3 \downarrow$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

1.5

Equations:

$2\,Fe^{3+} + 2\,I^- = 2\,Fe^{2+} + I_2$

$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$

$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$

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 cm^3 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 cm^3 round bottom flask is equipped with reflux condensor 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 condensor 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 cm^3) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 cm^3) 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 cm^3 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 cm^3 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 cm^3 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}.

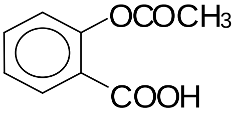
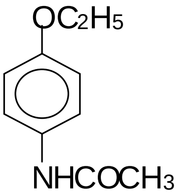
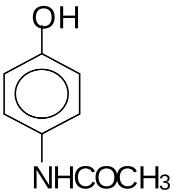
2.3 Calculate the yield of product obtained by you.

2.4 Calculate and compare the values of R_f of unknown drug and your product.

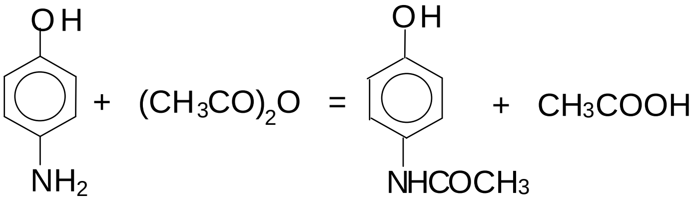
2.5 Is it likely that paracetamol is contained in the sample of drug?

SOLUTION

2.1

Acetylsalicylic acid	Phenacetine	Paracetamol
		

2.2



2.5 Yes, the sample is likely to contain paracetamol.

29th

International Chemistry Olympiad

8 theoretical problems
2 practical problems

THE TWENTY-NINTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–22 JULY 1997, MONTREAL, CANADA

THEORETICAL PROBLEMS

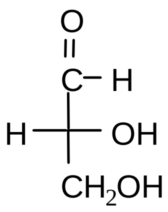
PROBLEM 1

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**).

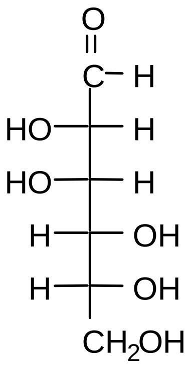
1.1 On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.

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

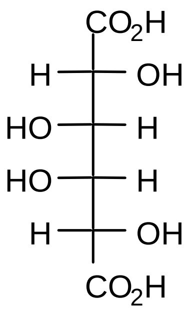


Compound **1**

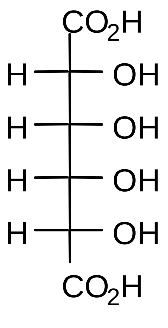
SOLUTION

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:

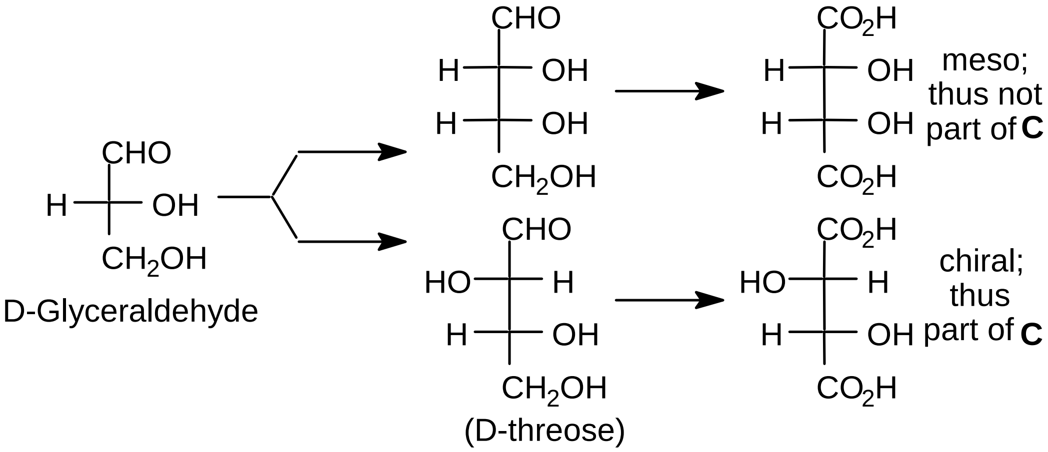


AA1 (=D)



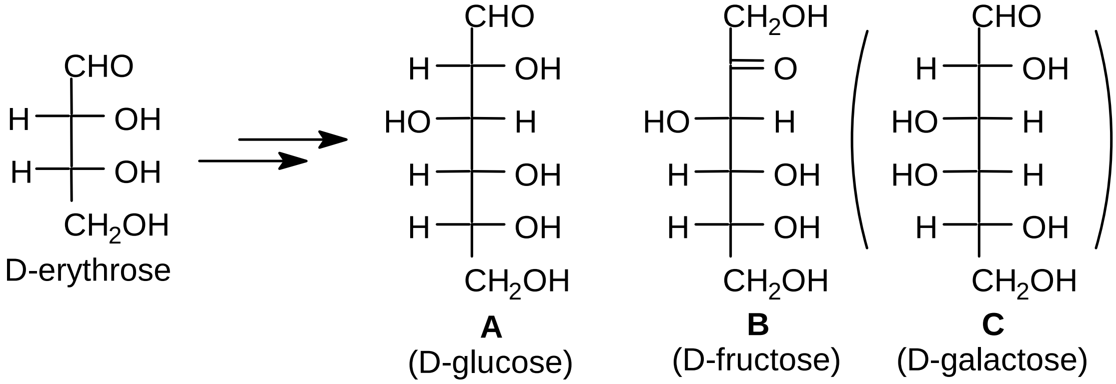
AA2

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:



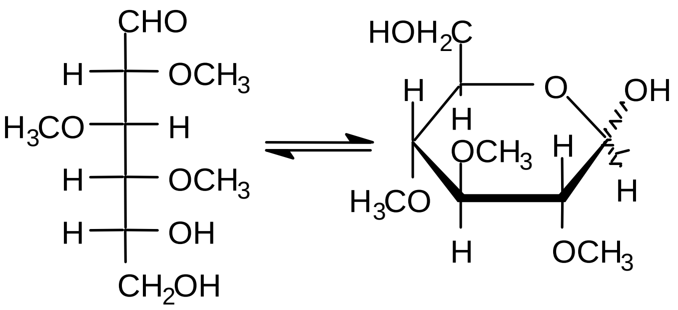
It follows from this that the aldaric acid **D** produced from **C** above is **AA1** and thus that **C** must be D-galactose. Compound **A** reacts with 5 moles of HI to give 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) suggesting that it is an aldohexose while **B** reacts 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.

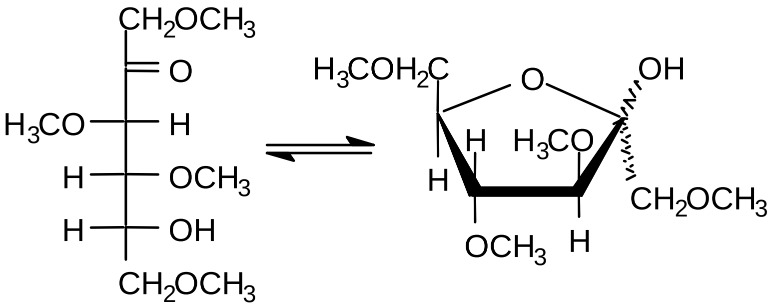


Methylation of **X** followed by hydrolysis yields **E**, **F** and **G** below:

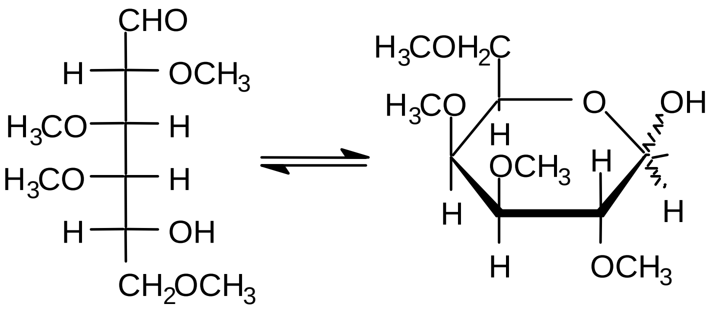
1.2



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.

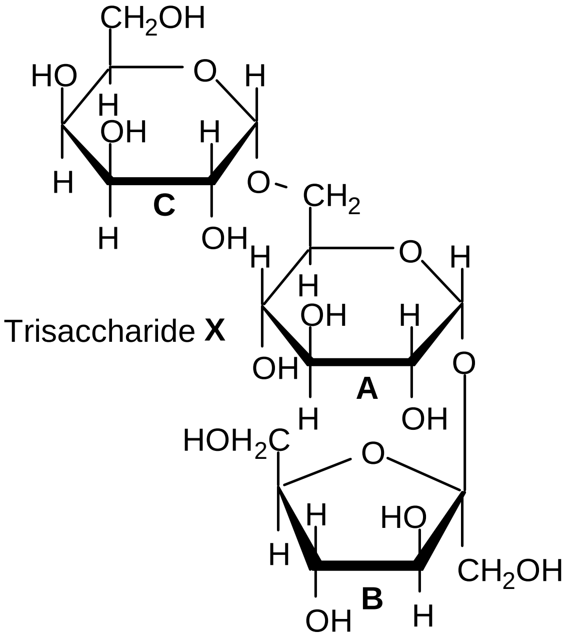
These results indicate that the sequence of monosaccharides in **X** is **C-A-B** (or **B-A-C**).

If: **A**5 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:

Proposal A: $H_2O\ (g) + SO_3\ (g) \rightarrow H_2SO_4\ (g)$

Proposal B: $2\ H_2O\ (g) + SO_3\ (g) \rightarrow H_2SO_4\ (g) + H_2O\ (g)$

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:

$$SO_3 + 2\ H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3 \bullet 2\ H_2O \qquad \text{(fast)}$$

$$SO_3 \bullet 2\ H_2O \xrightarrow{k_2} H_2SO_4 + H_2O \qquad \text{(slow)}$$

($SO_3 \bullet 2\ H_2O$ is a complex which is stabilized by hydrogen bonds and $k_2 << k_1$ 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:

$E_A = +\ 80\ \text{kJ mol}^{-1}$ for Proposal A $\qquad E_B = -\ 20\ \text{kJ mol}^{-1}$ 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 K) than at the earth's surface (T = 300 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: $\dfrac{d[H_2SO_4]}{dt} = k[H_2O]\,[SO_3]$

Summing the exponents gives a second order process

Proposal B: $\dfrac{d[H_2SO_4]}{dt} = k\,[SO_3][H_2O]^2$

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.

$$\frac{d[SO_3\cdot 2\,H_2O]}{dt} = k_1[SO_3][H_2O]^2 - k_{-1}[SO_3\cdot 2\,H_2O] - k_2[SO_3\cdot 2\,H_2O] = 0$$

Thus: $k_{-1}[SO_3\cdot 2\,H_2O] + k_2\,[SO_3\cdot 2\,H_2O] = k_1\,[SO_3]\,[H_2O]^2$

and therefore: $[SO_3\cdot 2\,H_2O] = \dfrac{k_1\,[SO_3][H_2O]^2}{k_{-1} + k_2}$

Also: $\dfrac{d[H_2SO_4]}{dt} = k_2\,[SO_3\cdot 2\,H_2O]$ and substituting from above yields

$$\frac{d[H_2SO_4]}{dt} = k_2\,[SO_3\cdot 2\,H_2O] = \frac{k_1 k_2 [SO_3]\,[H_2O]^2}{k_{-1} + k_2}$$

However, since $k_2 \ll k_{-1}$ the above reduces to:

$$\frac{d[H_2SO_4]}{dt} = \frac{k_1 k_2\,[SO_3][H_2O]^2}{k_{-1}} = K_{eq}\,k_2\,[SO_3][H_2O]^2 = k\,[SO_3][H_2O]^2$$

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*.

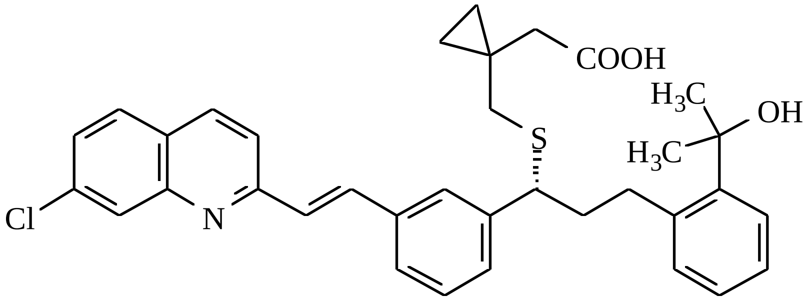
For proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

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 rational for Proposal B which involves the relative sizes of the rate constants is nonsense and was included to balance the choices. The rational 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

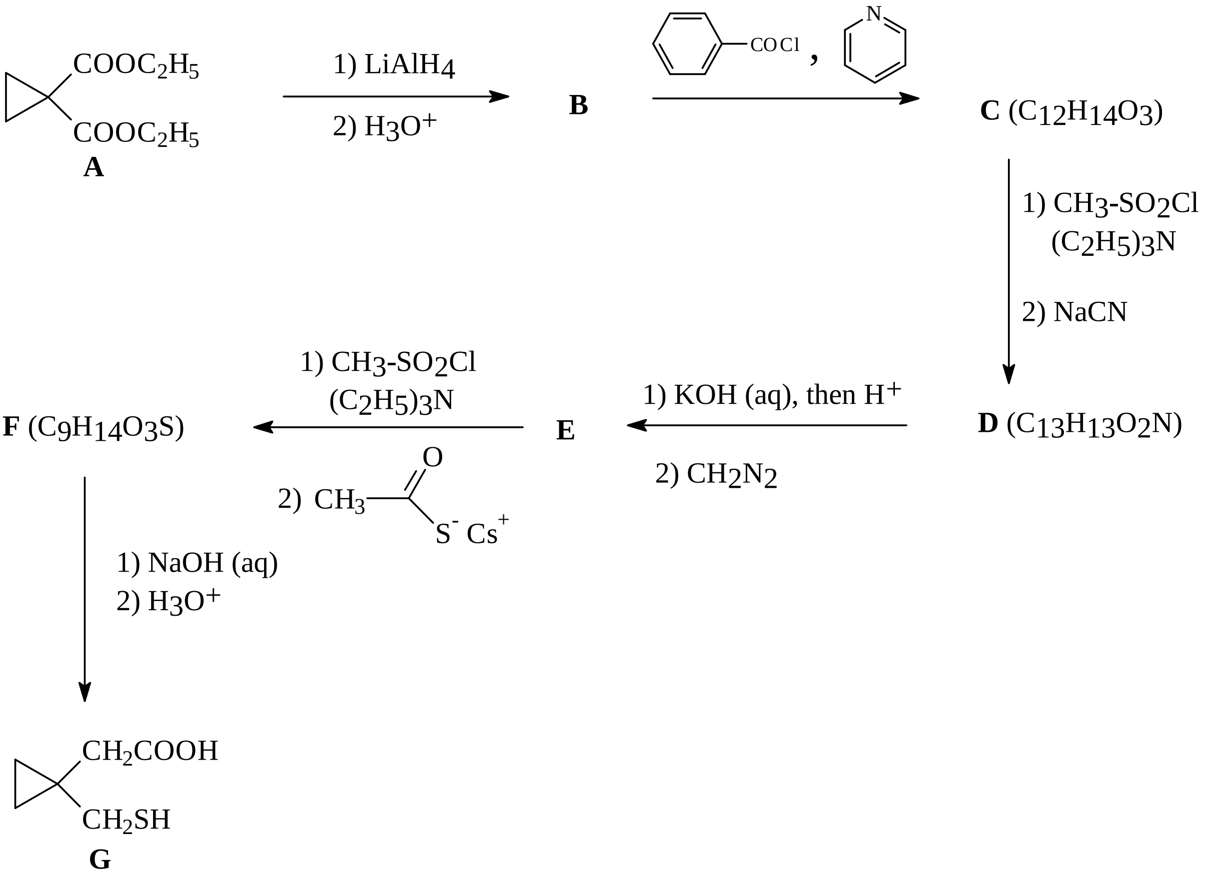
Chemists at Merck Frosst Canada in Montréal have developed a promising drug which is useful against asthma. The structure of MK-0476 is shown below.



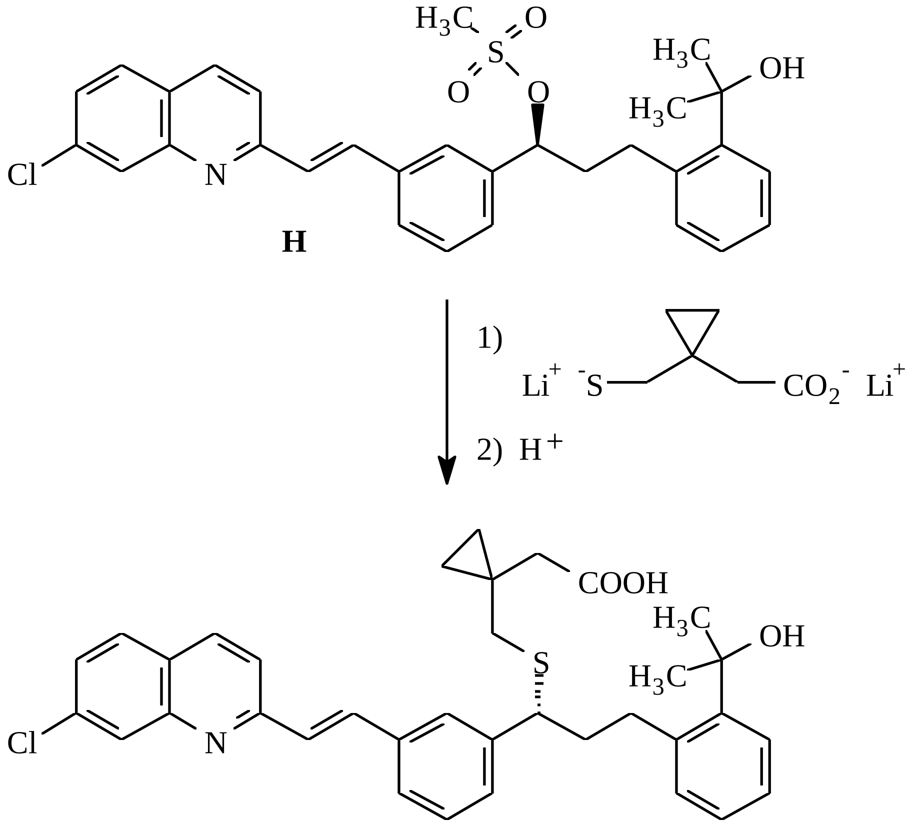
MK-0476

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:

a) **G** plus two molar equivalents of base

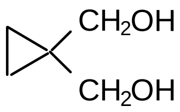
b) **G** plus one molar equivalent of base

3.5 A side reaction of **G** is its oxidative dimerization.

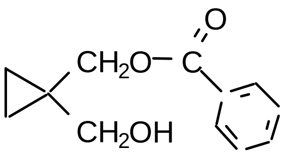
Draw the structure of the dimeric product, showing all non-bonded electrons.

SOLUTION

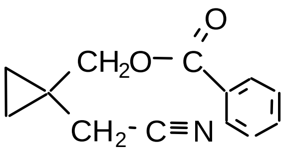
3.1



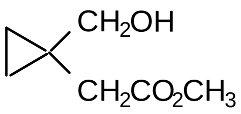
B



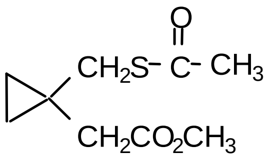
C ($C_{12}H_{14}O_3$)



D ($C_{13}H_{13}O_2N$)



E



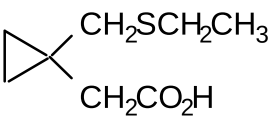
F ($C_9H_{14}O_3S$)

3.2 S_N2 Bimolecular Nucleophilic Substitution

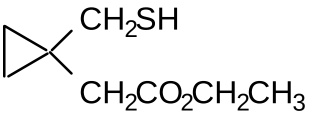
3.3 Rate = k[substrate] [nucleophile]

The overall rate is directly dependent on the concentration of <u>both</u> 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

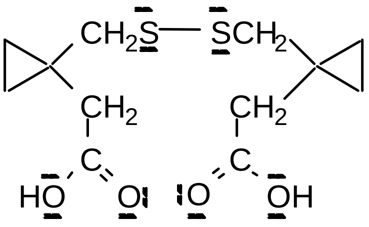


From 2 equiv base



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.

$HIn + Na+OH- \rightleftharpoons Na+In- + H_2O$

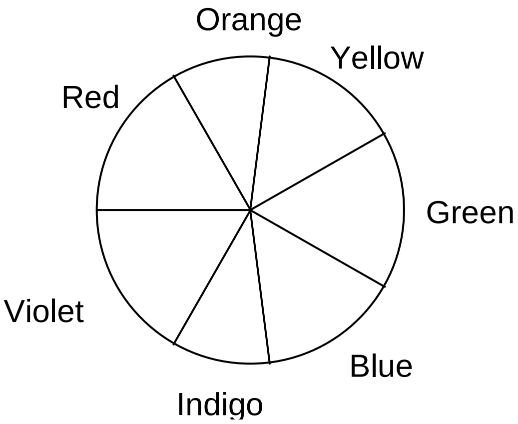
also written as

$HIn \rightleftharpoons In- + H^+$

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)

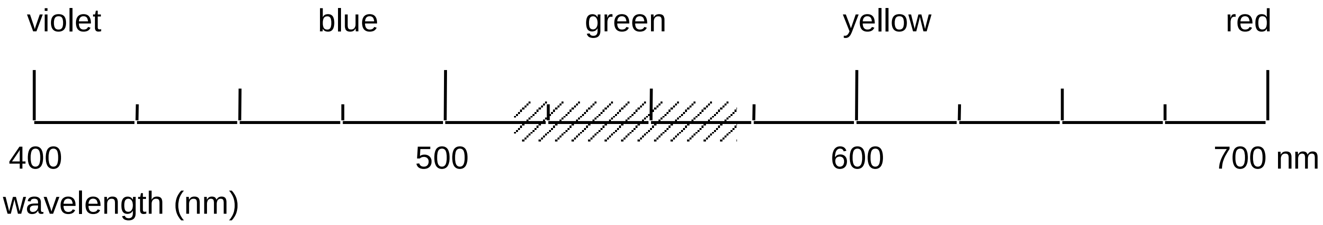
λ, nm	*pH* = 1.00	*pH* = 13.00
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



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:

	λ = 490 nm	λ = 625 nm
HIn (HCl)	9.04×10^2 M^{-1} cm^{-1}	3.52×10^2 M^{-1} cm^{-1}
In- (NaOH)	1.08×10^2 M^{-1} cm^{-1}	1.65×10^3 M^{-1} 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.

$A = \varepsilon\, l\, c$ (Beer's Law)

where l = length of cell, c = concentration of analyte, ε = molar absorptivity.

Therefore $$\varepsilon = \frac{A}{l\,c} = \frac{0.256}{1.0 \times 5.00\times10^{-4}} = 5.12\times10^{2}\ \text{M}^{-1}\ \text{cm}^{-1}$$

Absorbance of a 1.00×10^{-4} M basic solution of the indicator using a 2.50 cm cell is:

$A = 5.12\times10^{2} \times 2.50 \times 1.0\times10^{-4} = 0.128$

4.5 The dissociation reaction of the indicator is:

$[\text{HIn}] = [\text{H}^+] + [\text{In}^-]$

accordingly,

$[H+] = [In-]$ (1)

and

$[HIn] + [In-] = 1.80\times10^{-3}$ M (2)

$$K_a = \frac{[H^+][In^-]}{[HIn]} \qquad (3)$$

Substitute (1) and (2) into (3)

$$K_a = \frac{[In^-]^2}{1.8\times10^{-3} - [In^-]} \; = \; 2.93\times10^{-5}$$

Rearrangement yields the quadratic expression

$[In-]^2 + 2.93\times10^{-5}\,[In-] - 5.27\times10^{-8} = 0$

which results in

$[In-] = 2.15\times10^{-4}$ M

$[HIn] = 1.80\times10^{-3}$ M $- 2.15\times10^{-4}$ M $= 1.58\times10^{-3}$ M

The absorbance at the two wavelengths are then:

$A_{490} = (9.04\times10^2 \times 1 \times 1.58\times10^{-3}) + (1.08\times10^2 \times 1 \times 2.15\times10^{-4}\ ) = 1.45$

$A_{625} = (3.52\times10^2 \times 1 \times 1.58\times10^{-3}) + (1.65\times10^3 \times 1 \times 2.15\times10^{-4}) = 0.911$

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 is it 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(Fe) = 55.847 g mol^{-1}

M(C) = 12.011 g mol^{-1}

$N_A = 6.02214\times10^{23}$ 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*(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*(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".

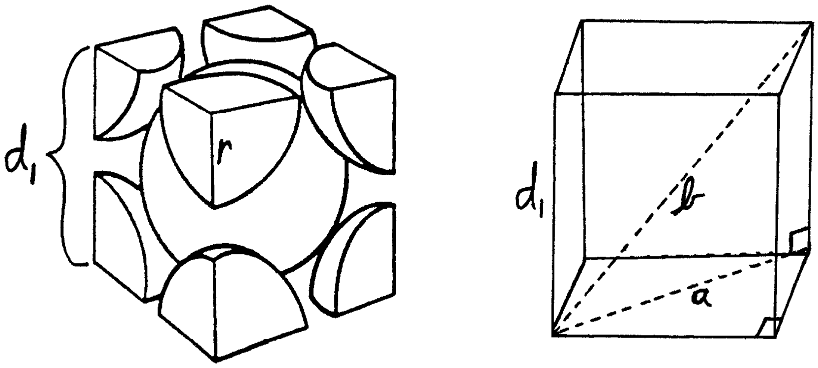
An alternative route to ρ_{fcc} of γ-iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

5'. Calculate the percent space filling ratio of the bcc unit cell.

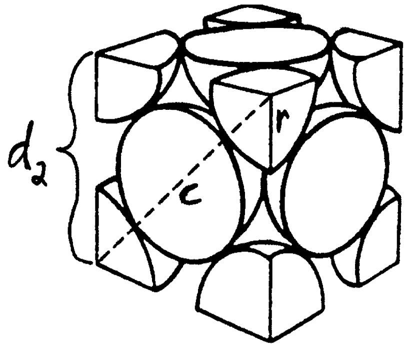
6'. Calculate the percent space filling ratio of the fcc unit cell.

7'. Calculate the ρ_{fcc}/ρ_{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)

<u>Calculations in details</u>

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.

$V_a = (4/3)\ \pi\ r^3$ $\qquad V_{a1} = 2\ V_a$ $\qquad V_{a2} = 4\ V_a$

$b = 4\ r;$ $\qquad a^2 = 2\ d_1^2;$ $\qquad b^2 = d_1^2 + a^2 = 3\ d_1^2$

$d_1 = (b^2/3)^{1/2} = (16\ r^2/3)^{½};$ $\qquad V_1 = d_1^3 = [(16\ r^2/3)^{1/2}]^3$

$c = 4\ r;$ $\qquad c^2 = 2\ d_2^2$

$d_2 = (c^2/2)^{1/2} = (16\ r^2/2)^{½};$ $\qquad V_2 = d_2^3 = [(16\ r^2/2)^{½}]^3$

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 cm^3 or 1 mole of iron will occupy a volume of 7.093 cm^3

1 mole corresponds to 6.02214×10^{23} atoms

V_1 = (7.093 cm^3 mol^{-1}) × (2 atoms/unit cell) / (6.02214×10^{23} atoms mol^{-1})

$V_1 = 2.356\times10^{-23}$ cm^3 per unit cell

3. $d_1 = (V_1)^{1/3} = (2.356\times10^{-23}\ \text{cm}^3)^{1/3}$

$d_1 = 2.867\times10^{-8}$ cm

4. For a bcc structure, the value of d_1 can be expressed as: $d_1 = [(16\ r^2)/3]^{1/2}$

so the value of "r" will be: $r = (3\ d_1^{\ 2}/16)^{1/2}$

$r = [3\ (2.867\times10^{-8}\ \text{cm})^2/16]^{1/2}$

$r = 1.241\times10^{-8}$ cm

5. At 1250 K, in the fcc structure, the value of "d_2" is given by: $d_2 = (16\ r^2/2)^{1/2}$

$d_2 = [16\ (1.241\times10^{-8}\ \text{cm})^2/2]^{1/2}$

$d_2 = 3.511\times10^{-8}$ cm

6. $V_2 = d_2^{\ 3} = (3.511\times10^{-8}\ \text{cm})^3$

$V_2 = 4.327\times10^{-23}$ cm^3

7. The mass "m" of the 4 iron atoms in the fcc unit cell will be:

m = (55.847 g mol^{-1}) × (4 atoms/unit cell) / (6.02214×10^{23} atoms mol^{-1})

$m = 3.709\times10^{-22}$ g per unit cell

8. $\rho_{fcc} = m / V_2 = (3.709\times10^{-22}\ \text{g}) / (4.327\times10^{-23}\ \text{cm}^3)$

$\rho_{fcc} = 8.572$ g/cm^3

Alternative route to ρ_{fcc} of γ-iron:

5'. $R_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2\ V_a) / (V_1)] \times 100\%$

$R_1 = ([2 \times (4/3)\ \pi\ r^3] / [(16\ r^2/3)^{1/2}]^3) \times 100\%$

$R_1 = ([(8/3)\ \pi\ r^3] / [(16/3)^{3/2}\ r^3]) \times 100\%$

$R_1 = ([(8/3)\ \pi] / [(16/3)^{3/2}]) \times 100\%$

$R_1 = [(8.378) / (12.32)] \times 100\%$

$R_1 = 68.02\ \%$

6'. $R_2 = [(V_{a2}) / (V_2)] \times 100\% = [(4\ V_a) / (V_2)] \times 100\%$

$R_2 = ([4 \times (4/3)\ \pi\ r^3] / [(16\ r^2/2)^{1/2}]^3) \times 100\%$

$R_2 = ([(16/3)\ \pi\ r^3] / [8^{3/2}\ r^3]) \times 100\%$

$R_2 = ([(16/3)\ \pi] / [8^{3/2}]) \times 100\%$

$R_2 = [(16.76) / (22.63)] \times 100\%$

$R_2 = 74.05\%$

7'. $\rho_{fcc} / \rho_{bcc} = (74.05\%) / (68.02\%)$

$\rho_{fcc} / \rho_{bcc} = 1.089$

8'. $\rho_{fcc} = 1.089 \times \rho_{bcc}$

$\rho_{fcc} = 1.089 \times 7.874$ g cm^{-3}

$\rho_{fcc} = 8.572$ 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 [ρ(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. In 100.0 g of martensite at 4.3 % C: (4.3 g C) / (12.011 g mol^{-1}) = 0.36 mol C

   (95.7 g Fe) / (55.847 g mol^{-1}) = 1.71 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 C atom) / (4.8 Fe atoms)] × (2 Fe atoms / unit cell)

   or: 0.42 carbon atoms per unit cell

3. 5 carbon atoms [(0.42 C atom / 0.42) × 5] in 12 unit cells [(1 unit cell/0.42) × 5].

   5 carbon atoms dispersed in 12 unit cells

4. [(55.847 g/mol) / (6.02214×10^{23} atoms/mol)] × (2 atoms/unit cell of α-iron)

   1.8547×10^{-22} g Fe per unit cell of α-iron

5. (12.011 g/mol) / (6.02214×10^{23} atoms/mol)

   1.9945×10^{-23} g C per atom

6. [1.8547×10^{-22} g Fe + (0.42 C at. × 1.9945×10^{-23} g / C at.)] per unit cell

   1.938×10^{-22} g C and Fe per unit cell

7. Each unit cell of α-iron occupies a volume, $V_1 = 2.356 \times 10^{-23}$ cm^3

   (*cf.* Question i)

   ρ(martensite at 4.3 % C) = (1.938×10^{-22} g C and Fe) / (2.356×10^{-23} cm^3)

   ρ(martensite at 4.3 % C) = 8.228 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 $Pd(NH_3)_2Cl_2$. 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 $Pd(NH_3)_2Cl_2$ 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.

n **A**wClx + m NH_3 $\rightarrow$ p NH_4Cl + q **A** + r **A**yNz

(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:

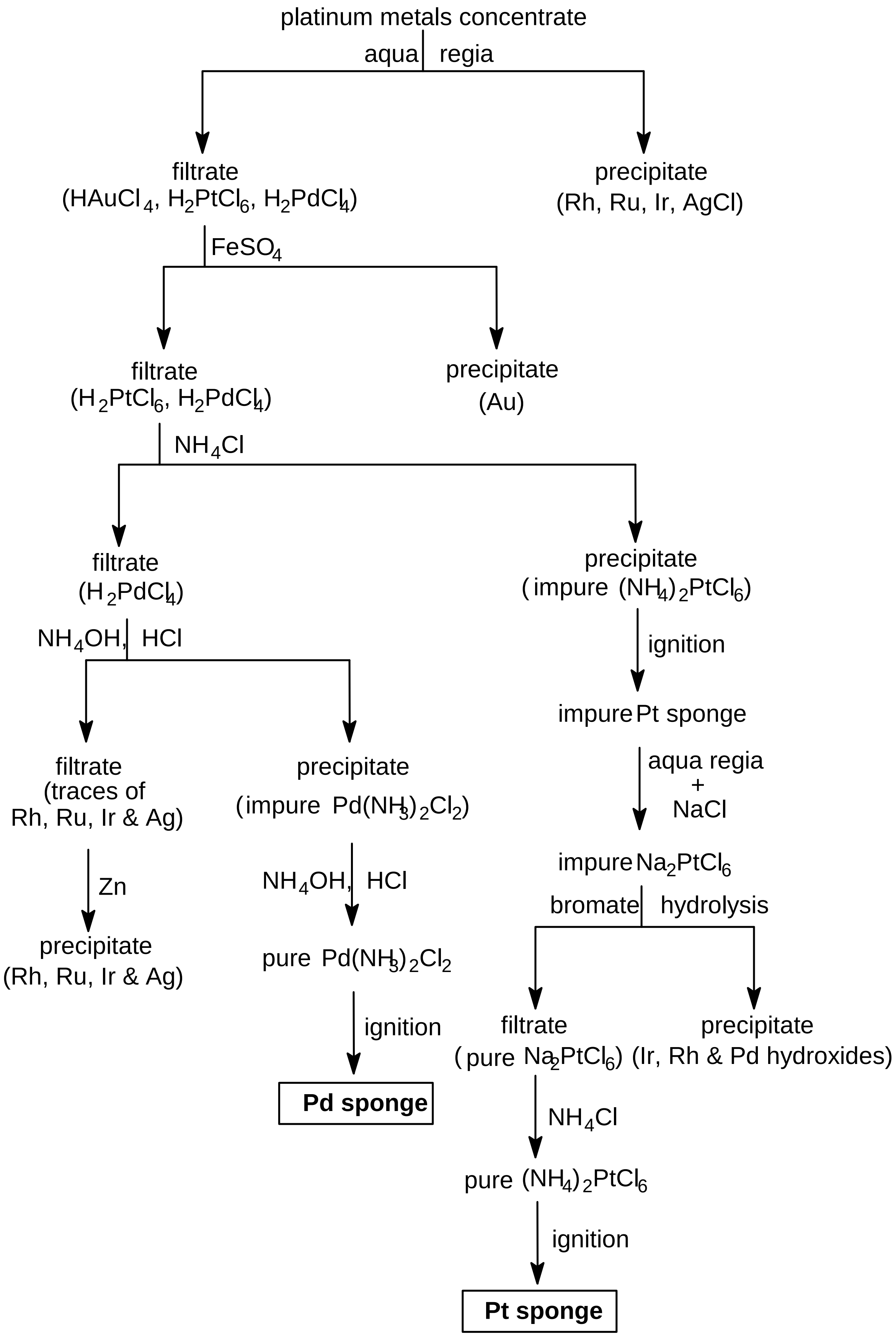
$M(\text{Cl}) = 35.453 \text{ g mol}^{-1}$ $M(\text{N}) = 14.007 \text{ g mol}^{-1}$ $M(\text{H}) = 1.008 \text{ g mol}^{-1}$

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.

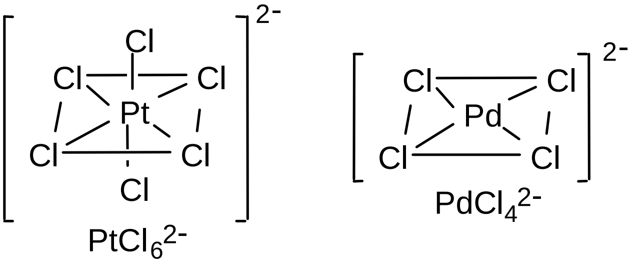
Method of Purification of Platinum and Palladium



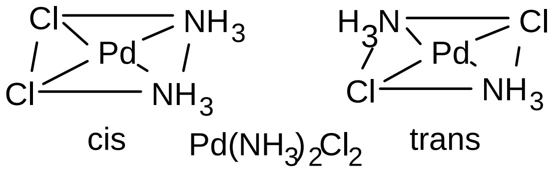
SOLUTION

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 Pt(II) centred in a square of Cl^- ions.



ii) Like $PdCl_4^{2-}$, $Pd(NH_3)_2Cl_2$ 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).

$HAuCl_4 + 3\ FeSO_4 \rightarrow Au^0 + HCl + FeCl_3 + Fe_2(SO_4)_3$

iv) $Pd(NH_3)_2Cl_2 + O_2 \rightarrow Pd^0 + N_2 + 2\ H_2O + 2\ HCl$

$Pd^{2+} + 2\ e^- \rightarrow Pd^0$ reduction

$2\ O^0 + 4\ e^- \rightarrow 2\ O^{2-}$ reduction

$2\ N^{3-} - 6\ e^- \rightarrow 2\ N^0$ oxidation or

$Pd(NH_3)_2Cl_2 + 2\ O_2 \rightarrow Pd^0 + 2\ NO + 2\ H_2O + 2\ HCl$

$Pd^{2+} + 2\ e^- \rightarrow Pd^0$ reduction

$4\ O^0 + 8\ e^- \rightarrow 4\ O^{2-}$ reduction

$2\ N^{3-} - 10\ e^- \rightarrow 2\ N^{2+}$ oxidation

or

$Pd(NH_3)_2Cl_2 + 3\ O_2 \rightarrow Pd^0 + 2\ NO_2 + 2\ H_2O + 2\ HCl$

$Pd^{2+} + 2\ e^- \rightarrow Pd^0$ reduction

$6\ O^0 + 12\ e^- \rightarrow 6\ O^{2-}$ reduction

$2\ N^{3-} - 14\ e^- \rightarrow 2\ N^{4+}$ oxidation

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 $(NO)_x$. 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:

53.492 g NH_4Cl → 35.453 g Cl

25.68 g NH_4Cl → ? g Cl

? = 25.68 × 35.453 / 53.492 = 17.02 g Cl

Total amount of A in the reaction is 24.71 g Cl – 17.02 g Cl = 7.69 g A There is 2.57 g free A and (7.69 – 2.57) = 5.12 g A in the nitride.

The amount of N bound in nitride is therefore

7.37 g nitride – 5.12 g A bound in nitride = 2.25 g N bound in nitride

The amount of nitrogen bound in NH_4Cl is 25.68 – 17.02 = 8.66 g

The rule of multiple proportions is applied:

Proportions of 1 : 1

Chloride:

7.69 g A binds → 17.02 g Cl

? g A binds → 35.453 g Cl

? = 35.453 × 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 → 2.25 g N

? g A binds → 14.007 g N

? = 14.007 × 5.12/2.25 = 31.87* g

A could be is sulphur, fits the physical description and M_r(S) = 32.064

(*Phosphorus, M_r(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 → 17.02 g Cl

? g A binds → 2 × 35.453 g Cl

? = 2 × 35.453 × 7.69 / 17.02 = 32.03 g. Again A could be sulphur.

Nitride:

5.12 g A binds → 2.25 g N

? g A binds → 2 × 14.007 g N

? = 2 × 14.007 × 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.

ii) $3\ SCl_2 + 8\ NH_3 \rightarrow 6\ NH_4Cl + S + S_2N_2$

or

$6\ SCl_2 + 16\ NH_3 \rightarrow 12\ NH_4Cl + 2\ S + S_4N_4$

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 $(SN)_n$, 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 S_8 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 (S_2Cl_2 and SCl_4) do not fit the stoichiometry of the reaction.)

iii) A disproportionation reaction involving sulphur occurs:

$2\ S^{2+} - 2\ e^- \rightarrow 2\ S^{3+}$

$S^{2+} + 2\ e^- \rightarrow S^0$

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 kJ mol^{-1} at the normal boiling point, the molar heat capacity of Cl_2 (g) at constant volume is C_v = 28.66 J K^{-1} 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 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

i) 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.

ii) 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:

$[Ni(H_2O)_6]^{2+} + 2\ NH_3 \rightleftharpoons [Ni(NH_3)_2(H_2O)_4]^{2+} + 2\ H_2O$ (1)

$\ln K_c = 11.60$ and $\Delta H^0 = -33.5$ kJ mol^{-1}

$[Ni(H_2O)_6]^{2+} + en \rightleftharpoons [Ni(en)(H_2O)_4]^{2+} + 2\ H_2O$ (2)

$\ln K_c = 17.78$ and $\Delta H^0 = -37.2$ kJ mol^{-1}

Note: *en* is ethylenediamine (a neutral bidentate ligand)

(R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

Calculate ΔG^0, ΔS^0 , and K_c at 298 K for reaction [3] occurring in a dilute aqueous solution:

$[Ni(NH_3)_2(H_2O)_4]^{2+} + en \rightleftharpoons [Ni(en)(H_2O)_4]^{2+} + 2\ NH_3$ (3)

SOLUTION

7.1

i) Electronic configuration of a Cl atom:

$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^1$

Significant atomic orbitals (AO) = 1(K) + 4(L) + 4(M) = 9 AO

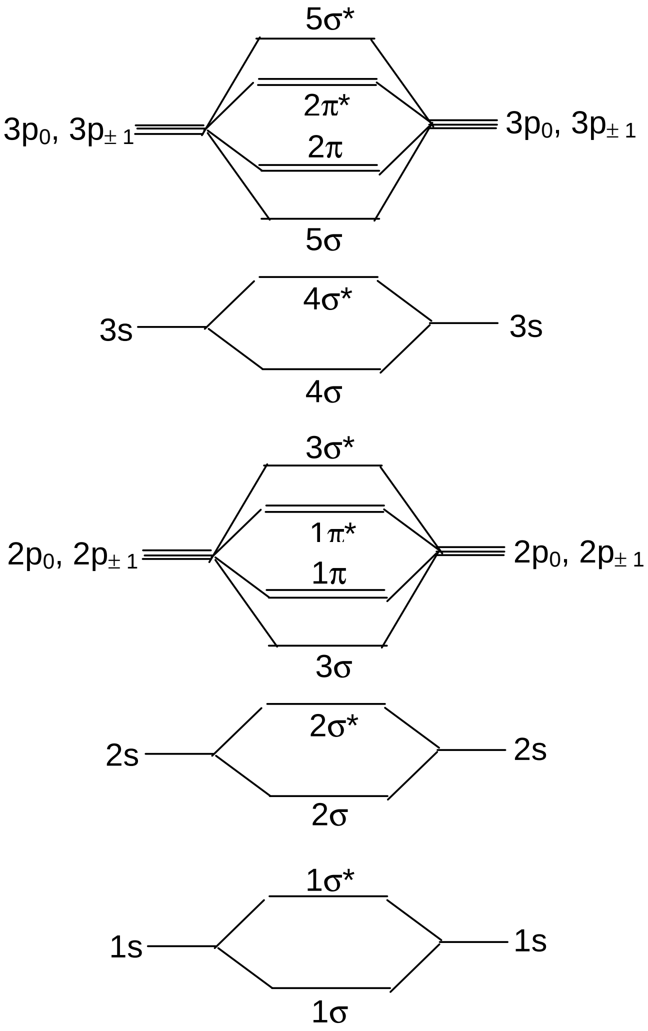
Number of electrons in these AOs: 17

Number of molecular orbitals (MO) equals number of AOs:

Thus 2 x [1(K) + 4(L) + 4(M)] = 18 MOs are present in a Cl_2 molecule

In the formation of Cl_2: 2 x 17 = 34 electrons to go into the 18 MOs.

MO description of Cl_2:



$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*4} 3\sigma^{*2} 4\sigma^2 4\sigma^{*2} 5\sigma^2 2\pi^4 2\pi^{*4}$

or

$(KK)(LL)(\sigma 3s)^2(\sigma^* 3s)^2(\sigma 3p)^2(\pi 3p)^4\ (\pi^* 3p)^4$

or

$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2(\sigma^* 2p_z)^2$
$(\sigma 3s)^2(\sigma^* 3s)^2(\sigma 3p_z)^2(\pi 3p_x)^2(\pi 3p_y)^2(\pi^* 3p_x)^2(\pi^* 3p_y)^2(\sigma^* 2p_z)^0$

or

$(KK)(LL)\ (\sigma 3s)^2(\sigma^* 3s)^2(\sigma 3p_z)^2(\pi 3p_x)^2(\pi 3p_y)^2(\pi^* 3p_x)^2(\pi^* 3p_y)^2(\sigma^* 2p_z)^0$

*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; 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:

$$\begin{array}{c}Cl_2\ (g)\\ 1\ \text{mol}\\ 300\ \text{K}\end{array} \xrightarrow[\substack{\text{cooled}\\ 1.013\times10^7\ \text{Pa}\\ (100\ \text{atm})}]{\Delta E_1} \begin{array}{c}Cl_2\ (g)\\ 1\ \text{mol}\\ 239\ \text{K}\end{array} \xrightarrow[\substack{1.013\times10^5\ \text{Pa}\\ (1\ \text{atm})}]{\Delta E_2} \begin{array}{c}Cl_2\ (l)\\ 0.1\ \text{mol}\\ 239\ \text{K}\end{array}$$

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: a) ΔE for a perfect gas is a function only of T

b) C_v is constant

c) "–" 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

$V = n\,R\,T\,/\,P = (0.1 \times 0.0820584 \times 239) / 1 = 1.96\ \text{dm}^3$

Volume of liquid Cl_2: $(0.1 \times 2 \times 35.454) / 1.56 = 4.54\ \text{cm}^3$

$$\Delta E_2 \;=\; \Delta H_2 - \int P_{\text{ext}} \Delta V (\text{phase change}) \;=\; \Delta H_2 - P_{\text{ext}} (V_{\text{l}} - V_{\text{g}})$$

but V_l is approximately 0 and can be neglected

(ca. 4.5 cm^3 liquid volume vs. ca. 17.6 dm^3; ca. 0.03 % error)

$\Delta E_2 = (0.1)\,(-\Delta H_{vap}) + P_{\text{ext}} V\text{g}$

$= 0.1 \times (-20420) + (1 \times 1.96\ \text{L}) \times 101.325\ \text{J dm}^{-3}\ \text{atm}^{-1} = -2042.0 + 198.5 = -1843.5$

$\Delta E = \Delta E_1 + \Delta E_2 = -1748.3 + (-1843.5) = -3591.8$

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 $S(T,P)$.

$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2$ and

$$\overline{C}_p \;=\; \overline{C}_v + R \;=\; 28.66 + 8.314 \;=\; 36.97\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_1 = n\,C_p \ln\frac{T_2}{T_1} - n\,R \ln\frac{P_2}{P_1} = 1.0 \times 36.97 \ln\frac{239}{300} - 8.314 \ln\frac{1}{100} == \;-8.40\;+\;38.29\;=$$

$= 29.89\ \text{J K}^{-1}$

For the phase transition (constant temperature), by definition $\Delta S_2 = Q / T$

Since the pressure is constant in this case, $Q / T = Q_\text{p} / T = \Delta H / T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{0.1 \times (-20420)}{239} = -8.54\ \text{J K}^{-1}$$

$\Delta S_{\text{sys}} = 29.89 - 8.54 = 21.35\ \text{J K}^{-1}$

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 $\Delta G_3 = \Delta G_2 - \Delta G_1$
$\Delta G^0_1 = -R\,T \ln K_{c1} = -8.314 \times 298 \times 11.60 = -28740$ J mol^{-1} = -28.74 kJ mol^{-1}
$\Delta H^0_1 = -33.5$ kJ mol^{-1}
$\Delta S^0_1 = (\Delta H^0_1 - \Delta G^0_1) / T$
$= (-33.5) - (-28.74)) / 298 = -0.0161$ kJ K^{-1} mol^{-1} = -16.1 J K^{-1} mol^{-1}
Similarly:
$\Delta G^0_2 = -44.05$ kJ mol^{-1}
$\Delta H^0_2 = -37.2$ kJ mol^{-1}
$\Delta S^0_2 = -22.98$ J K^{-1} mol^{-1}
Reaction 3 = Reaction 2 – Reaction 1, thus
$\Delta H^0_3 = \Delta H^0_2 - \Delta H^0_1 = -3.7$ kJ
$\Delta S^0_3 = \Delta S^0_2 - \Delta S^0_1 = 39.08$ J K^{-1}
$\Delta G^0_3 = \Delta H^0_3 - \mathrm{T}\,\Delta S^0_3 = -15.35$ kJ mol^{-1}

Thus $K_{c3} = \mathrm{e}^{\frac{15.35}{RT}} = 4.90 \times 10^2$

Alternatively:
$\Delta G^0_3 = \Delta G^0_2 - \Delta G^0_1 = -44.05 - (-28.74) = -15.31$ kJ mol^{-1} thus $K = 4.82 \times 10^2$)
$\Delta S^0 = (\Delta H^0 - \Delta G^0) / \mathrm{T} = (-3700 - (-15311)) / 298 = 38.96$ 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 $c(H^+) = 1.000$ M (mol dm^{-3}) and $c(Cu^{2+}) = 1.000\times10^{-2}$ 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):

$T = 273.15$ K and $P(H_2) = 1.01325\times10^4$ 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 $a(Pt) = 3.9236\times10^{-8}$ cm.

Both Pt and Cu have the *fcc* (face centred cubic) crystallographic structure.

Molar masses and constants:

$M(H) = 1.00795$ g mol^{-1}

$M(Cu) = 63.546$ g mol^{-1}

$e = 1.60218\times10^{-19}$ C

$F = 96485.3$ C mol^{-1}

$R = 8.314510$ J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1}

$V_m = 22.4141$ dm^3

1 atm = 1.01325×10^5 Pa

$N_A = 6.02214\times10^{23}$ mol^{-1}

SOLUTION

Approach

- Determine the number of H_2 moles generated by the electrolysis.
- Calculate the charge required for the H_2 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 cm^2; during an epitaxial growth the number of Cu atoms per 1 cm^2 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

(a) Anode: $2\ H_2O \rightarrow H^+ + O_2 + 4\ e^-$

(b) Cathode:

Two reactions occur simultaneously at the cathode:

$2\ H^+ + 2\ e^- \rightarrow H_2$

$Cu^{2+} + 2\ e^- \rightarrow Cu$

8.2 Determination of the charge necessary to generate 2.0000 cm^3 of H_2 gas

(T = 273.15 K, p = 10.1325 kPa)

Two approaches to determination of the number of H_2 gas moles

(a) *Determination of n(H$_2$)*: $p\,V = n(H_2)\,R\,T$

$$n(H_2) = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6}\ \text{mol}$$

$$n(H_2) = \frac{V(H_2)}{V_m}$$

V_m = 22.4141 dm^3 mol^{-1} (V_m refers to the pressure of 1 atm or at $p(H_2)$ = 101.325 kPa and because the pressure of H_2 is ten times smaller, one knows right away that the volume occupied under 1 atm would be 0.2000 cm^3)

$$n(H_2) = \frac{0.20000 \times 10^{-3}}{22.4141} = 8.9230 \times 10^{-6}\ \text{mol}$$

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 = 1.4412×10^{-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:

$$s_{\mathrm{Pt(100)}} = \frac{n_u}{A_u} = \frac{2}{1.5395\times10^{-15}\,\mathrm{cm}^2} = 1.2991\times10^{15}\,\mathrm{cm}^{-2}$$

The number of Cu atoms per 1 cm^2 equals the number of Pt atoms - epitaxial growth

$$\sigma_{\mathrm{Cu(100)}} = \sigma_{\mathrm{Pt(100)}} = 1.2991\times10^{15}\,\mathrm{cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{\mathrm{ML}} = 2\times e\times1.2991\times10^{15}$$

$$q_{\mathrm{ML}} = 4.1628\times10^{-4}\,\mathrm{C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{\mathrm{ML}} = \frac{0.2780\,\mathrm{C}}{4.1628\times10^{-4}\,\mathrm{C}}$$

$$n_{\mathrm{ML}} = 668\ \mathrm{ML}$$

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: $M(Ca) = 40.08$ g mol^{-1} $M(Mg) = 24.31$ 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 mg Mg^{2+}/cm^3 solution, 0.0382 moles Mg^{2+}/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 cm^3 of the standardized magnesium solution to a final volume of 100.0 cm^3. Add 40 cm^3 of distilled water, 5 cm^3 of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm^3 of diluted magnesium solution. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

C. Titration of Mg^{2+} and Ca^{2+}

Add 40 cm^3 of distilled water, 5 cm^3 of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm^3 of the "Bottled Water" sample. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

D. Titration of Mg^{2+}

Add 40 cm^3 of distilled water, 5 cm^3 of *pH* 10 buffer solution, and some Calmagite indicator to 5.00 cm^3 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 Mg^{2+} (in mg dm^{-3}) in the "Bottled Water" sample.

Calculate the concentration of Ca^{2+} (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.

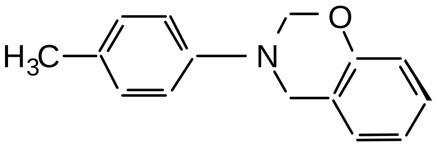
Chemicals Available
litmus paper, red and blue
aqueous ceric ammonium nitrate
aqueous chromic-sulfuric acid
aqueous 2,4-dinitrophenylhydrazine
aqueous 0.2% $KMnO_4$
acetone (2-propanone)

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

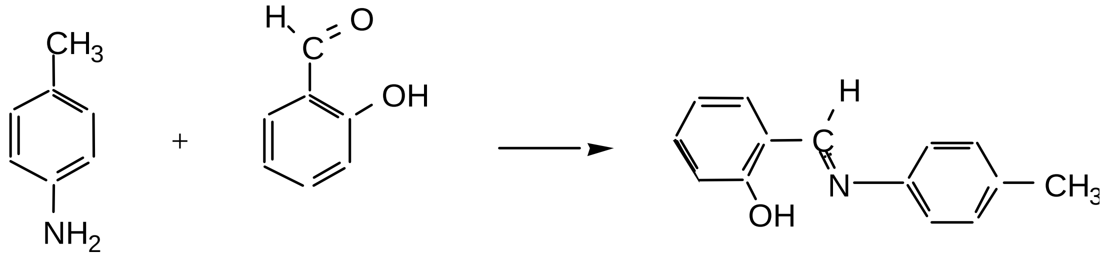
5 cm^3 reaction vial containing 2.5 cm^3 of ethanolic 1-amino-4-methylbenzene (0.22 g),
vial containing 0.25 g of 2-hydroxybenzaldehyde,
vial containing 0.1 g of sodium borohydride,
vial containing 0.042 g of paraformaldehyde,
test tube containing dilute ethanolic KOH,
(50 mg of KOH dissolved in 10 cm^3 of ethanol),
wash bottle containing dry ethanol,
Ice is available in each laboratory room.

Molar masses:

M(H) = 1.008 g mol^{-1} M(C) = 12.011 g mol^{-1} M(N) = 14.007 g mol^{-1}
M(O) = 15.999 g mol^{-1} M(Na) = 22.990 g mol^{-1} M(B) = 10.811 g mol^{-1}

Procedure

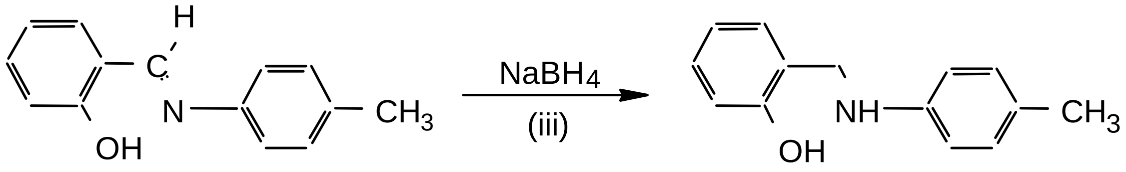
STEP I



(i) (ii) **A**

1. Place the small magnetic stirbar in the 5 cm^3 reaction vial containing solution (i) and stir.
2. Add the 2-hydroxybenzaldehyde from vial (ii) dropwise to the stirred solution in vial (i). After a short period of time a yellow solid will crystallize out. This is intermediate product **A**.
3. Isolate the yellow solid (**A**) by vacuum (suction) filtration and wash it with ice-cold ethanol.

STEP II



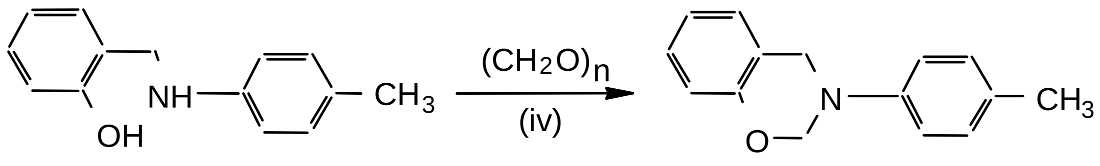
A **B**

1. Add the impure Product A from Step I to a 5 cm^3 reaction vial containing approximately 1.5 cm^3 of ethanol.
2. Surround the vial with ice/water, and stir the reaction vigorously with the spatula while carefully adding small amounts of sodium borohydride (iii) over a period of about

   5 minutes until the bright yellow colour disappears. The reaction will bubble.

   Note that you have been given more sodium borohydride than is required for this reaction.
3. Isolate the intermediate Product B by vacuum (suction) filtration, wash it with ice-cold ethanol, and air dry the solid for approximately 5 minutes.

STEP III



B **C**

1. Dissolve all of the paraformaldehyde (iv) in approximately 2.5 cm^3 of ethanolic potassium hydroxide (v) in a 5 cm^3 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 cm^3 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

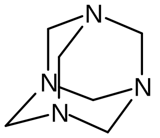
THEORETICAL PROBLEMS

PROBLEM 1

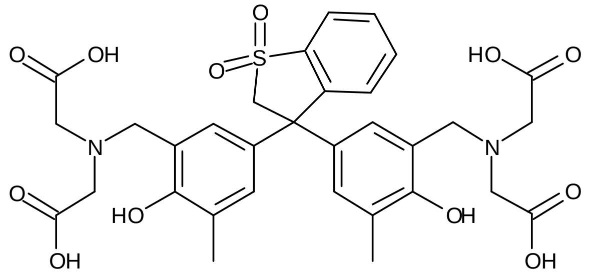
The following 8 steps describe the procedure for analysing a sample of alloy that contains both tin and lead.

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 cm^3 aliquot of 0.2000 M Na_2H_2EDTA solution was added. The precipitate dissolved and a clear, colourless solution was obtained.
4. This solution was quantitatively transferred to a 250.0 cm^3 volumetric flask and made up to the mark with distilled water.
5. A 25.00 cm^3 aliquot of this solution was treated with 15 cm^3 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 cm^3.
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 cm^3.

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.



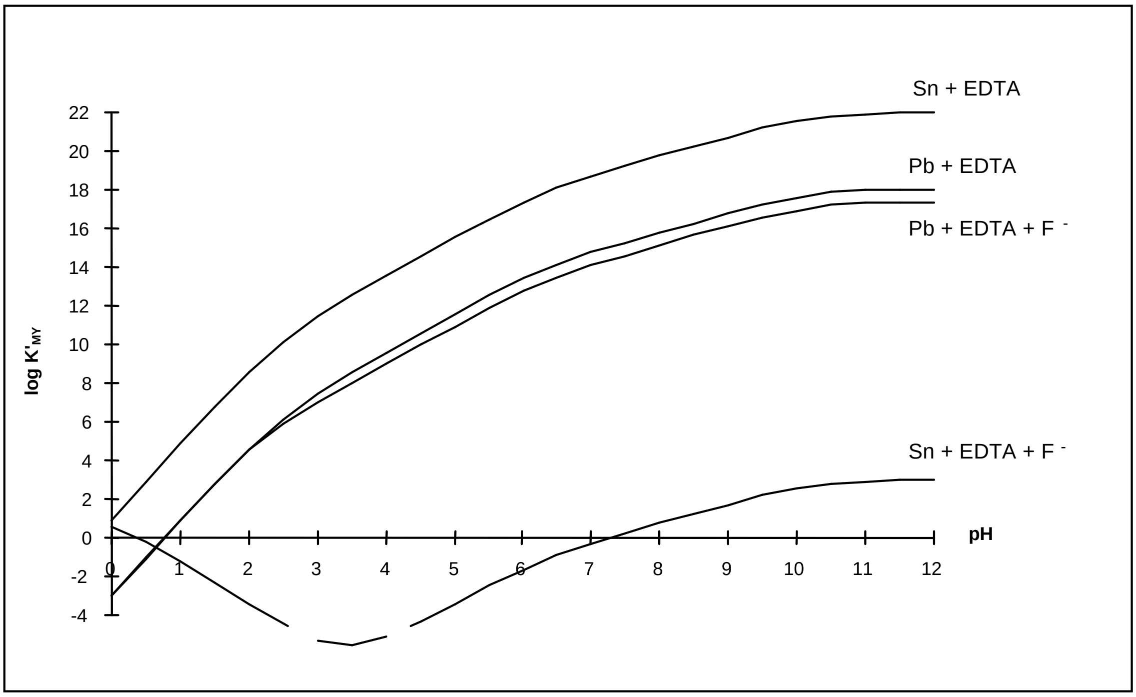
Hexamine



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 $PbCl_2$ 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 Pb^{2+} forms a red complex with the xylenol orange indicator:

Pb^{2+} + XO (yellow) $\rightarrow PbXO^{2+}$ (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 Sn^{4+} but not with Pb^{2+} 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 (yellow) + 2 H^+

1.9 Below *pH* 2, F^- is protonated and does not compete effectively with Y for Pb^{2+}

$H^+ + F^- \rightarrow HF$.

1.10 The percentage by mass of Sn and Pb in the alloy:

The amount of EDTA in excess from the amount of standard Pb^{2+} titrant:

$n(\text{EDTA}) = n(Pb^{2+}) = 0.02405\ dm^3 \times 0.009970\ mol\ dm^{-3} = 2.398 \times 10^{-4}$ mol.

The original amount of EDTA:

$n(\text{EDTA}_{)\text{init.}} = 0.1 \times 25.00 \text{ dm}^3 \times 0.2000 \text{ mol dm}^{-3} = 5.000\times10^{-4}$ mol

EDTA consumed by the Pb^{2+} and Sn^{4+} in a 25 cm^3 aliquot:

$n(\text{EDTA})_{\text{consumed}} = 5.000\times10^{-4} – 2.398\times10^{-4} \text{ mol} = 2.602\times10^{–4} \text{ mol} = n(Pb^{2+} + Sn^{4+})$ in a 25 cm^3 aliquot.

The amount of EDTA released from SnY by reaction with fluoride:

$n(\text{EDTA})_{\text{ released}} = n(Pb^{2+})_{\text{stand.}} = 15.00 \text{ cm}^3 \times 0.009970 \text{ mol dm}^{-3} = 1.496\times10^{-4} \text{ mol} =$

$= n(Sn^{4+})$ in the 25 cm^3 aliquot

in a 25 cm^3 aliquot $n(Pb^{2+}) = (2.602\times10^{–4} – 1.496\times10^{–4}) \text{ mol} = 1.106\times10^{–4}$ mol

In the original 0.4062 g sample of alloy:

$m(\text{Sn}) = 10 \times 1.496\times10^{–4} \text{ mol} \times 118.69 \text{ g mol}^{–1} = 0.1776$ g

$m(\text{Pb}) = 10 \times 1.106\times10^{–4} \text{ mol} \times 207.19 \text{ g mol}^{–1} = 0.2292$ g

The percentages of tin and lead:

Sn: $100 \times (0.1776 / 0.4062) = 43.7$ %

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.

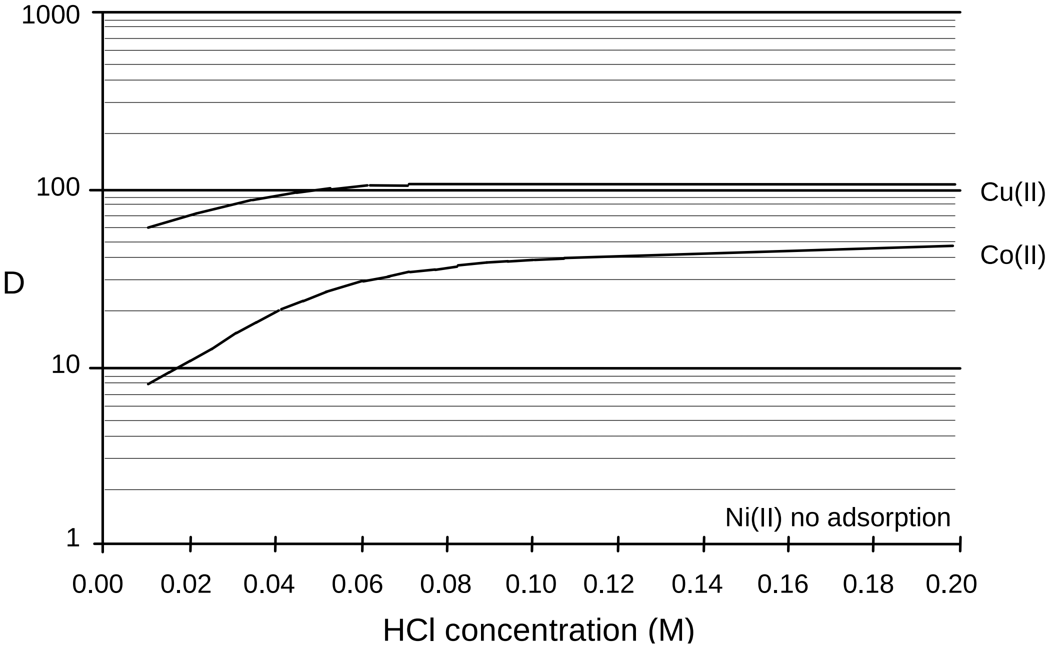


Figure 1. Distribution coefficients, *D* of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note *D* value for Zn > 1000)

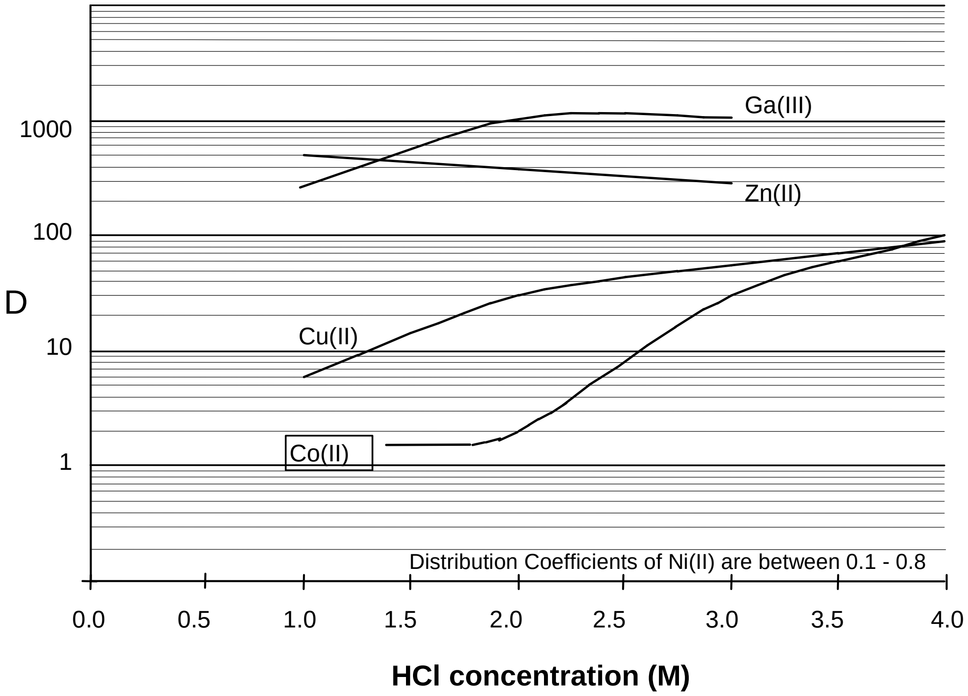


Figure 2. Distribution coefficients, *D* of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

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 (±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 HC1 55% isopropyl alcohol	to remove Co-55 followed by
	1.0 M HC1 55% isopropyl alcohol	to remove Cu-64
D	0.2 M HC1 96% methanol	to remove Ni-57 followed by
	3.0 M HC1 55% isopropyl alcohol	to remove Co-55 followed by
	4.0 M HC1 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

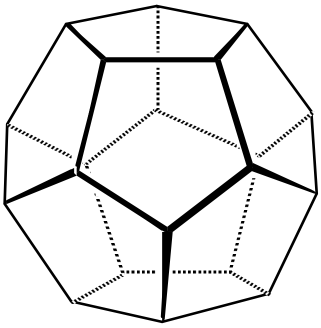
b) True

c) False

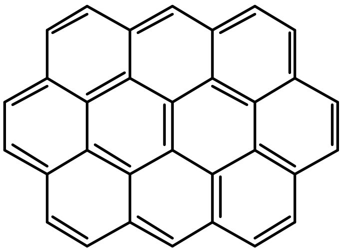
d) True

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, $C_{20}H_{20}$



and Ovalene, $C_{32}H_{14}$.

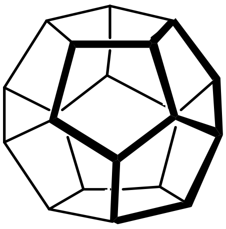
Each C_5 ring of dodecahedrane is a regular pentagon, while each C_6 ring of ovalene can be regarded as a regular hexagon.

3.1 What are the $\angle$(CCC) angles for each of these rings?

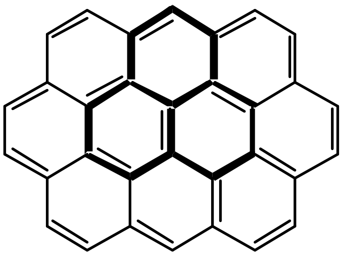
3.2 Which configuration (trigonal planar, 120°, tetrahedral, 109.5°, or octahedral, 90°) do the above $\angle$ (CCC) angles most closely match?

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?

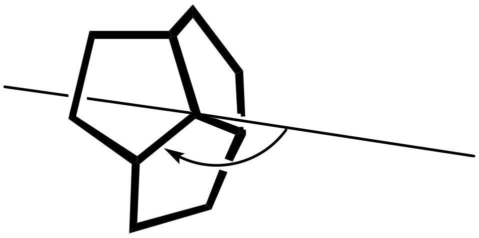
A "juncture" is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctures (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:



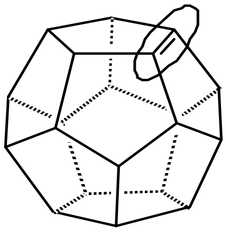
Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.



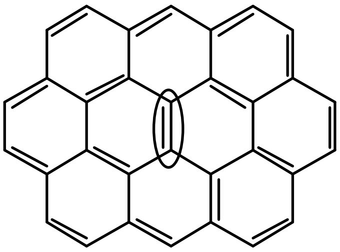
3.4 What is the value of this angle for dodecahedrane (make an "educated guess", to the nearest three degrees), and for ovalene?

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 ($C_{20}H_{18}$):



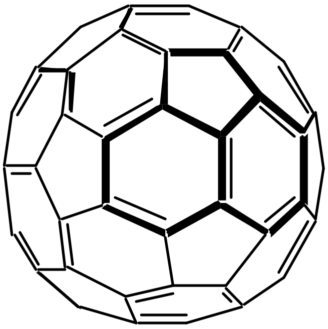
and ovalene:



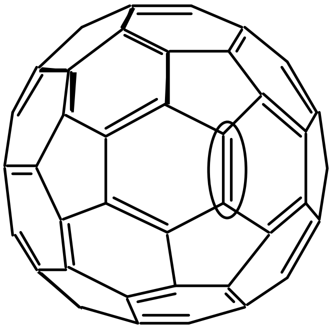
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

3.6 Compare the indicated pairs of carbon atoms (encircled above). For which C=C pair is H_2 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 dodecadedrane.



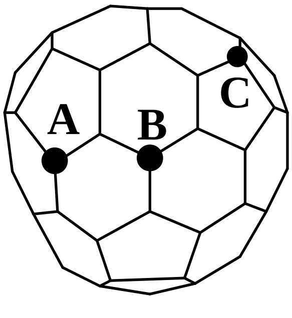
For C_{60}, all junctures are entirely equivalent. Now consider H_2 addition at a C=C bond of C_{60}:



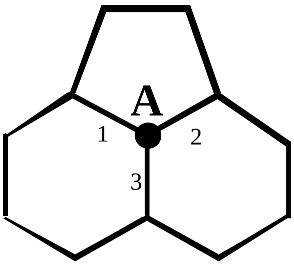
3.7 For which of C_{60}, dodecahedrene, or ovalene is H_2 addition most exothermic? (Again, assume localization of double bonds.)

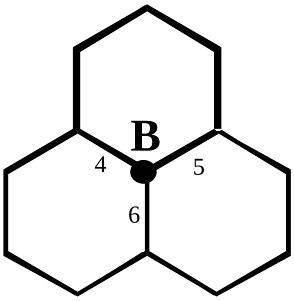
3.8 For which of C_{60}, dodecahedrene, or ovalene is H_2 addition least exothermic?

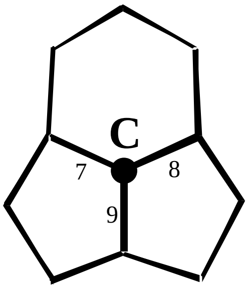
There is evidence for fullerenes smaller than C_{60}, such as C_{58}. The C_{58} structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:



The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:





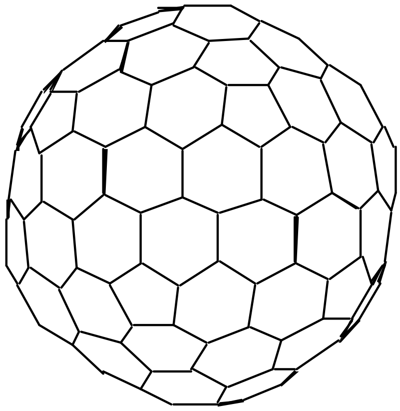


3.9 Which juncture has the least deviation from planarity ?

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 H_2 addition?

Finally, consider a larger fullerene, C_{180}:



To a first approximation, both C_{60} and C_{180} are "perfect" spheres.

3.12 Which has the larger average deviation from planarity at each juncture? C_{60} or C_{180}?

3.13 Compare the geometries of C_{60} and C_{180}, 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:

reactants $\rightleftharpoons$ $3C_{60}$

and

reactants $\rightleftharpoons$ C_{180}

SOLUTION

3.1 Dodecahedrane: 108 °

Ovalene 120 °

3.2 Dodecahedrane: tetrahedral

Ovalene: trigonal planar

The ∠(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, $C_{20}H_{20}$ 109 -115 degrees

ovalene, $C_{32}H_{14}$ 90 degrees

Reasoning: For dodecahedrane, the three rings are not coplanar. Determination of the exact axis angle is complicated; but note that the ∠(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, $C_{32}H_{14}$

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 H_2 addition from among C_{60}, dodecahedrene, ovalene is most exothermic for dodecahedrene.

Reasoning: The deviation from planarity, in a C_{60} 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 C_{60} is intermediate between dodecahedrene and ovalene in its preference for hydrogenated versus dehydrogenated structures. The junctures in dodecahedrene are all pentagons [C_5,C_5,C_5]. The junctures in ovalene are all [C_6,C_6,C_6]. Those in C_{60} are [C_5,C_6,C_6]. 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 H_2 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 H_2 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 sp^2 hybridization) and is closest to the dodecahedrane skeleton (for which the bond angles are almost ideal for sp^3 hybridization). Thus, bond 9 is the most favourable site for dihydrogenation.

3.12 The larger average deviation from planarity at each juncture is in C_{60} .

Reasoning: C_{180} obviously has a larger diameter than C_{60}, so its average deviation from planarity at a given juncture is less than that found for C_{60}. [To visualize this, it may help to note that the 'equator' of C_{180} will be defined by more atoms than are found along C_{60}'s 'equator'.]

3.13 The correct statement:

$\Delta_f H^0$ (C_{60}) > $\Delta_f H^0$(C_{180}) > $\Delta_f H^0$ (graphite)

Reasoning: C_{60} has a larger average deviation from planarity than C_{180}, so sp^2 hybridization is less favourable for the smaller fullerene. However, both fullerenes are non-planar and therefore less amenable to sp^2 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).

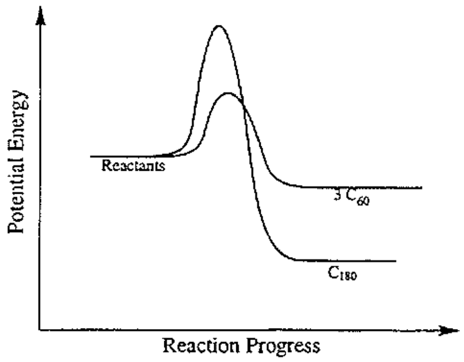
3.14 Which of graphs best represents the dependence of potential energy upon reaction progress for the two processes:

$$\text{reactants} \rightleftharpoons 3\,C_{60}$$

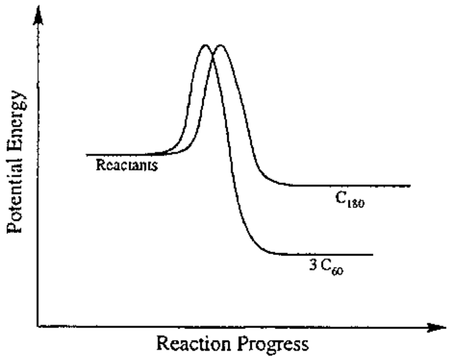
and

$$\text{reactants} \rightleftharpoons C_{180}$$

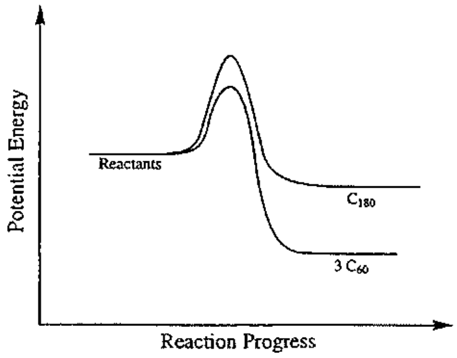
a).



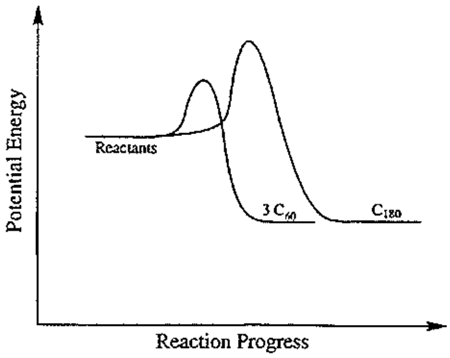
b).



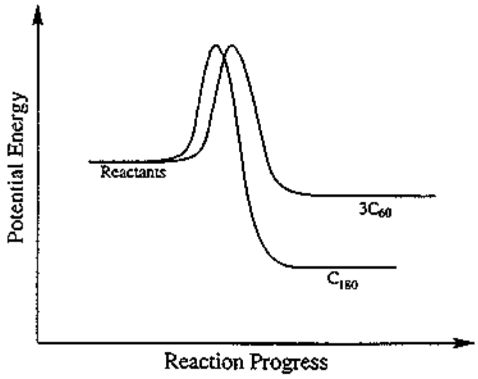
c).



d).



e).



The best graph is: <u>a)</u>

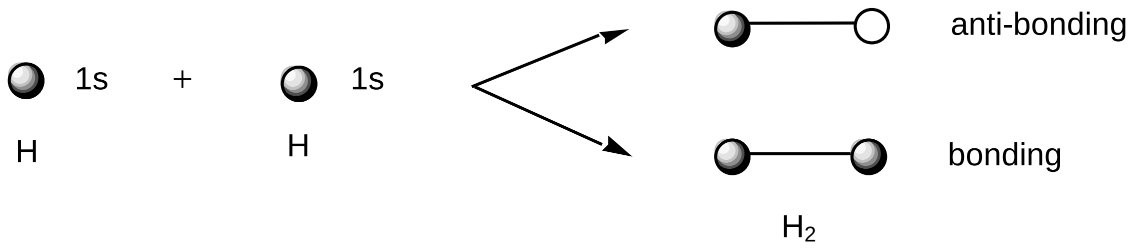
<u>Reasoning</u>: The equilibrium reaction

$$C_{60} \rightleftharpoons \quad \text{reactants} \rightleftharpoons 3\ C_{60}$$

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.

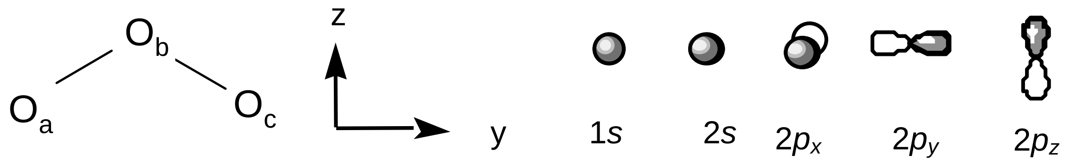
PROBLEM 4

When two hydrogen atoms come together, the 1s atomic orbitals combine to form bonding and anti-bonding molecular orbitals:



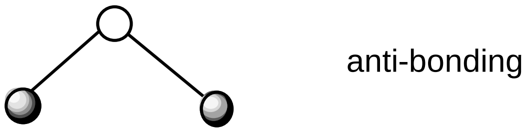
In a similar way, we may combine the atomic orbitals of more complicated atoms to form molecular orbitals, taking into account the symmetry of the molecule.

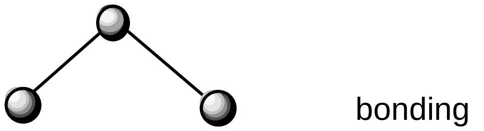
Consider the ozone molecule, O_3, which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the *yz* plane) and assume that there are 1*s*, 2*s*, 2p_x, 2p_y and 2p_z orbitals on each atom.



The atoms O_a and O_c are "related by symmetry" and the 1*s* orbitals on these atoms form symmetric and anti-symmetric combinations:

In this molecule the 1*s* 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:

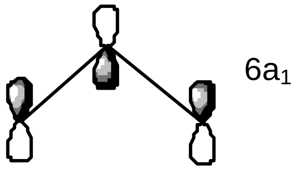




4.1 On the answer sheet, use a similar approach to construct the molecular orbitals arising from the separate interaction of the 2*s*, 2p_x, 2p_y, and 2p_z atomic orbitals. (Remember to form the symmetric and anti-symmetric combinations of Oa and Oc first.)

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 2*s*, $2p_x$, $2p_y$, 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)

a) Because the bonding character decreases.

b) Because the anti-bonding character increases.

c) Both (a) and (b).

d) Because the overlap decreases.

The correct answer is c).

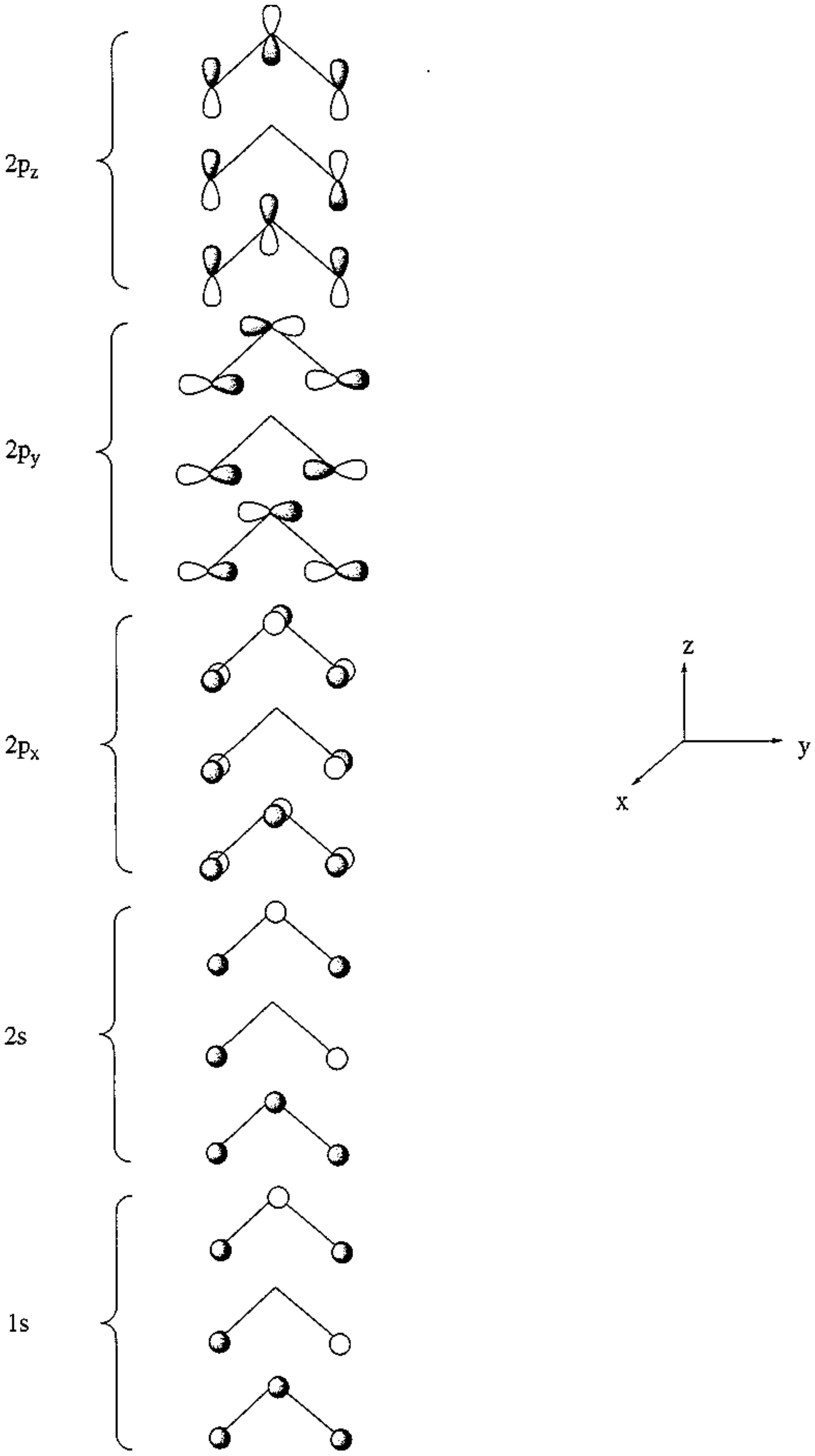
Reasoning: The energy changes so rapidly because the overlap is bonding between all three atoms in the bent molecule, but becomes more and more anti-bonding as the molecule approaches linearity:

4.3

O_3	BO_2	CO_2	NO_2	FO_2
$\boxed{6a_x\ (24e\text{-})}$	$\boxed{4b_2\ (21e\text{-})}$	$\boxed{4b_2\ (22e\text{-})}$	$\boxed{6a_1\ (23e\text{-})}$	$\boxed{2bx\ (25e\text{-})}$

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 $[Au(CN)_2]^-$, 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 $[Zn(CN)_4]^{2-}$ (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 $[Au(CN)_2]^-$ and 0.0030 M in $[Ag(CN)_2]^-$ 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 $[Au(CN)_2]^-$ and of $[Ag(CN)_2]^-$ after reaction has ceased.

$[Zn(CN)_4]^{2-} + 2\ e^- \rightarrow Zn + 4\ CN^-$ $\quad E° = -1.26$ V

$[Au(CN)_2]^- + e^- \rightarrow Au + 2\ CN^-$ $\quad E° = -0.60$ V

$[Ag(CN)_2]^- + e^- \rightarrow Ag + 2\ CN^-$ $\quad E° = -0.31$ V

5.3 $[Au(CN)_2]^-$ 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? $\{[Au(CN)_2]^- : K_f = 4 \times 10^{28}\}$

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:

$4\ Au + 8\ CN^- + O_2 + 2\ H_2O \rightarrow 4\ [Au(CN)_2]^- + 4\ OH^-$

reaction 2:

$Zn + 2\,[Au(CN)_2]^- \rightarrow [Zn(CN)_4]^{2-} + 2\,Au$

5.2 E^0(Ag/Zn) = –0.31 – (–1.26) = 0.95 V

E^0(Au/Zn) = –0.60 – (– 1.26) = 0.66 V

E^0(Ag/Zn) > E^0(Au/Zn)

Therefore the Ag(I) complex will be reduced first.

(i) mol Ag(I) in 500 dm^3 = 500 × 0.0030 = 1.5 mol

(ii) mol Au(I) in 500 dm^3 = 500 × 0.010 = 5.0 mol

(iii) mol Zn in 40 g = 40 / 65.38 = 0.61 mol

1 mol zinc reacts with 2 mol of Ag(I) or Au(I)

Therefore 0.61 mol Zn will consume 1.2 mol $[Ag(CN)_2]^-$

$[Ag(CN)_2]^-$ remaining = 1.5 – 1.2 = 0.3 mol

$[Au(CN)_2]^-$ will not be reduced.

Concentration of $[Au(CN)_2]^-$ when reaction has ceased = 0.010 × 3 = 0.030 M

Concentration of $[Ag(CN)_2]^-$ when reaction has ceased = 0.3 × (3 / 500) = 0.002 M

$[Zn(CN)_4]^{2-} + 2\,e^- \rightarrow Zn + 4\,CN^-$ $E^0 = -1.26$ V

$[Au(CN)_2]$" + e^- $\rightarrow$ Au + 2CN~ $E^0 = -\,0.60$ V

$[Ag(CN)_2]$" + e^- $\rightarrow$ Ag + 2CN- $E^0 = -\,0.31$ V

5.3 $Au^+ + 2\,CN^- \rightarrow [Au(CN)_2]^-$ $K_f = 4\times10^{28}$

99 mol % $[Au(CN)_2]^-$

$$K_f = \frac{[Au(CN)_2^-]}{[Au^+]\,[CN^-]^2}$$

$$\frac{[Au(CN)_2^-]}{[Au^+] + [Au(CN)_2^-]} = 99/100$$

Thus: $100 \times [Au(CN)_2^-] = 99 \times [Au^+] + 99 \times [Au(CN)_2^-]$

Therefore $[Au^+] = [Au(CN)_2^-]$ / 99

Substituting into K_f:

$4\times10^{28} = 99 / [CN"]^2$

$[CN^-] = 5\times10^{-14}$

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.

$SnCl_4 + Cl^- \rightarrow SnCl_5^-$

and

$SnCl_4 + 2\ Cl^- \rightarrow SnCl_6^{2-}$

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.

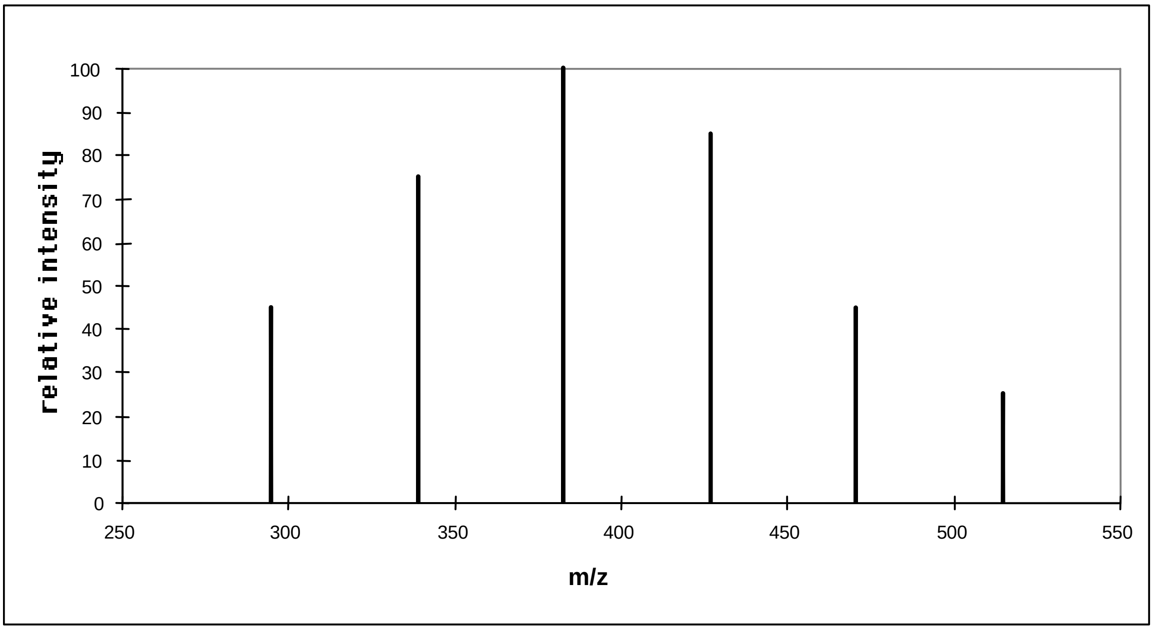
A solution containing $SnBr_6^{2-}$ (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at m/z=515.

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



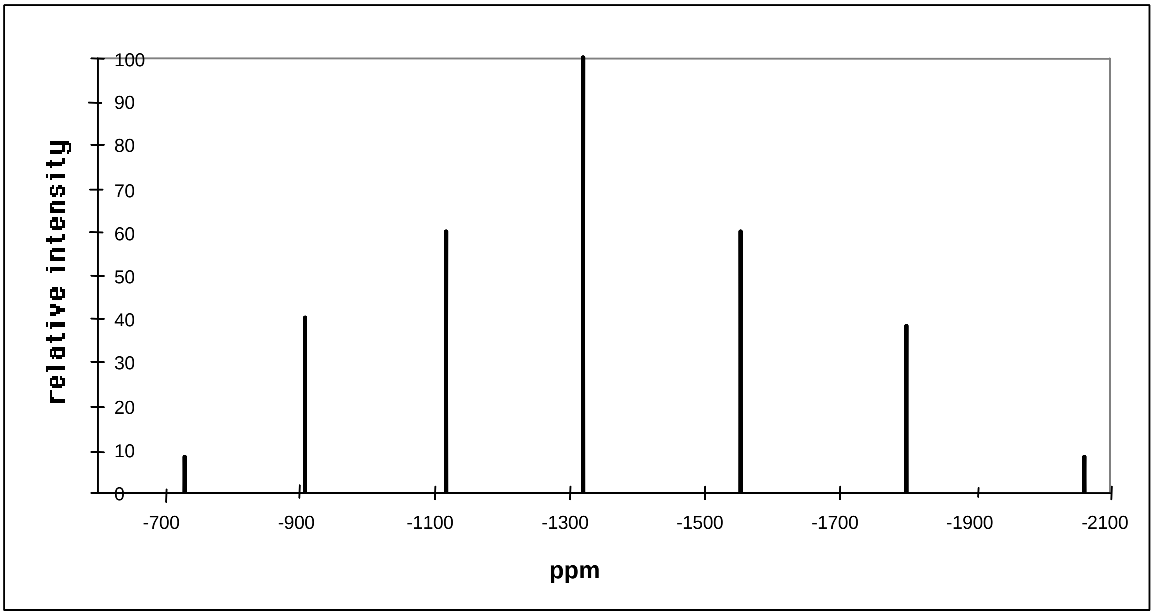
6.8 Write the empirical formula for each of the four new species.

^{1}H 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).

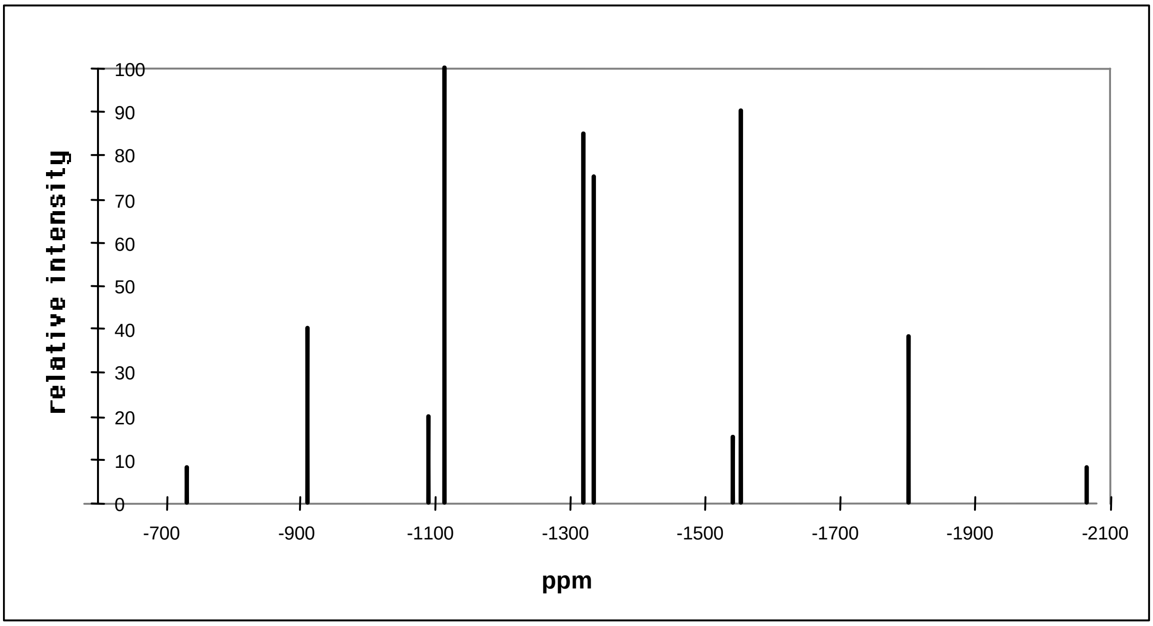
6.9 Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed on the answer template.

Fig. 2



Cooling the solution causes a change to this ^{119}Sn NMR spectrum and at -30 °C ten peaks are observed (Fig. 3).

Fig. 3

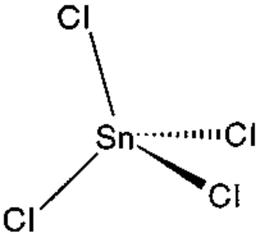


6.10 Draw the geometry for the four tin-containing species present in this solution at –30 °C that give rise to the peaks at –1092 and –1115, –1322 and –1336 ppm.

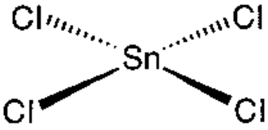
SOLUTION

6.1

A

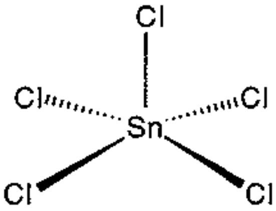


B

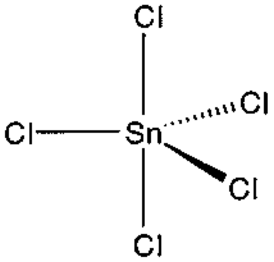


6.2

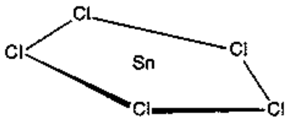
C



D



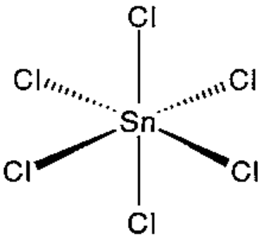
E



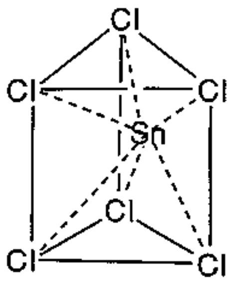
6.3 In accordance with VSEPR theory geometry D is likely to be preferred for $SnCl_5^-$.

6.4

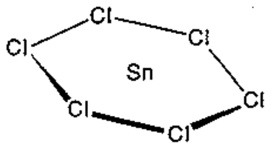
F



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: $SnCl_2Br_3^-$

m/z = 383: $SnCl_3Br_2^-$ - m/z = 471: $SnClBr_4^-$

6.9

- 912 ppm: $SnCl_5Br^{2-}$
-1117 ppm: $SnCl_4Br_2^{2-}$
-1322 ppm: $SnCl_3Br_3^{2-}$
-1554 ppm: $SnCl_2Br_4^{2-}$
-1800 ppm: $SnClBr_5^{2-}$

6.10

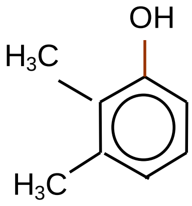
-1092 ppm and -1115 ppm (2 compounds)

-1322 ppm and -1336 ppm (2 compounds)

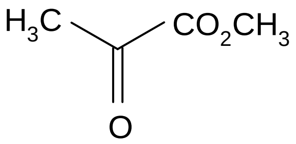
PROBLEM 7

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

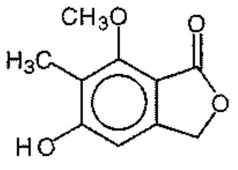
Compound **D** was synthesised as follows: The phenol **E** was methylated (MeI/K_2CO_3) to afford **F** ($C_9H_{12}O_2$) which in turn was reduced with lithium metal in liquid ammonia and 2-methyl-propan-2-ol to give the symmetrical unconjugated diene **G**. Conjugation of this diene was achieved by 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**.

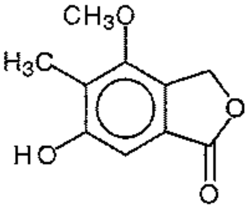
7.2 Using the last space on the answer template provide a second structure for **B**.

SOLUTION

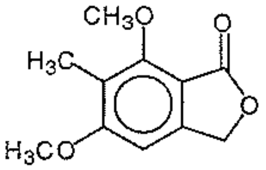
7.1 and **7.2**



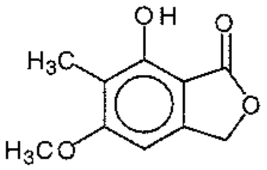
A



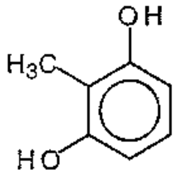
B



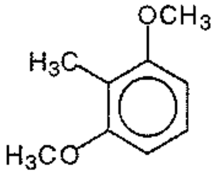
C



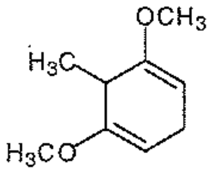
D



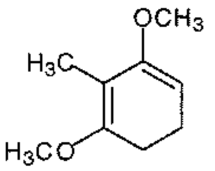
E



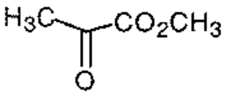
F



G

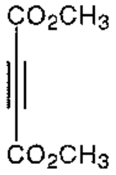


H



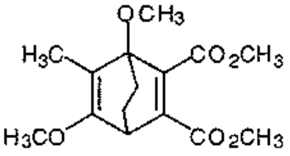
$H_3C-C(=O)-CO_2CH_3$

I

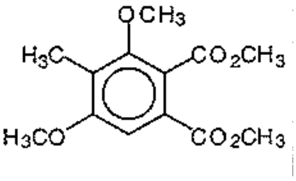


$CH_3O_2C-C\equiv C-CO_2CH_3$

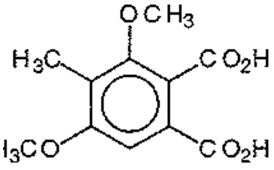
J



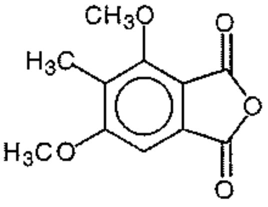
K



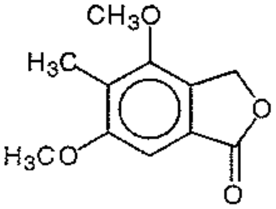
L



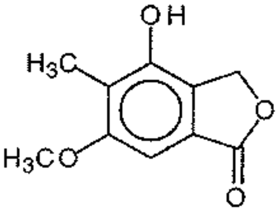
M



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.

$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4\ (s)$$

The precipitate must then be re-dissolved in acid:

$$CaC_2O_4\ (s) + 2\ H^+ \rightarrow Ca^{2+} + H_2C_2O_4$$

The liberated oxalic acid is titrated with standard permanganate solution:

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2 + 2\ Mn^{2+} + 8\ H_2O$$

Formation of the calcium oxalate precipitate

1. Use a 25.00 cm^3 pipette and 250.0 cm^3 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 cm^3 aliquot of the dilute calcium/magnesium solution into a 250 cm^3 beaker, add approximately 10 cm^3 of 3 M H_2SO_4 and about 50 cm^3 of water.

CARE! 3 M H_2SO_4 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 H_2SO_4 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 <u>for at least 60 minutes</u> 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 cm^3 conical flask. Rinse the paper with a few cm^3 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 cm^3 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 cm^3 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 <u>before</u> 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 cm^3 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 cm^3 3 M sulphuric acid, collecting the acid in the conical flask. Finally, rinse the paper with ~ 20 cm^3 water.

Titration with permanganate

16. Make the volume up to about 100 cm^3 with water, heat the solution to about 60 ℃, 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 ℃ 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 <u>original</u> 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 $KMnO_4$ 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 cm^3 aliquot of dilute Ca/Mg solution:

$n(KMnO_4)$ required to titrate oxalate from dissolved calcium oxalate precipitate

$n(KMnO_4) = 0.0198$ mol dm^{-3} $\times$ 0.0277 dm^3 = 5.485×10^{-4} mol

n(oxalate) from dissolved calcium oxalate precipitate:

n(oxalate) = 5/2 $\times$ 5.485×10^{-4} mol = 1.371×10^{-3} mol

$n(Ca^{2+})$ from dissolved calcium oxalate precipitate = n(oxalate) = 1.371×10^{-3} mol

c(Ca) = 1.371×10^{-3} mol / 0.02500 dm^3 = 0.0548 mol dm^{-3}

In original Ca/Mg solution:

c(Ca) = 0.0548 mol dm^{-3}

PROBLEM 2 (Practical)

Analysis of a Mixture of Cobalt(III) Complexes

When the complex $[Co(NH_3)_5NO_2]Cl_2$ is prepared in the laboratory, it often contains a considerable amount of $[Co(NH_3)_6]Cl_3$ by-product.

In this exercise, you must determine the amount of $[Co(NH_3)_5NO_2]Cl_2$ in a sample that also contains only $[Co(NH_3)_6]Cl_3$ 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 $–SO_3H$ 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 $\underline{n}$ 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 cm^3 beaker, washing it from the container with about 50 cm^3 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 cm^3 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 (*pH* ~5). You should not need to use more than 200 cm^3 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 cm^3 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 cm^3 aliquots of the diluted NaOH solution, using phenolphthalein indicator.

Analysis Procedure

You are provided with approximately 40 cm^3 of a 0.00500 M solution of HCl that contains 0.2000 g of a mixture of the cobalt(III) complexes $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_6]Cl_3$ in 40.00 cm^3.

6. Use a pipette to transfer a 25.00 cm^3 aliquot of the cobalt complex solution into a 250 cm^3 beaker (beaker No 1) and add ~25 cm^3 water.
7. 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.
8. Carefully wash the acidic solution into a second 250 cm^3 beaker (beaker No 2) with about 20 cm^3 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.
9. 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.
10. Filter the two resin samples through a carefully washed filter paper, and collect the acidic filtrate in a 100 cm^3 volumetric flask. Carefully wash the resin with small portions of water into the volumetric flask and make up to the mark with water.
11. With this acid solution titrate 25.00 cm^3 aliquots of your standardized NaOH solution.

Calculate the number of moles of H^+ liberated by the 25 cm^3 aliquot of your mixture of cobalt(III) complexes and report the percentage of $[Co(NH_3)_5NO_2]Cl_2$ 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(NaOH) = 0.01250 mo! dm^{-3} × 0.02412 dm^3 = 0.01206 mol dm^{-3}

Aliquot of cobalt complex solution used for ion-exchange: 25 cm^3

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

$c(H^+)$ collected in 100 cm^3 flask:

$c(H^+)$ = 0.01206 mol dm^{-3} × (25.00 cm^3) / (22.32 cm^3) = 0.01351 mol dm^{-3}

total $n(H^+)$ collected from column:

$n(H^+)$ = 0.01351 mol dm^{-3} × 0.100 dm^3 = 1.351×10^{-3} mol

$n(H^+)$ from aliquot put onto column:

$n(H^+)$ = 0.00500 mol dm^{-3} × 0.02500 dm^3 = 1.250×10^{-4} mol

$n(H^+)$ ion-exchanged from complexes in aliquot put onto column:

$n(H^+)$ = 1.351×10^{-3} mol – 1.250×10^{-4} mol = 1.226×10^{-3} mol

let y = mass $[Co(NH_3)_5NO_2]Cl_2$ in 25.00 cm^3 aliquot of mixture added to column mass of mixture added to column = (25.00 cm^3 / 40 cm^3) × 0.2000 g = 0.1250 g

then mass $[Co(NH_3)_6]Cl_3$ in aliquot = (0.1250 - y) g

$n(H^+)$ ion-exchanged from $[Co(NH_3)_5NO_2]Cl_2$:

$n(H^+)$ = 2 y / 261.00 g mol^{-1} = 0.007663*x* mol

$n(H^+)$ ion-exchanged from $[Co(NH_3)_6]Cl_3$:

$n(H^+)$ = 3 (0.1250 – y) g / 267.50 g mol^{-1} = (0.001402 – 0.011214 y) mol

Thus, 0.007663 y + (0.001402 – 0.011214 y) = 0.001226 or y = 0.04956 g

% $[Co(NH_3)_5NO_2]Cl_2$ = 100 (0.04956 g / 0.1250 g) = 39.6 %