THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Volume 2

21st – 40th IChO
1989 – 2008

Edited by Anton Sirota

IUVENTA, Bratislava, 2009

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS,

Volume 2
21st – 40th IChO (1989 – 2008)

Editor: Anton Sirota

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VOLUME 2

The competition problems of the:

Preface

This publication contains the competition problems (Volume 2) from the 21st – 40th International Chemistry Olympiads (IChO) organized in the years 1989 – 2008 and is a continuation of the publication that appeared last year as Volume 1 and contained competition problems from the first twenty IChOs. The whole review of the competition tasks set in the IChO in its fourty-year history is a contribution of the IChO International Information Centre in Bratislava (Slovakia) to the development of this world known international competition. This Volume 2 contains 154 theoretical and 46 practical competition problems from the mentioned years. The review as a whole presents altogether 279 theoretical and 96 practical problems.

In the elaboration of this collection the editor had to face certain difficulties because the aim was not only to make use of past recordings but also to give them such a form that they may be used in practice and further chemical education. Consequently, it was necessary to make some corrections in order to unify the form of the problems. However, they did not concern the contents and language of the problems.

Unfortunately, the authors of the particular competition problems are not known and due to the procedure of the creation of the IChO competition problems, it is impossible to assign any author's name to a particular problem. As the editor I would appreciate many times some discussion with the authors about any critical places that occurred in the text. On the other hand, any additional amendments to the text would be not correct from the historical point of view. Therefore, responsibility for the scientific content and language of the problems lies exclusively with the organizers of the particular International Chemistry Olympiads.

Some parts of texts, especially those gained as scanned materials, could not be used directly and thus, several texts, schemes and pictures had to be re-written or created again. Some solutions were often available in a brief form and necessary extent only, just for the needs of members of the International Jury.

Recalculations of the solutions were made in some special cases only when the numeric results in the original solutions showed to be obviously not correct. Although the numbers of significant figures in the results of several solutions do not obey the criteria generally accepted, they were left without change.

In this publication SI quantities and units are used and a more modern method of chemical calculations is introduced. Only some exceptions have been made when, in an effort to preserve the original text, the quantities and units have been used that are not SI. There were some problems with the presentation of the solutions of practical tasks, because most of the relatively simple calculations were based on the experimental results of contestants. Moreover, the practical problems are accompanied with answer sheets in the last years and several additional questions and tasks have appeared in them that were not a part of the text of the original experimental problems. Naturally, answer sheets could not be included in this publication and can only be preserved as archive materials.

When reading the texts of the IChO problems one must admire and appreciate the work of those many known and unknown people – teachers, authors, pupils, and organizers – who contributed so much to development and success of this important international competition.

I am sure about the usefulness of the this review of the IChO problems. It may serve not only as archive material but, in particular, this review should serve to both competitors and their teachers as a source of further inspiration in their preparation for this challenging competition.

Bratislava, July 2009

Anton Sirota, editor

21st

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE TWENTY-FIRST
INTERNATIONAL CHEMISTRY OLYMPIAD
2–10 JULY 1989, HALLE, GERMAN DEMOCRATIC REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

To determine the solubility product of copper(II) iodate, $Cu(IO_3)_2$, 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):

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

From (2) and (1):

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

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

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

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

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

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

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:

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

$m(CaCO_3/d) = n(SO_2/h) \times M(CaCO_3) \times 24 \text{ h} \cdot \text{d}^{-1} \times 0.95 = 1.53 \times 10^3 \text{ kg/d}$

$$m(\mathrm{CaSO_4\,.\,2\,H_2O}) = \frac{M(\mathrm{CaSO_4\,.\,2\,H_2O})}{M(\mathrm{CaCO_3})} \times m(\mathrm{CaCO_3})\,/\,\mathrm{d} = 2.63\times10^{3}\ \mathrm{kg/d}$$

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

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

Solving for $[\mathrm{H_3O^+}]$:

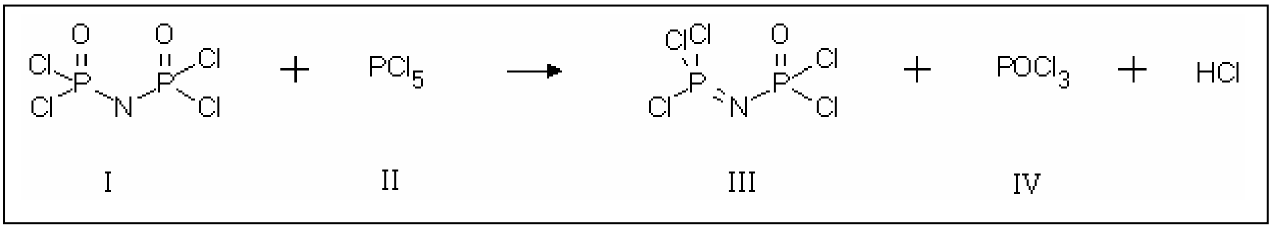
If $[\mathrm{SO_2}] = n(\mathrm{SO_2})\,/\,V = 1.34\times10^{-4}$ and $K_a = 1\times10^{-2.25}$, then $[\mathrm{H_3O^+}] = 1.32\times10^{-4}$ and $pH = 3.88$

3.4 $\mathrm{SO_2 + Na_2SO_3 + H_2O \rightarrow 2\ NaHSO_3}$

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.



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

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

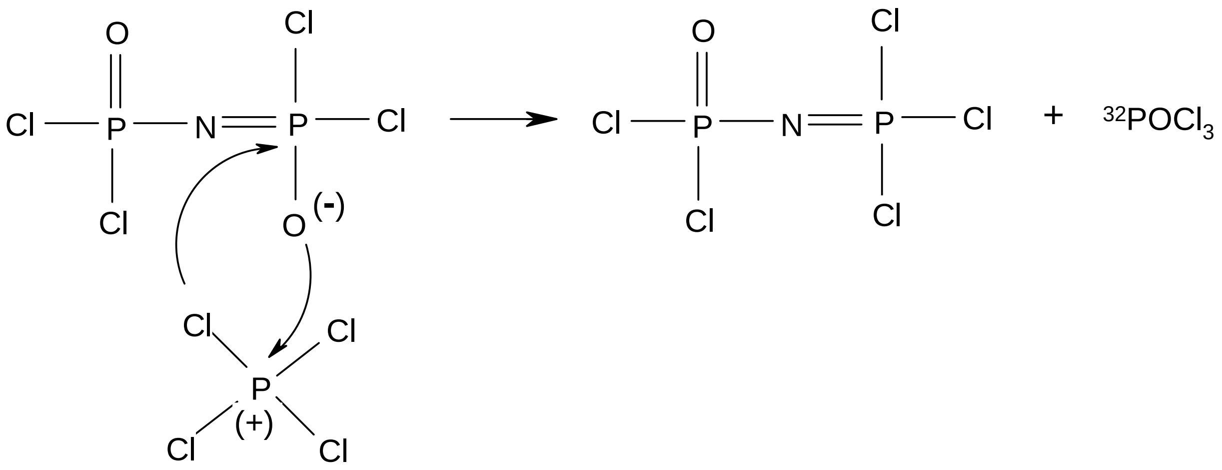
$PCl_5 + 8\ OH^- \rightarrow PO_4^{3-} + 5\ Cl^- + 4\ H_2O$

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

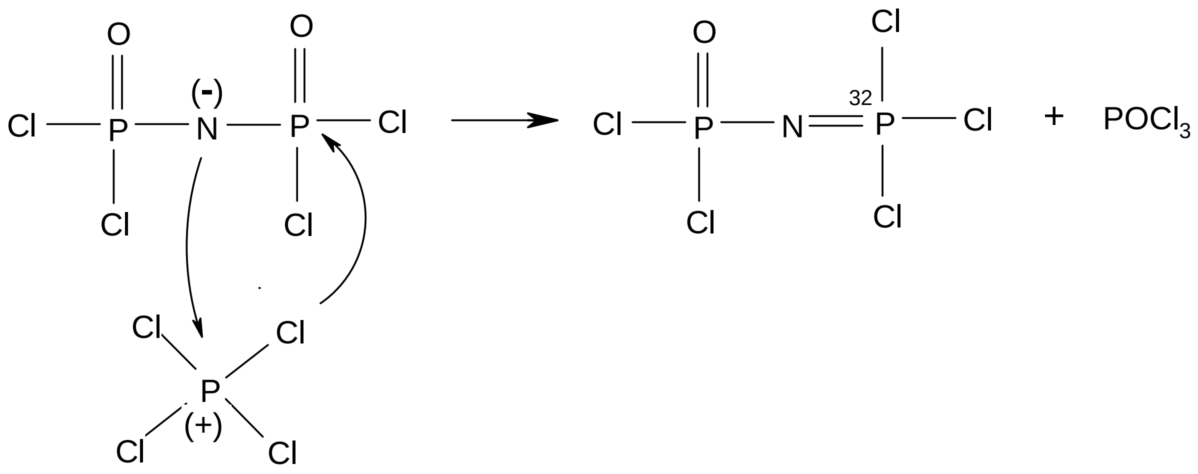
4.3 $A = A_0\, e^{-\lambda t}$ $t_{1/2}$: $A = 0.5\ A_0 \Rightarrow \lambda = \ln 2 / t_{1/2}$ $A = 10^{-3}\ A_0$

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

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?

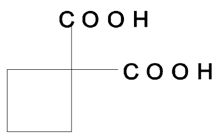
5.4 Which reaction can be used to determine the relative configuration of diastereoisomers?

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

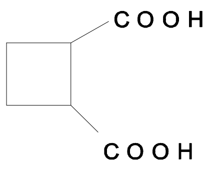
5.6 Indicate the absolute configurations of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (*R,S* system).

SOLUTION

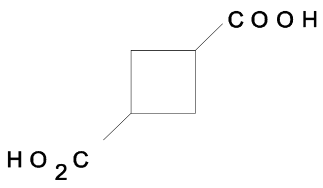
5.1 Constitutional isomers:



1,1 - cyclobutane -
dicarboxylic acid



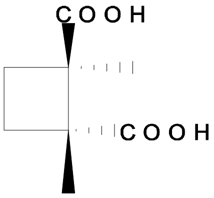
1,2 - cyclobutane -
dicarboxylic acid



1,3 - cyclobutane -
dicarboxylic acid

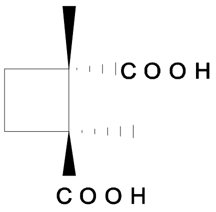
5.2 Stereoisomers:

I



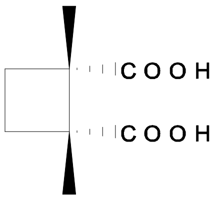
trans

II



trans

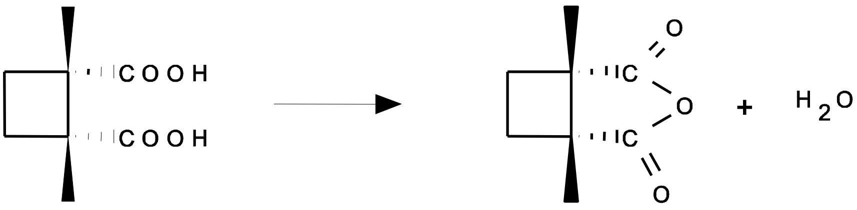
III



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).

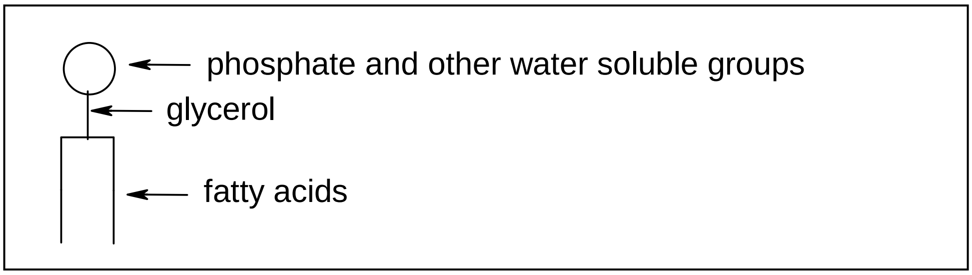
6.2 Using these three fatty acids in part 6.1 draw one possible structure of a triacyl glyceride.

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.

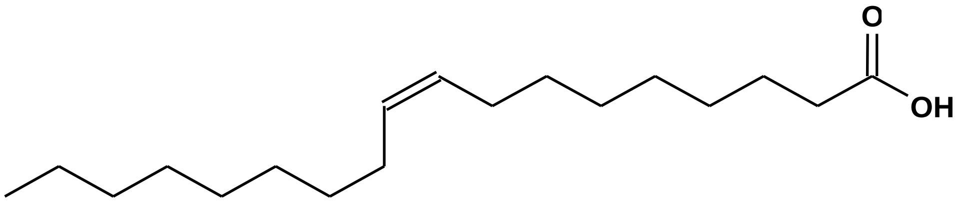
ii) Draw two possibilities for the association of six identical molecules of a phospholipid in water using the above diagram.

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

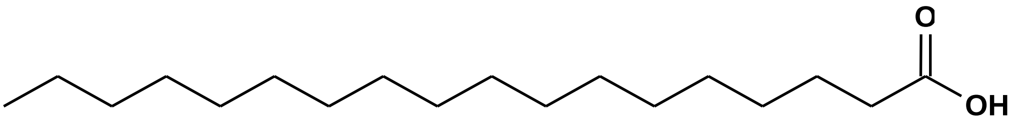
iv) Such a model (iii) is incomplete. What other bio-macromolecules are contained in such biomembranes?

SOLUTION

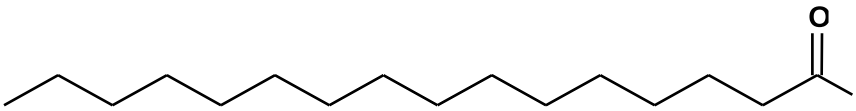
6.1



oleic acid

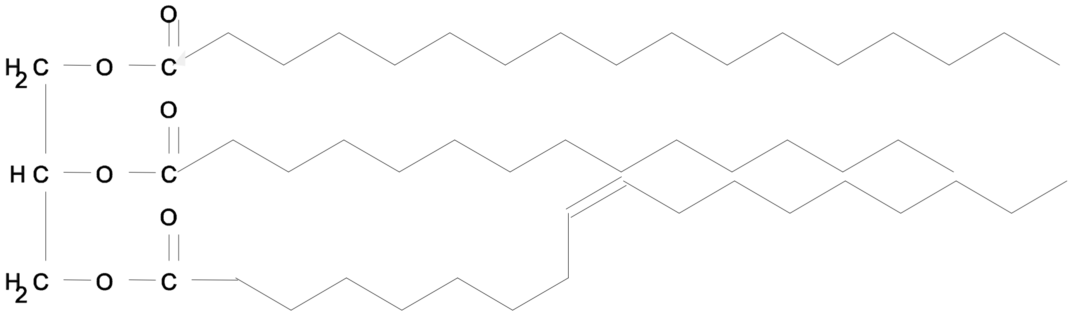


stearic acid

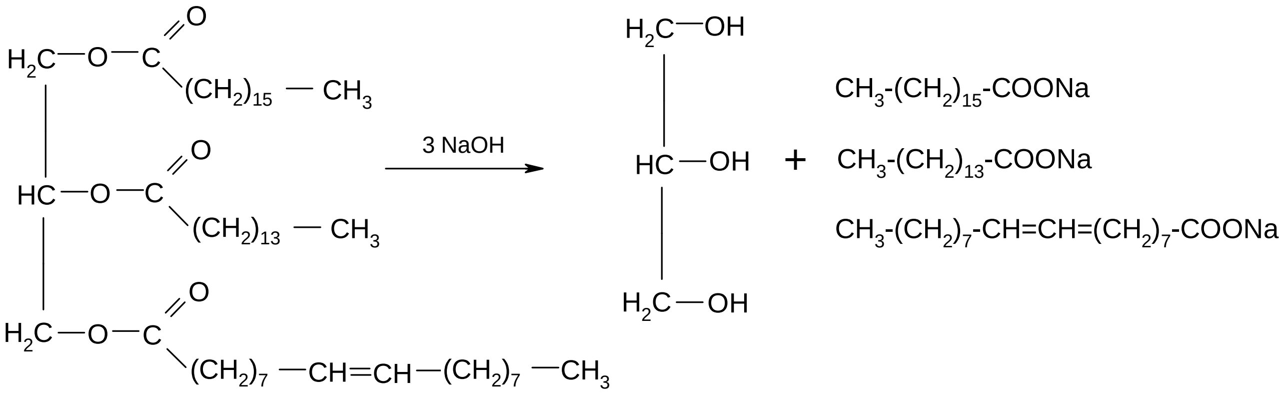


palmitic acid

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



6.3



$H_2C-O-C(=O)-(CH_2)_{15}-CH_3$

$HC-O-C(=O)-(CH_2)_{13}-CH_3$

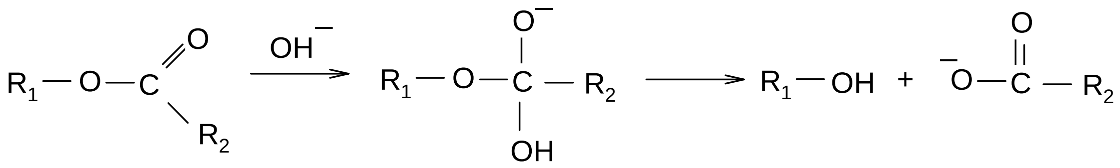
$H_2C-O-C(=O)-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$

H_2C-OH, $HC-OH$, H_2C-OH

$CH_3\text{-}(CH_2)_{15}\text{-}COONa$

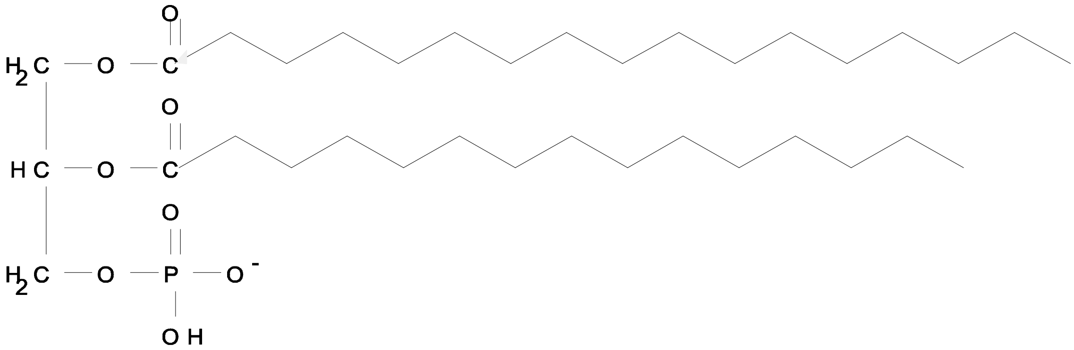
$CH_3\text{-}(CH_2)_{13}\text{-}COONa$

$CH_3\text{-}(CH_2)_7\text{-}CH=CH=(CH_2)_7\text{-}COONa$

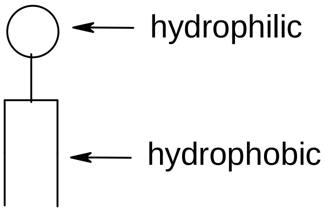


6.4 It is $C_{21}H_{43}COOH$.

6.5 An example for a phospholipid is:



6.6 i)



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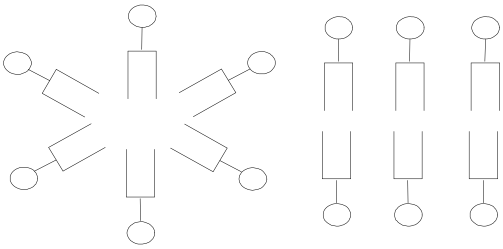

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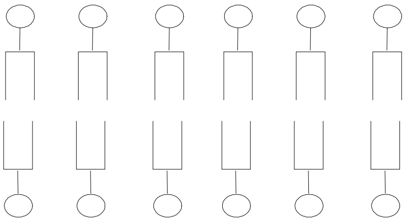


phospholipid bilayer

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.

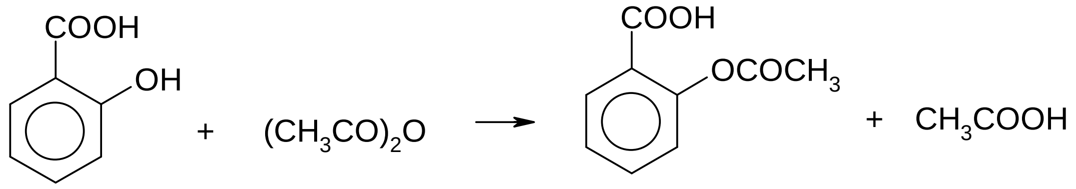
A technician should then weigh the cooled dish containing your product in your presence. Record the mass. The melting point will subsequently be taken by a technician to check the purity of your product.

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:

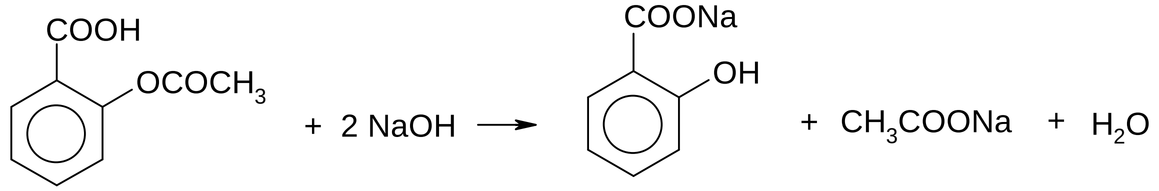
Pipette 50.00 cm^3 of your standardized sodium hydroxide solution into the Erlenmeyer flask I (with a ground glass joint) which contains your unknown mass of aspirin. Add 3 – 5 boiling stones to the flask and boil the reaction mixture for 15 minutes using a reflux condenser and the electrical hot plate. 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 $n(CaCO_3)$ = 12.56×10^{-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 $n(Ca_3(PO_4)_2)$ + $n(CaF_2)$ + $n(CaCO_3)$ = 6.28×10^{-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 × 2.00×10^{-3} mol of $Ca_3(PO_4)_2$, thus 3 × 2 × 2×10^{-3} = 1.2×10^{-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 $2 \times 0.8 \times 10^{-3} = 1.6 \times 10^{-3}$ mol of $Ca(H_2PO_4)_2$.

$m(Ca(H_2PO_4)_2 = 18.07 \times 10^{-3}$ mol = 4.230 g

Formation of gypsum: $n(CaSO_4) = n(H_2SO_4) = 5.00 \times 10^{-3}$ mol $\triangleq$ 0.86 g

The amount of $CaSO_4$ that was already present in 1 g of apatite and yielded gypsum is $0.434 \times 10^{-3} \times 172 = 0.075$ g. There remain also 0.034 g of silica, and thus the theoretical mass of the residue should be:

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

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 $0.856 / 234 = 3.66 \times 10^{-3}$ mol. For 5.49 g of residue it is 0.0201×10^{-3} mol of soluble product (n_2). The amount of acid used is 0.500 / 20 = 0.025 mol H_3PO_4 (equals 0.0125 mol P_2O_5) and 0.005 mol H_2SO_4. The amount of $Ca_3(PO_4)_2$ 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 $K_{sp} = 1 \times 10^{-20}$.

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 $[Cu^{2+}][OH^-]^2 = 1\times10^{-20}$; $[Cu^{2+}] = 1\times10^{-2} \Rightarrow [OH^-] = 1\times10^{-9}$; $\underline{pH = 5}$

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

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 = <u>12</u>

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

$[Cu(NH_3)_2]^{+} + e^- \rightarrow Cu + 2\,NH_3$ $E_0 = -\,0.14$ 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 $[Cu(NH_3)_2]^{+} + e^- \rightarrow Cu + 2\,NH_3$ $E_{f1} = -\,0.14$ V

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

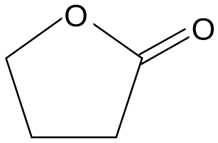
PROBLEM 3

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?

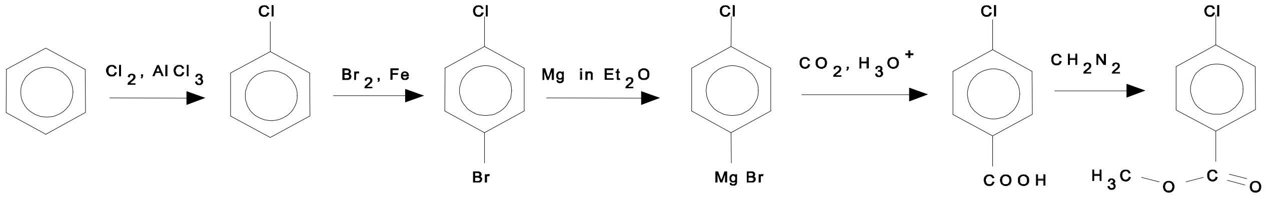
P reacts with **O** in basic media in a 1 : 1 molar ratio to give **H** that contains only one chlorine atom on the aromatic ring.

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

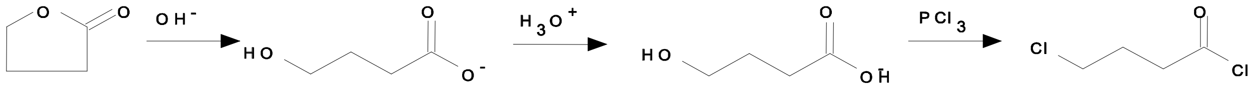
3.8 State the multiplicity of each resonance in the ^{1}H NMR spectrum of **K**. Assume that all coupling constants between protons and adjacent carbons are identical.

SOLUTION

3.1



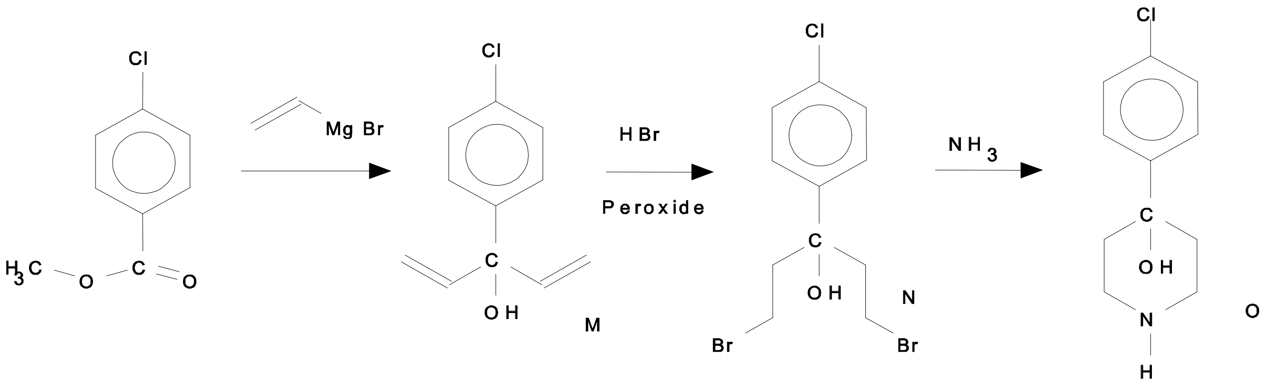
3.2 and **3.3**



J **K**

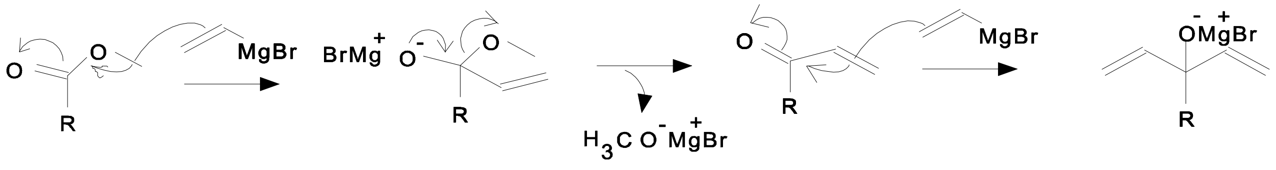
L

3.4

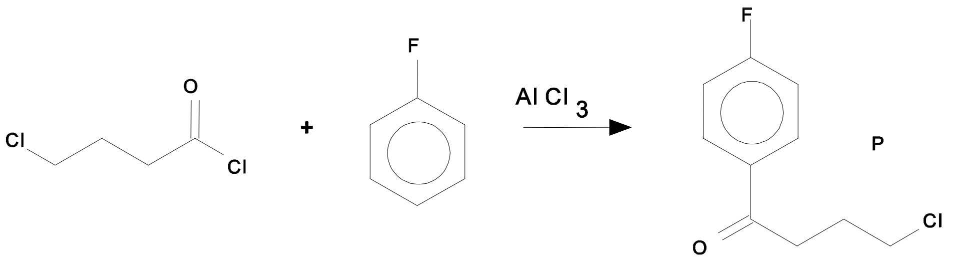


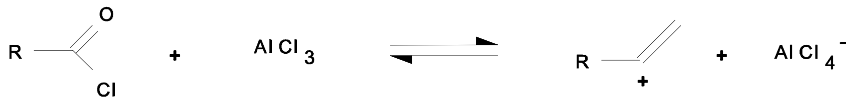
M **N** **O**

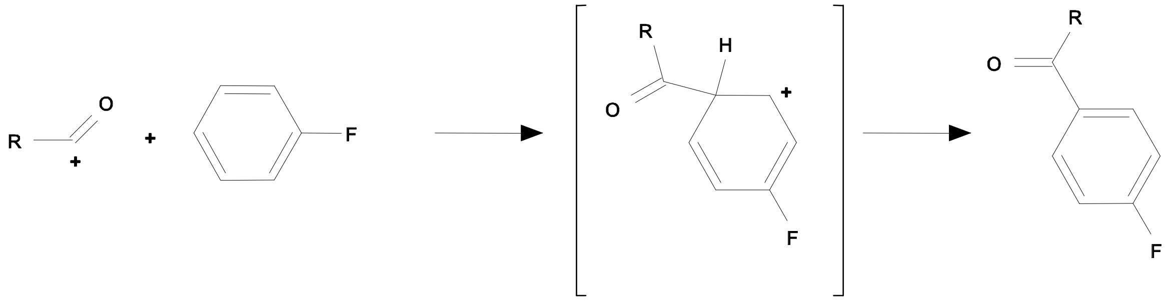
Mechanism of the Grignard reaction:



3.5





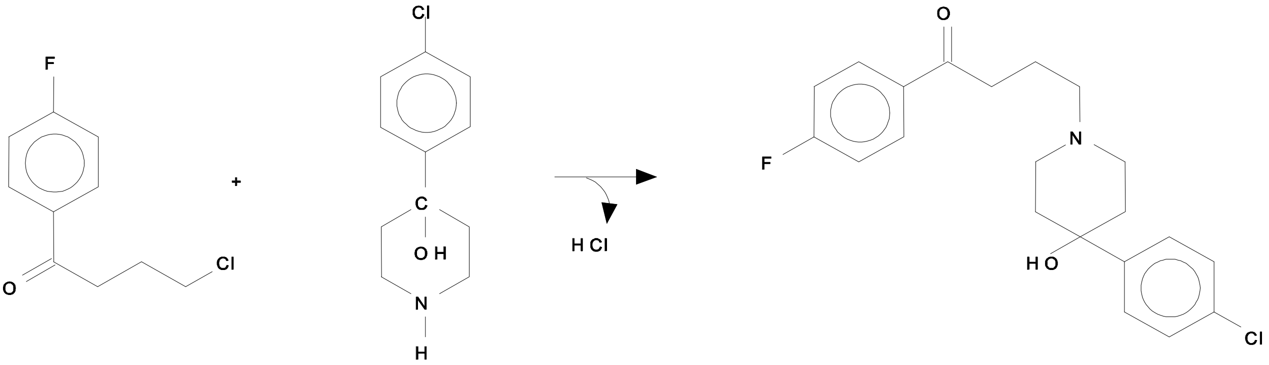


3.6 Chemical test: carbonyl groups react with phenylhydrazines to phenylhydrazones with a sharp, specific melting point.

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

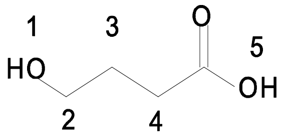
A possibility to distinguish between ketones and aldehydes is the Tollens-test (silver mirror). Ketones cannot be reduced whereas aldehydes easily reduce the silver ions to elementary silver.

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:

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

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:

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

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

Mechanism 3:

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

$NO_2NH^- \xrightarrow{k_5} N_2O + OH^-$ (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:

$v_1 = k_1 [NO_2NH_2]$

$$v_2 = k_3 [NO_2NH_3^+] = \frac{k_3 k_2}{k_{-2}} [NO_2NH_2] [H_3O^+]$$

$$v_3 = k_5 [NO_2NH^-] = \frac{k_5 k_4}{k_{-4}} \frac{[NO_2NH_2]}{[H_3O^+]}$$

Thus, it is the third mechanism that is correct.

5.3 $k = \dfrac{k_5 k_4}{k_{-4}}$

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

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

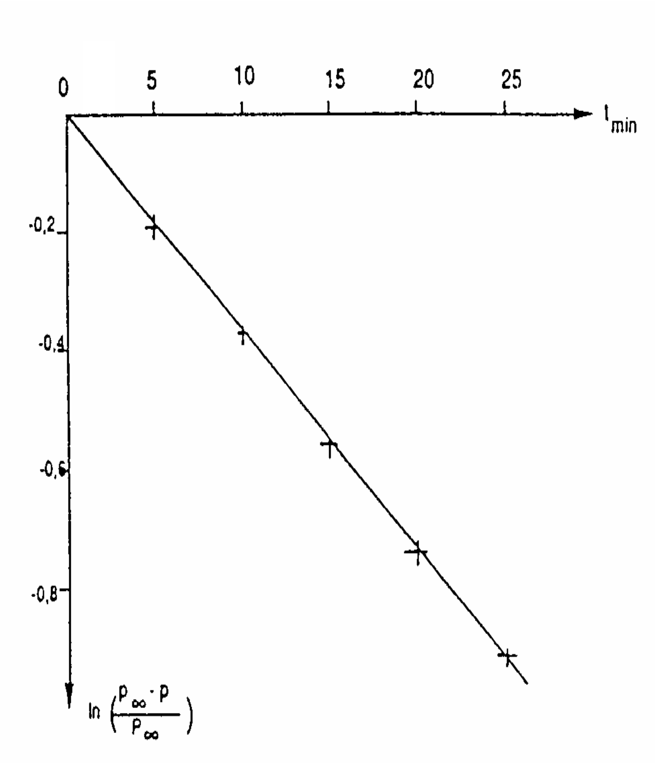
and thus

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

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

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

5.6

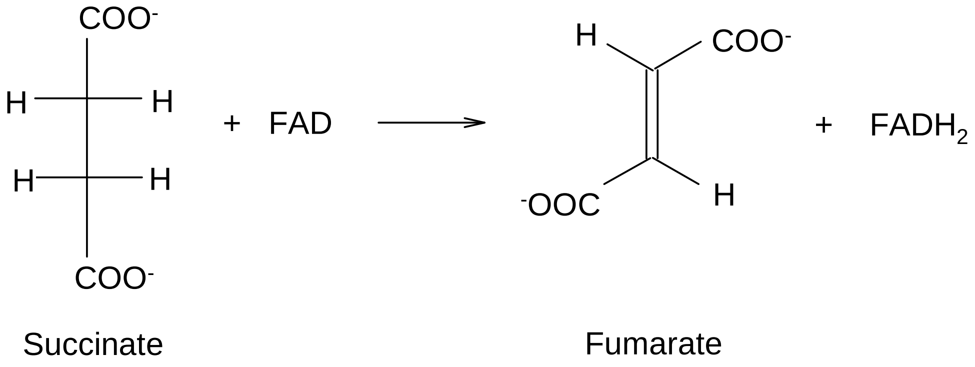


5.7 The graph of $f(x) = \ln(1 - p/p_\infty) = -k't$ is a straight line with the slope k' shown in Fig. k' was determined to be 3.7×10^{-2} min^{-1}.

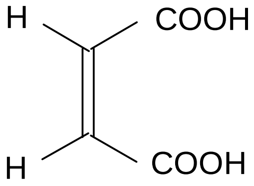
PROBLEM 6

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*.

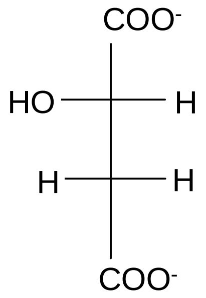
6.2 On the basis of the Newman projections of the most stable conformations of each isomer and the above facts, determine the percentage of dideuterated fumarate formed by *syn* and *anti* dehydrogenation.

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

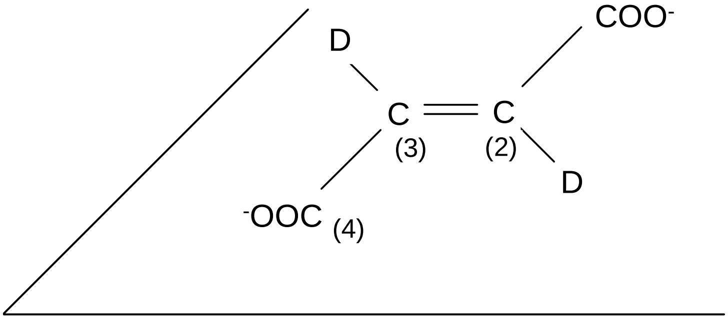
6.3 Show the stereochemistry of the enzymatic dehydrogenation.

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).

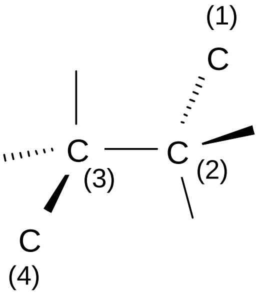
Fischer projection of (*S*)-malate:



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.

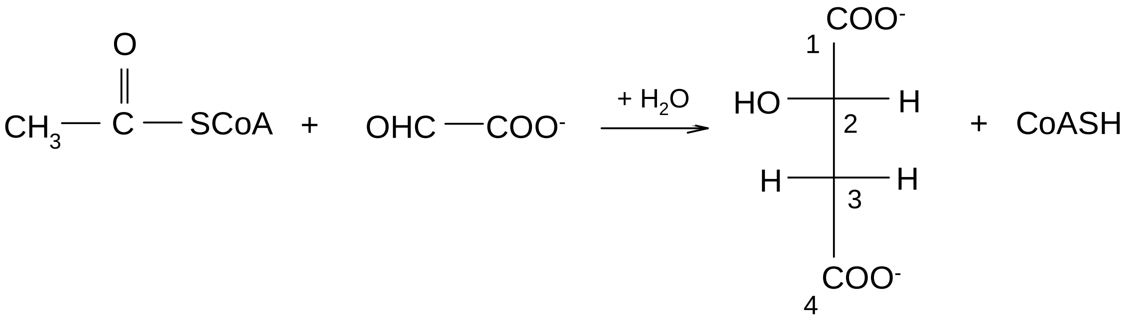


2,3-dideuteriofumarate

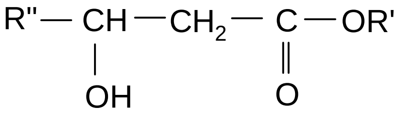


(2S,3S)-2,3-dideuteriomalate

The acetylcoenzyme A, $CH_3COSCoA$ reacts with glyoxylate, $OHC-CO_2^-$, 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 $R'\text{-}O^-$ ions. It leads to a β-hydroxyester.

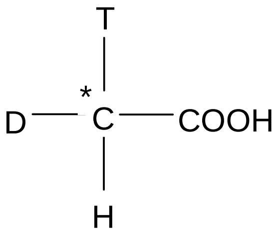


$$R''-CH(OH)-CH_2-C(=O)-OR'$$

($R'\text{-}O^-$ enter the reaction as a base to produce an intermediate carbanion from the ester)

6.5 Write the steps of the mechanism.

The enzymatic reaction is carried out using acetylcoenzyme A which is obtained from acetic acid CHDTCOOH having R-configuration.



$$D-\overset{*}{C}(T)(H)-COOH$$

(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?

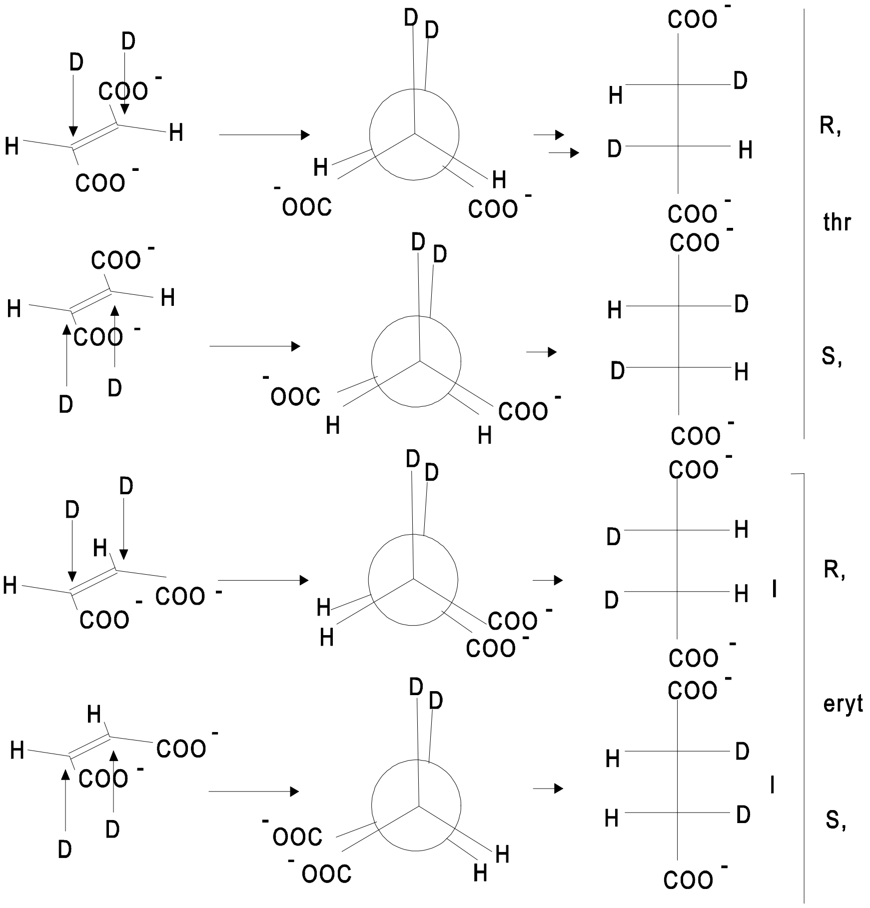
The major product is monotritiated fumarate (79%) with 21 % untritiated fumarate.

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.

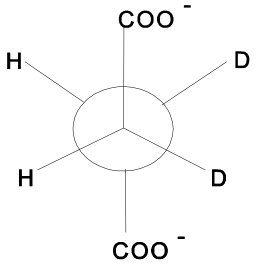
6.8 What would be the products if the starting material has a labelled acetyl group with *S*-configuration?

SOLUTION

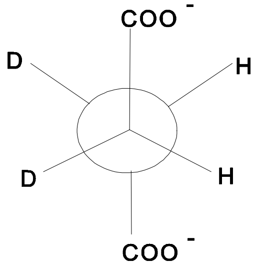
6.1 There are three isomers. The catalytic deuteration is a syn deuteration.



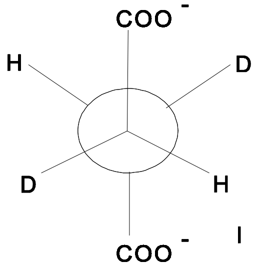
The most stable conformation for succinates is the anti form, since the distance between the bulky COO$^-$ groups is maximal:



I



II

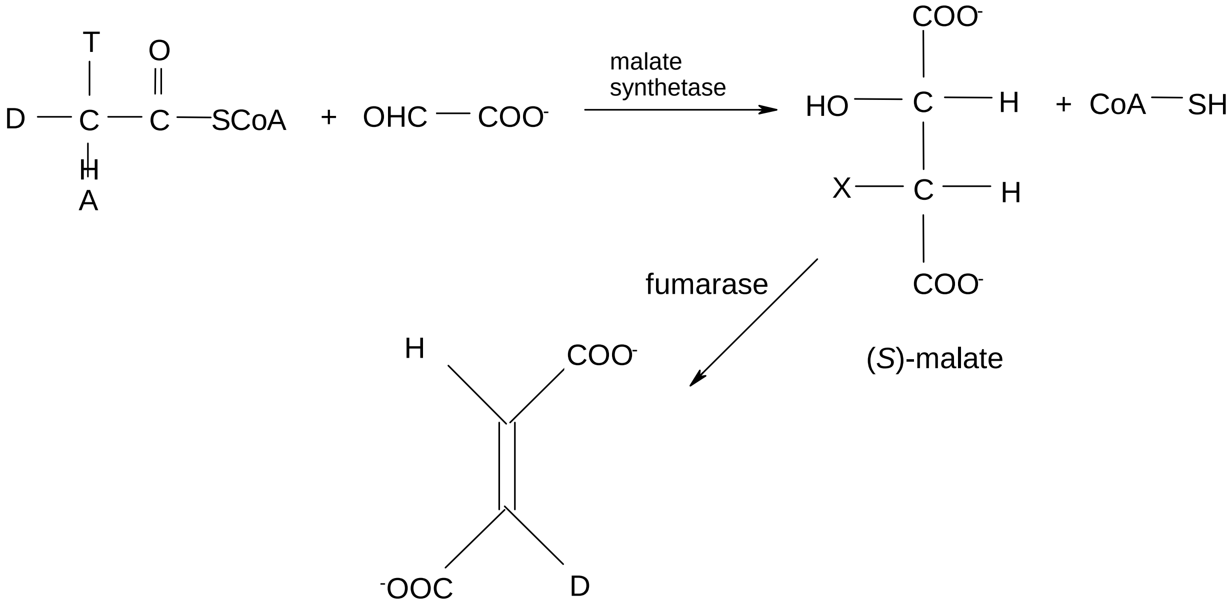


III

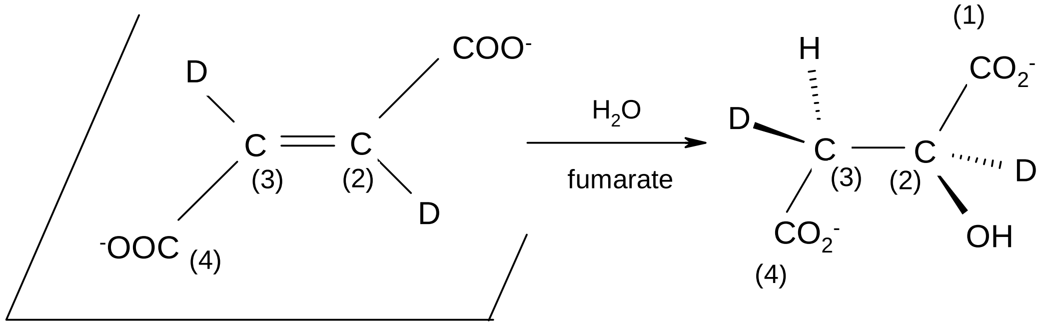
I and II are enantiomeres, II and III are a meso isomer, thus there are in total three isomers (two enantiomers and one meso form). Each threo and the meso form are diastereomers.

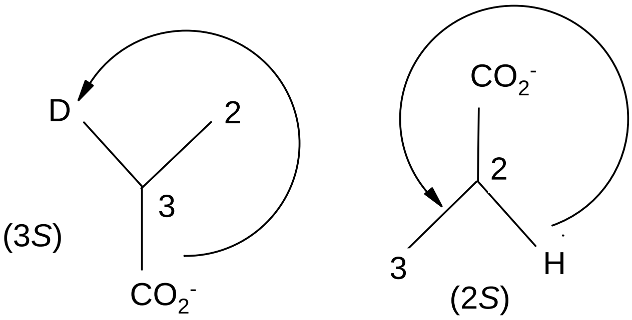
6.2 Considering the Newman projections of the three isomers it is clear that *syn* elimination of I and II leads either to fumarate containing no D or to dideuterated fumarate (percentage of dideuterated fumarate is thus 50 %) whereas *anti* elimination leads to monodeuterated fumarate. Concerning the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



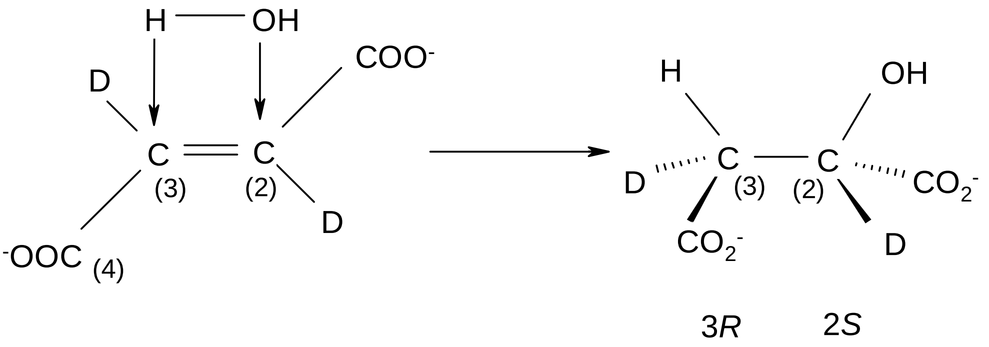
6.4





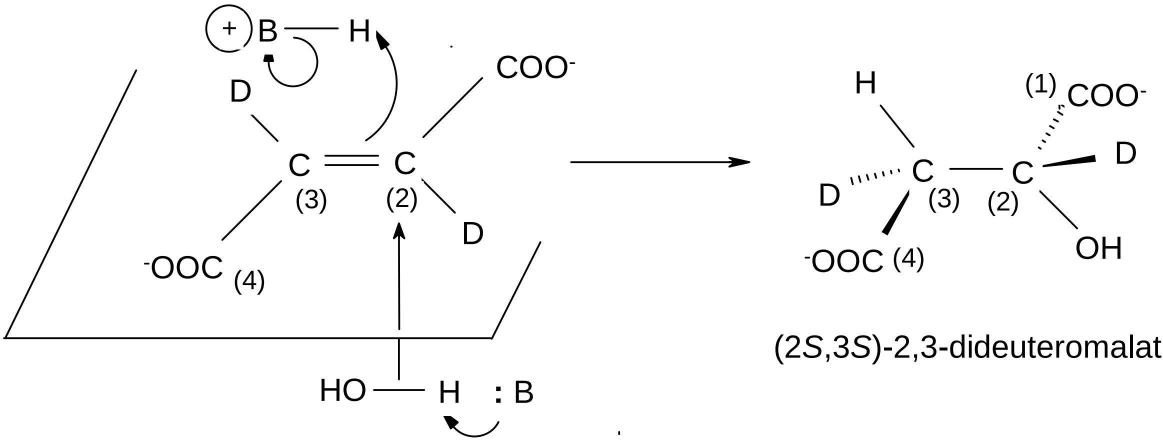
Stereospecific addition, *syn* or *anti*

Syn addition:



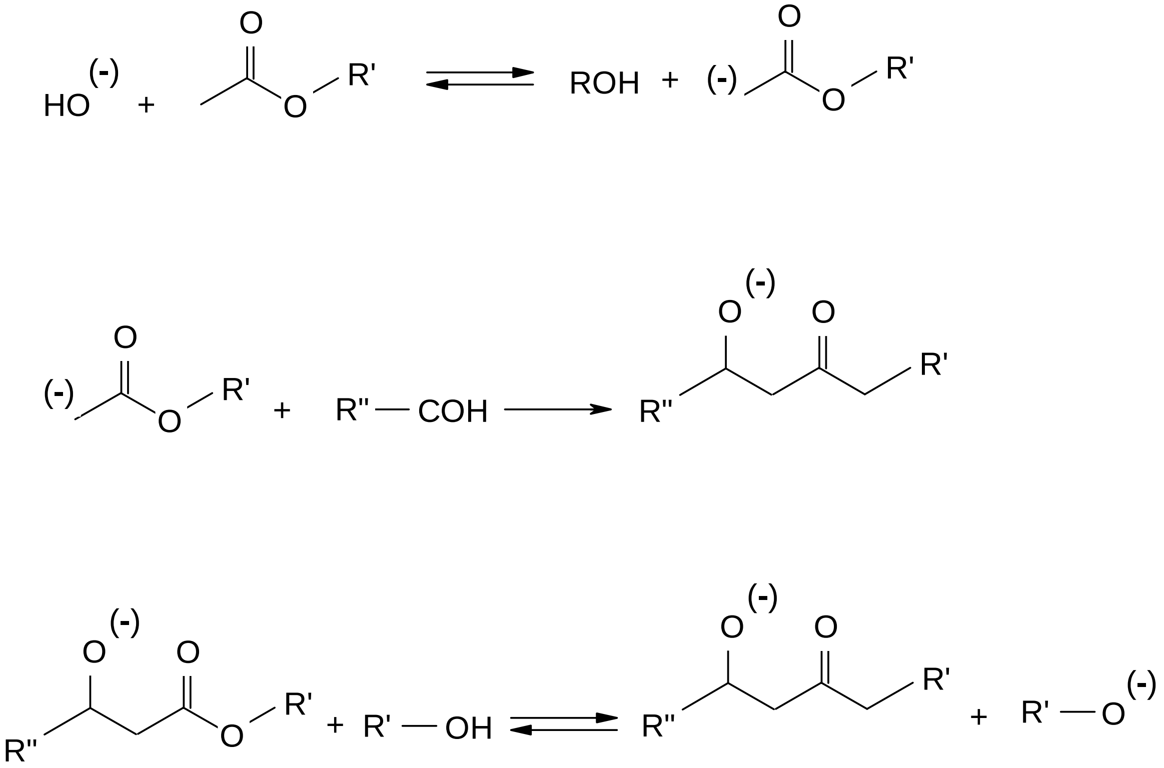
Syn addition would yield 2*S*, 3*R* or 2*R*, 3*S*

Anti addition:



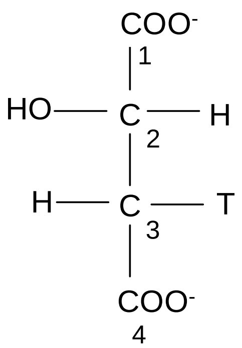
(2*S*,3*S*)-2,3-dideuteromalate

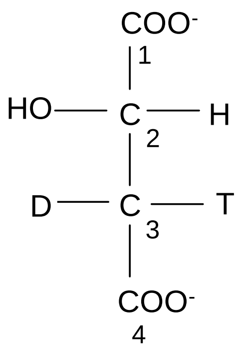
6.5



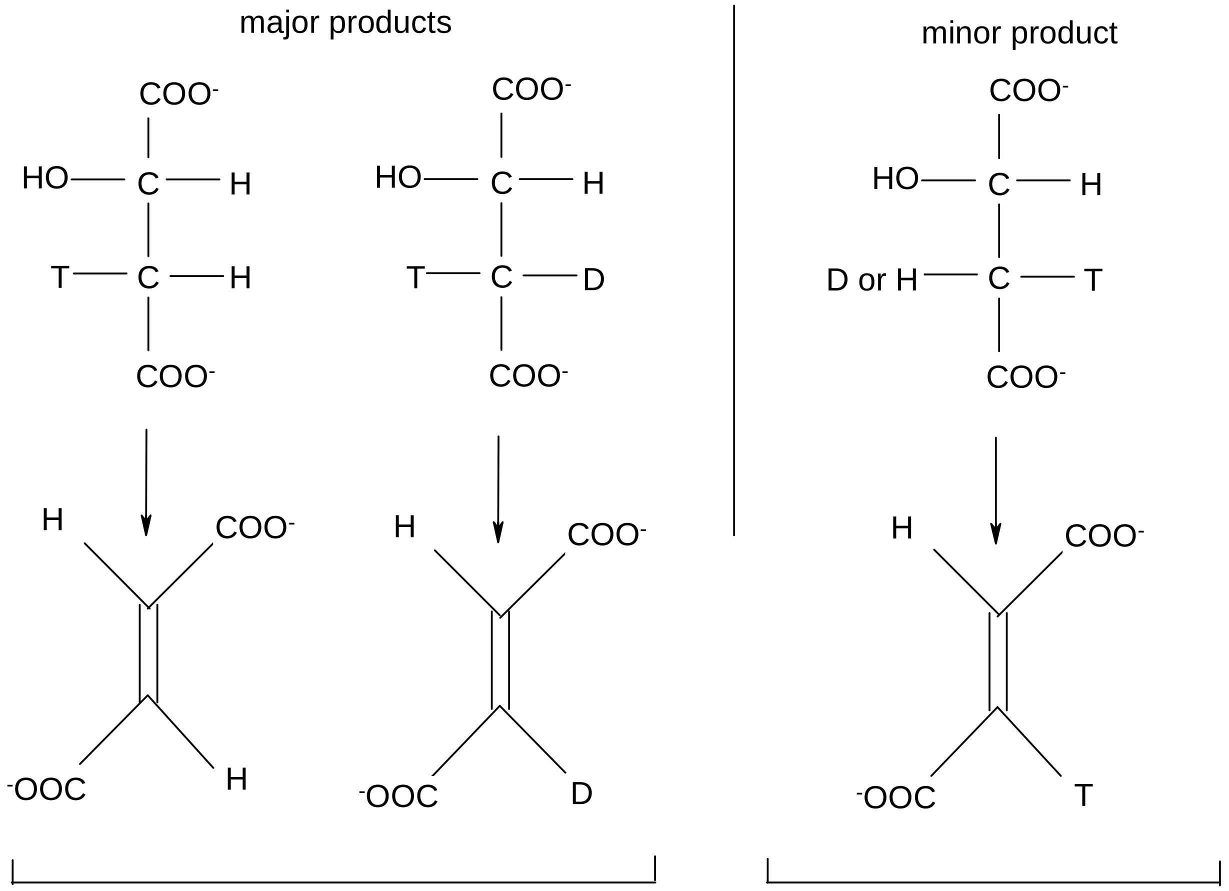
6.6 We would have (2*R*) (3*R*) if the enzyme did not produce enantiospecific addition. Thus: enantiospecific addition *anti*.

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:



79 % non tritiated fumarate

21 % monotritiated fumarate

PROBLEM 7

In this problem tick the appropriate box in the tables of the answer sheet.

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

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

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

The continuous plug flow reactor (Fig. 1)

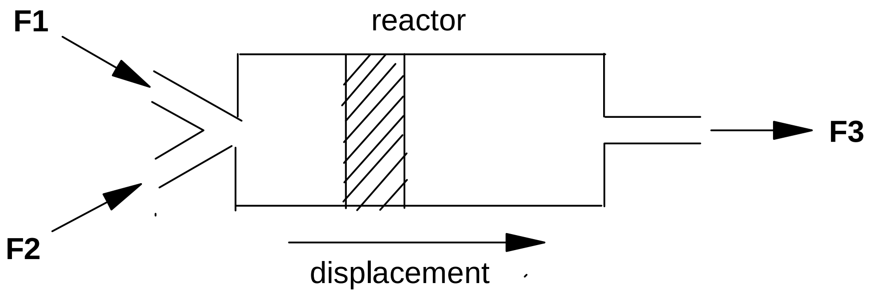


Fig. 1

The reagents are introduced and mixed at the inlet of the reactor (flow F1 and F2). Each slice of the reaction medium (marked zone in the diagram) moves along inside the plug flow reactor without mixing with the others and exits from the reactor (flow F3). When the flow has stabilized, concentrations and conditions are time-independent but dependent on the location in the reactor.

The continuous stirred reactor (Fig. 2)

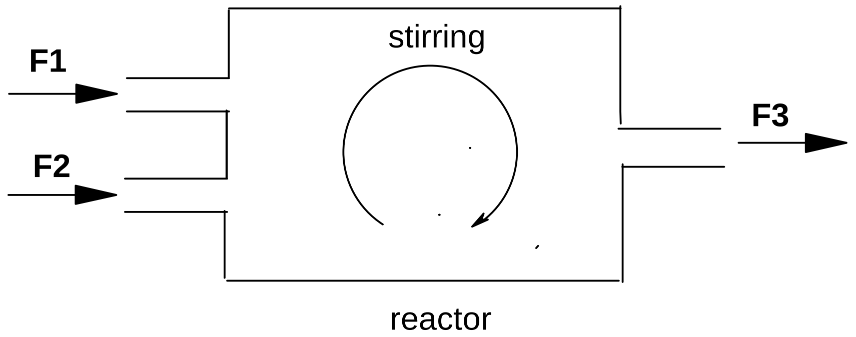


Fig. 2

The reagents are introduced into the reactor (flows F1 and F2). Inside the reactor they are stirred perfectly and instantaneously. When the flow is stabilized, concentrations and conditions are time-independent and identical at every point of the reactor.

The differential yield of hydrogenation (Y) is given by Y = $-\frac{d([C_6H_{12}])}{d([C_6H_6])}$.

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

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

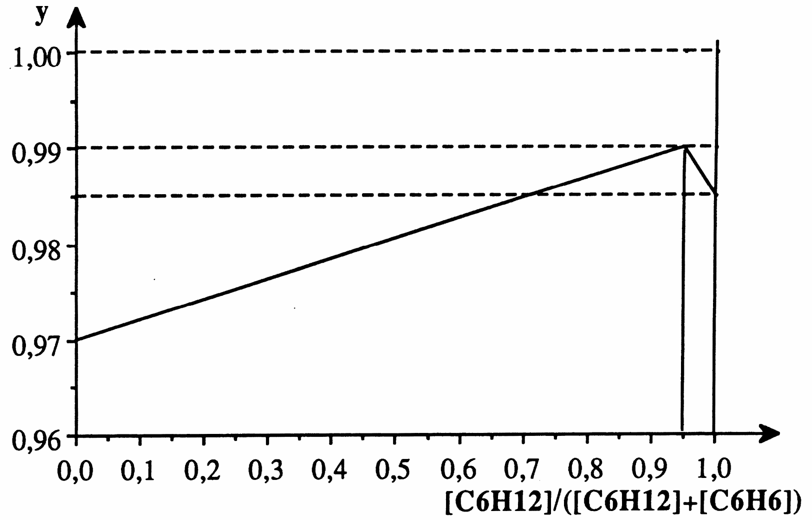


Fig. 3

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

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

7.1 What is the value of p in a continuous stirred reactor leading to the maximal mean yield of hydrogenation? What is the maximal value of Y?

7.2 For a continuous plug flow reactor, give a rough value of Y for 0.9 ≤ 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.

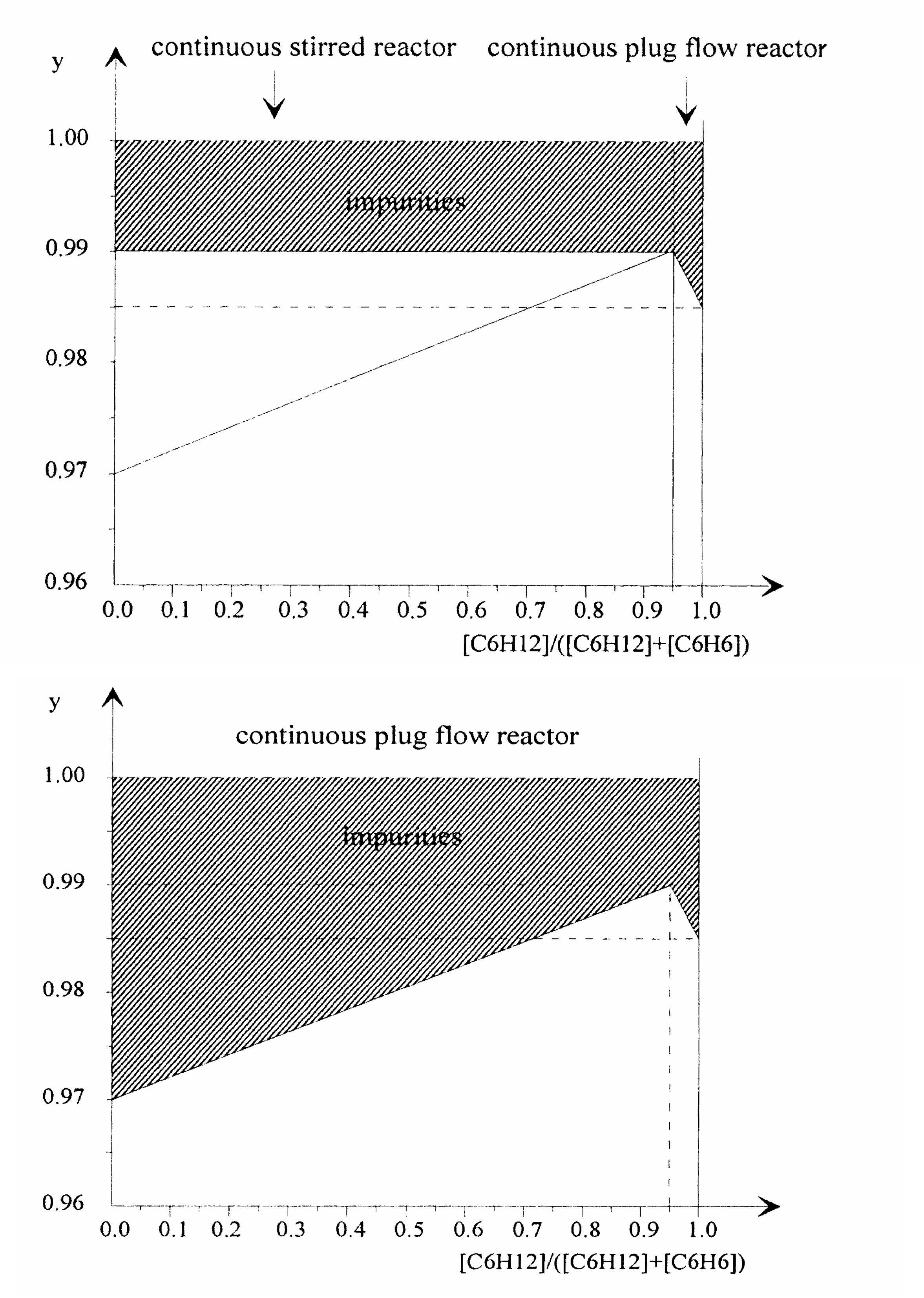
7.3 In the plug flow reactor, the quantity of benzene lost (not hydrogenated) is $1 – p$. Fig. 1 shows the area that represents the amount of benzene that is not hydrogenated and therefore lost. For the installation MP we first have the amount of benzene lost in the continuous stirred reactor which is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

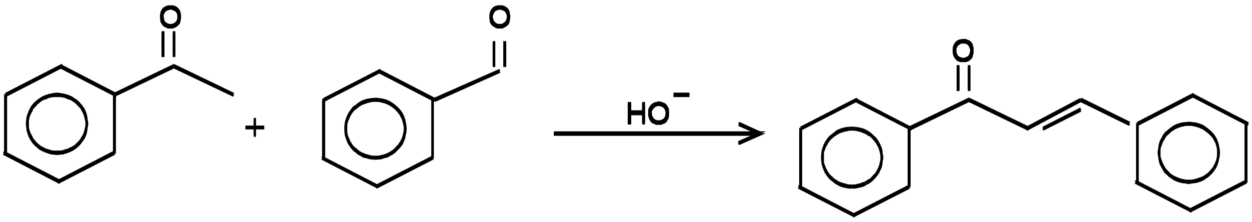

continuous stirred reactor
continuous plug flow reactor
y
1.00
0.99
0.98
0.97
0.96
impurities
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
[C6H12]/([C6H12]+[C6H6])
y
continuous plug flow reactor
1.00
0.99
0.98
0.97
0.96
impurities
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
[C6H12]/([C6H12]+[C6H6])

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:

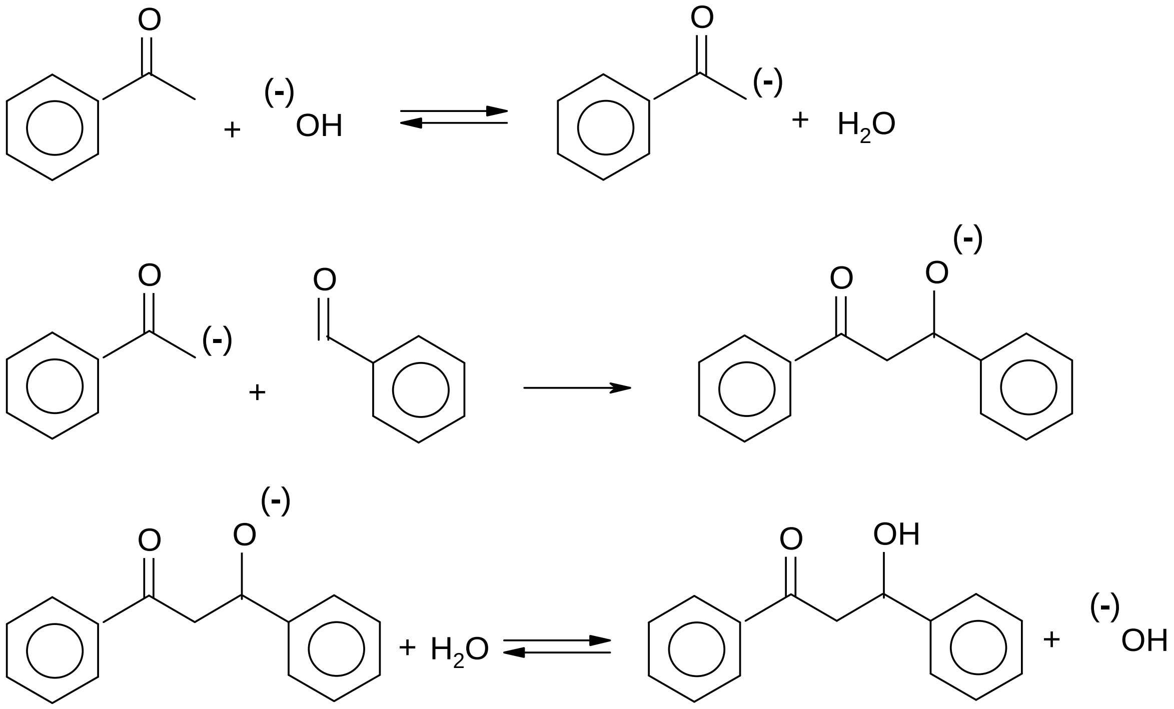
1.1 Write the mechanism for this reaction.

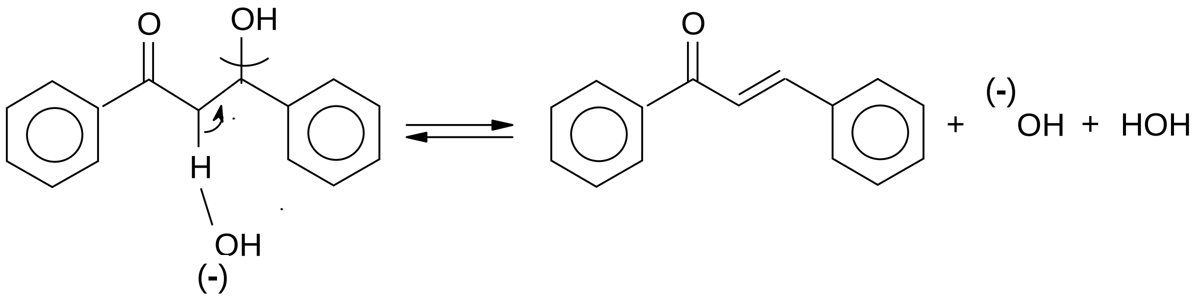
1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.

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 $1\text{ mol } O_2 \triangleq 4\text{ mol Mn(II)} \triangleq 4\text{ mol Mn(III)}$

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

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

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

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).

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

4.2 Calculate V(8) (density of *tert*-BuCl at 20 °C: 850 kg m^{-3}, molar mass of *tert*-BuCl: 92.5 g mol^{-1}).

4.3 Fill in the table on the answer sheet whose columns will be:

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

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 t-BuCl + H_2O $\rightarrow$ t-BuOH + HCl

t = 0	(t-BuCl)$_0$	
t	(t-BuCl)	(t-BuCl)$_0$ – (t-BuCl)
t(8)		(t-BuCl)$_0$

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

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

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

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International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE TWENTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
7–15 JULY 1991, LODZ, POLAND

THEORETICAL PROBLEMS

PROBLEM 1

1.1 Show that 0.1 mol of 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}

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

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

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

Then

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

$$[Tl^+]^2\,[S^{2-}] = \frac{(0.2)^2\times0.1}{1\times10^{20}} = 4\times10^{-23} < K_s(Tl_2S)$$

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):

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

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

  $$[Cu^{2+}]\,[S^{2-}] = \frac{(0.1)^2\times0.1}{1\times10^{20}} \approx 1\times10^{-23} > K_s(CuS)$$

  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) = <u>1.44 V</u>

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

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

$$K = \frac{[NO]^2}{[NO_3^-]^2\,[H^+]^8\,[S^{2-}]^3}$$

From the above equilibrium follows that $[S^{2-}] = \sqrt[3]{\frac{K\,[NO_3^-]^2\,[H^+]^8}{[NO]^2}}$

Since $[NO_3^-] = [H^+] = 1$

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

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

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

However

$$1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1\,K_2} \ll \sqrt[3]{\frac{K}{[NO]^2}} = \sqrt[3]{\frac{1\times10^{144}}{(0.0253)^2}} = 1.16\times10^{49}$$

$$[S^{2-}] = \frac{0.1}{1.16\times10^{49}} = 8.62\times10^{-51}$$

$[Cu^{2+}]\,[S^{2-}] = 0.1 \times 8.62\times10^{-51} = 8.62\times10^{-52} \ll K_{sp}(CuS)\ (= 1\times10^{-35})$

Conclusion: CuS dissolves in 1 M solution of 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** ($C_8H_{14}O_4$).

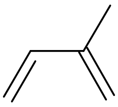
2.6 Sketch the structures of **C**, **D**, **E**, **F** and **Z.**

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**.

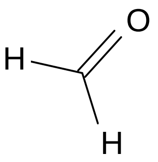
SOLUTION

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

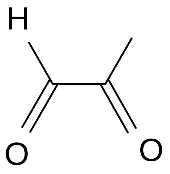
2.2



Y

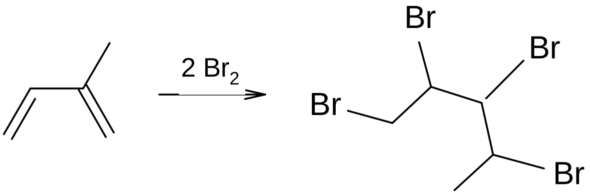


A



B

2.3

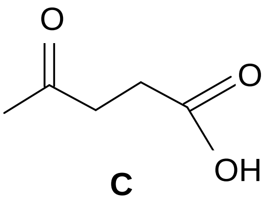


2.4 **Z** = $C_5H_8O_2$

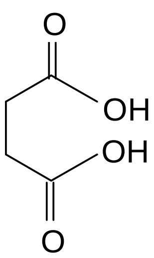
There is one double bond per monomer unit.

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.

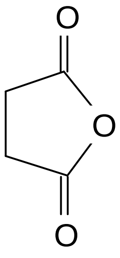
2.6



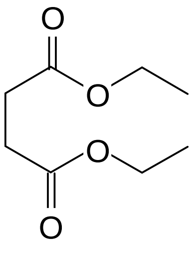
C



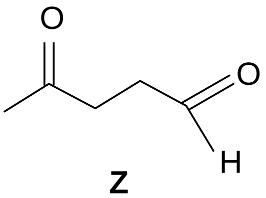
D



E

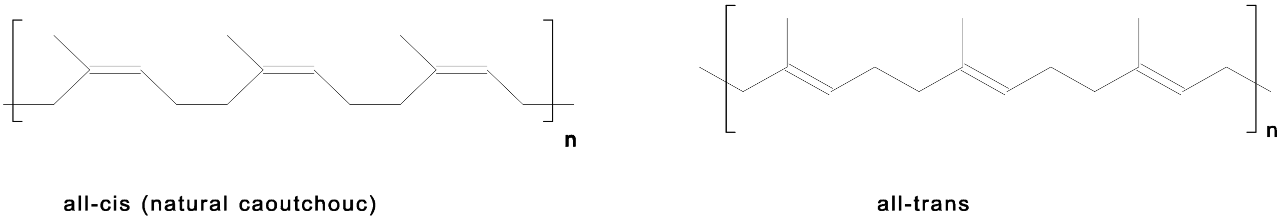


F



Z

2.7 There are two isomeric form (all cis or all trans) possible:



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

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

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

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

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

4.4 The wavelength of an electron is:

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

$(p = m_\text{e}v_\text{e}$ and $E_{\text{kin}} = \dfrac{p^2}{2\,m_\text{e}})$

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

- $k_{\text{ortho}} > k_{\text{para}}$ in compound **B**.
- The effect of the first halogen in the ring: $k_{\text{para}} > k_{\text{ortho}}$.
- 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 Φ = 0, π/2, π, and 3 π/2, where Φ denotes the dihedral or torsional angle in radians and ϑ = 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**.

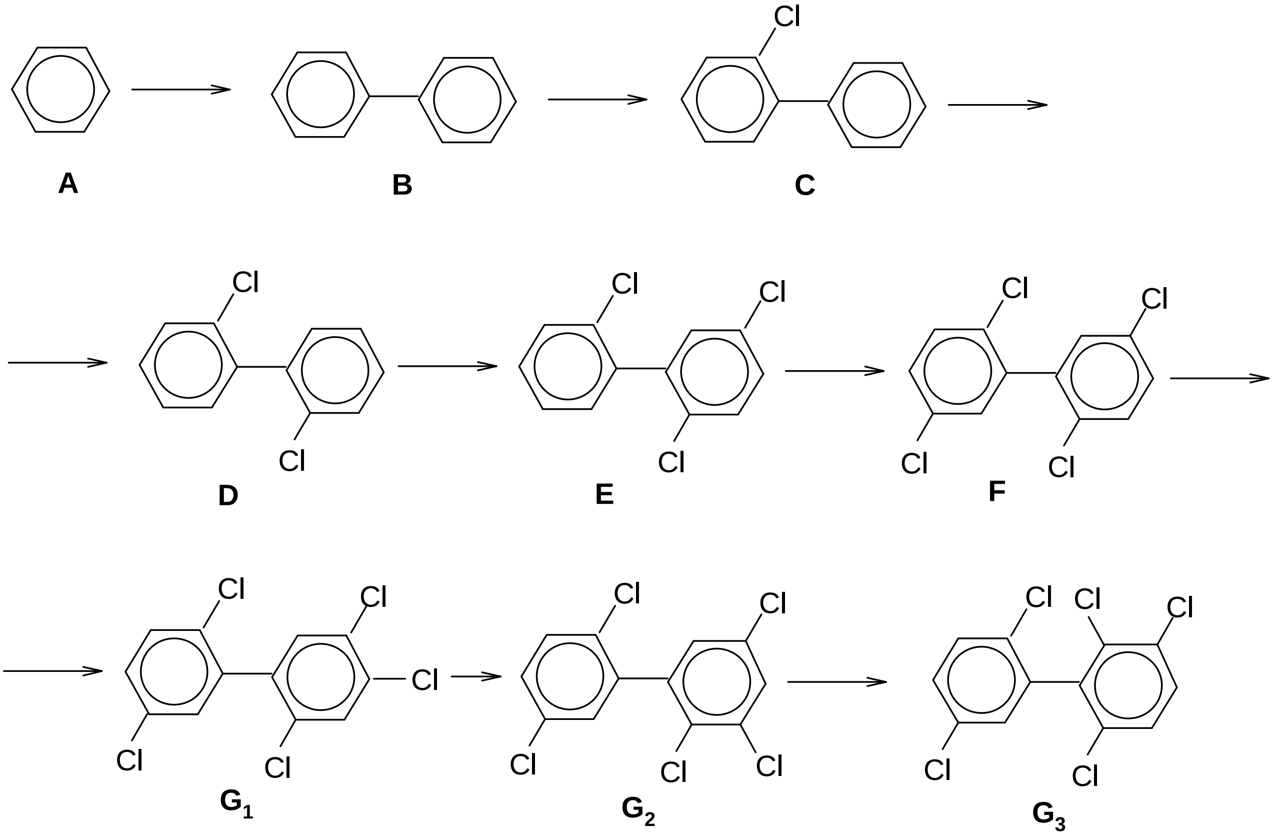
5.5 Give a sequence of $\mathbf{G_1}$, $\mathbf{G_2}$, $\mathbf{G_3}$ according to their increasing difficulty of racemization. Explain your answer.

5.6 Draw stereo-formulas of the enantiomers of $\mathbf{G_3}$.

5.7 Suggest a chemical reaction or a biological method by which compounds like these can be destroyed.

SOLUTION

5.1



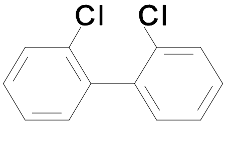
5.2 For the determination of the halogen of **E** we consider the ratio of the isotopic peaks in the mass spectrum.

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

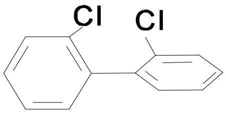
Therefore, with Br we would obtain: x : y = 50.54 : 49.46 ≅ 1 : 1 hence $(x + y)^3 = 1 + 3 + 3 + 1$ and the ratio would be 1 : 3 : 3 : 1 which is not in agreement with the text.

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

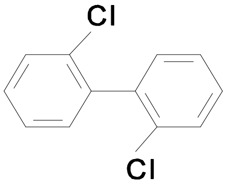
5.3



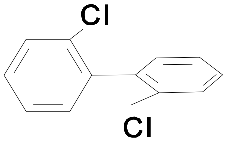
$\Phi = 0\ \pi$



$\Phi = 1/2\ \pi$

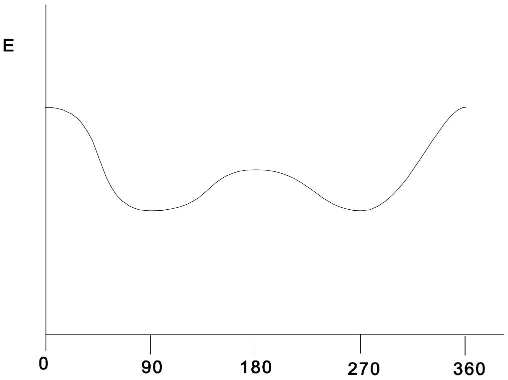


$\Phi = \pi$

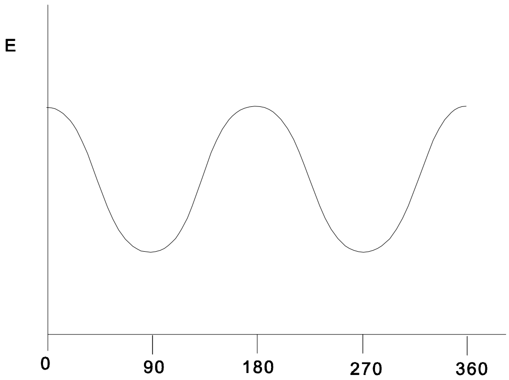


$\Phi = 3/2\ \pi$

5.4



Compound C

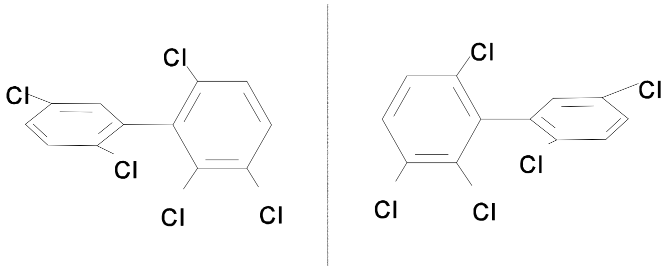


Compound D

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: $m_1 l m_2 = x$ 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)

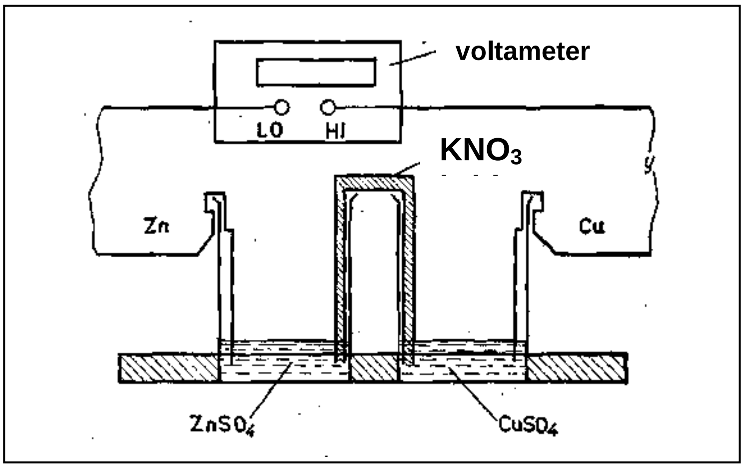


Fig. 1

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:

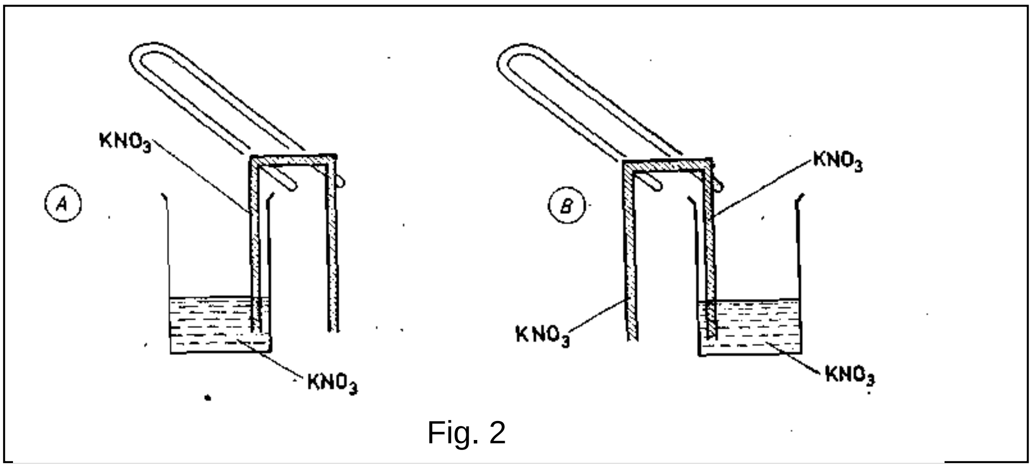


Fig. 2

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).

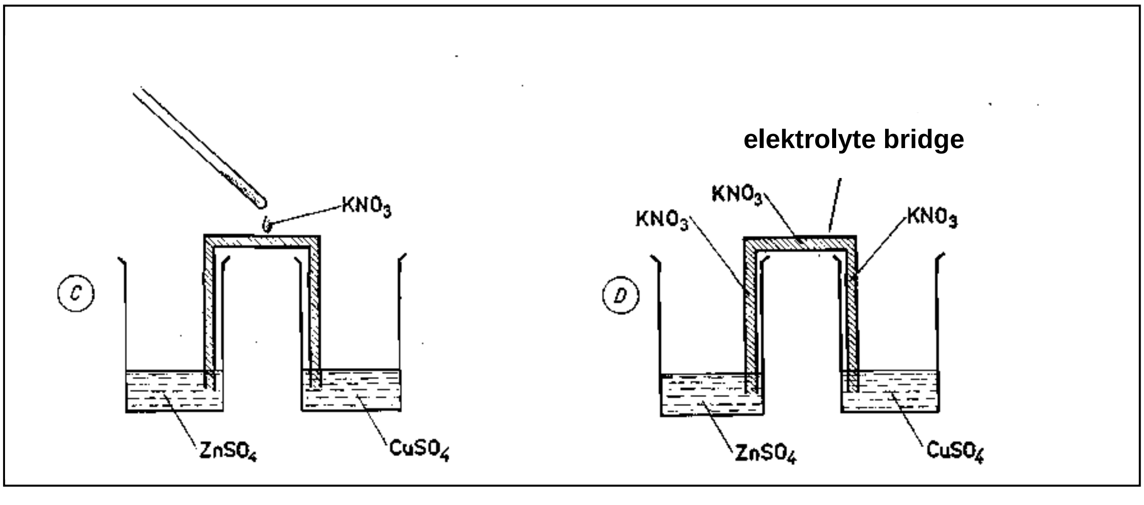


Fig. 3

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
$$E = \left(E^0(\mathrm{Cu^{2+}/Cu}) + \frac{RT}{2F}\ln([\mathrm{Cu^{2+}}]\times f_{Cu^{2+}}) \right) - \left(E^0(\mathrm{Zn^{2+}/Zn}) + \frac{RT}{2F}\ln([\mathrm{Zn^{2+}}]\times f_{Zn^{2+}}) \right) - E_{dif}$$

For $E_{dif} = 0$:

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

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:

$$[\mathrm{Cu(NH_3)_4^{2+}}] = \frac{c(\mathrm{Cu^{2+}})\times V}{V + V_1}$$

$$[\mathrm{NH_3}] = \frac{(c(\mathrm{NH_3})\times V_1) - (4\,c(\mathrm{Cu^{2+}})\times V)}{V + V_1}$$

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

$$\mathrm{Cu^{2+} + 4\ NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}}$$

$$\beta_4 = \frac{[\mathrm{Cu(NH_3)_4^{2+}}]\times f_{\mathrm{Cu(NH_3)_4^{2+}}}}{[\mathrm{Cu^{2+}}]\times f_{\mathrm{Cu^{2+}}} \times [\mathrm{NH_3}]^4}$$

Then the Nernst equation has the form:

$$E_1^{'} = E^0(\text{Cu}^{2+}/\text{Cu}) = \frac{RT}{2F}\ln\frac{[\text{Cu(NH}_3)_4^{2+}]\times f_{\text{Cu(NH}_3)_4^{2+}}}{\beta_4 \times [\text{NH}_3]^4}$$

$$E_B = E'_1 - E_2 = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F}\ln\frac{[\text{Cu(NH}_3)_4^{2+}]\times f_{\text{Cu(NH}_3)_4^{2+}}}{[\text{Zn}^{2+}]\times f_{Zn^{2+}} \times \beta_4 \times [\text{NH}_3]^4}$$

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 $\text{Zn(NH}_3)_4^{2+}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\text{Cu(NH}_3)_4^{2+}$.

24th

International Chemistry Olympiad

9 theoretical problems
1 practical problem

THE TWENTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
11–22 July 1992, PITTSBURGH, UNITED STATES OF AMERICA

THEORETICAL PROBLEMS

PROBLEM 1

Diatoms, microscopic organisms, are an abundant food source in the oceans producing carbohydrates from carbon dioxide and water by photosynthesis:

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

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.

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

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

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

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

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.

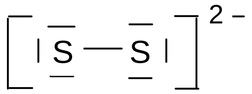
2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, FeO(OH).

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 =

$2 \text{ yr} \times 365 \text{ days yr}^{-1} \times 24 \text{ h day}^{-1} \times 60 \text{ min h}^{-1} \times 20.0 \text{ dm}^3 \text{ min}^{-1} =$

$= 2.10\times10^7 \text{ dm}^3$ of water

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

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

mass of deposited Fe_2O_3:

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

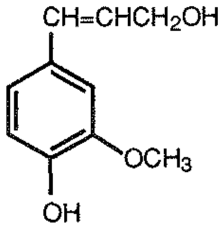
Coniferyl alcohol reacts with cold HBr to form **D** ($C_{10}H_{11}O_2Br$). Hot HI converts ArOR to ArOH and RI. Coniferyl alcohol reacts with excess hot HI to give **E** ($C_9H_9O_2I$) and CH_3I. CH_3I in aqueous base reacts with coniferyl alcohol to form **F** ($C_{11}H_{14}O_3$), which is not soluble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

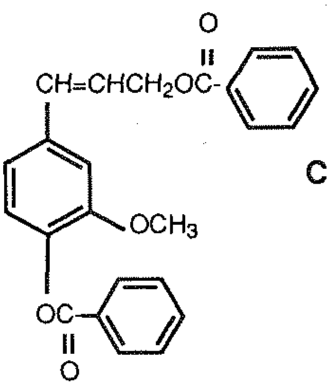
SOLUTION

3.1

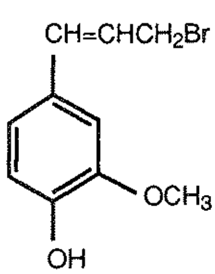


coniferyl alcohol

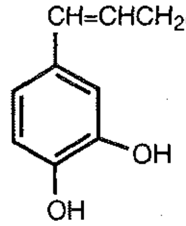
$O{=}CHCH_2OH$ **B**



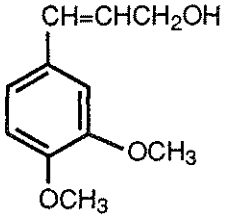
C



D

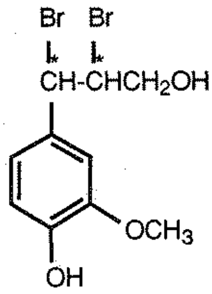


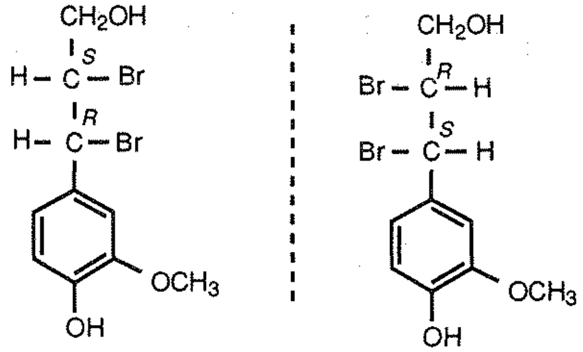
E

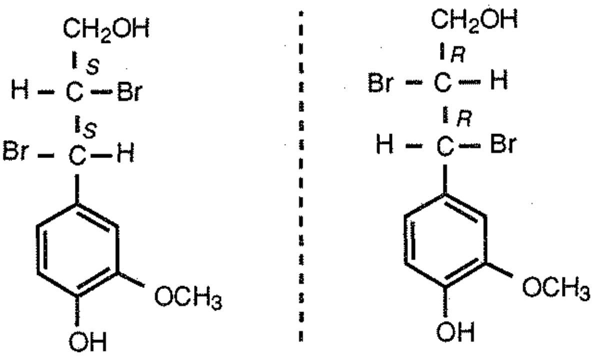


F

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



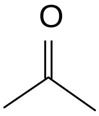


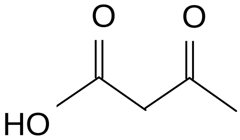


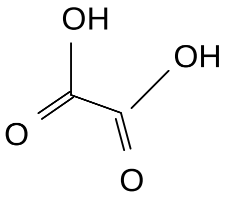
PROBLEM 4

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.**

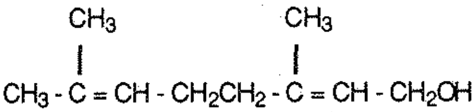
4.2 Give the structure of compound **B.**

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

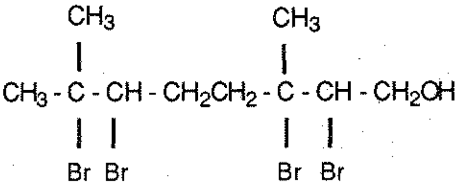
4.1



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

geraniol **A**

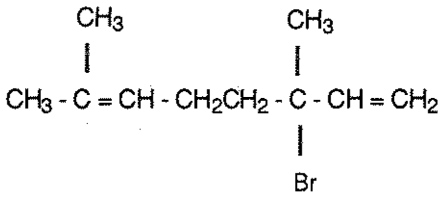
4.2



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

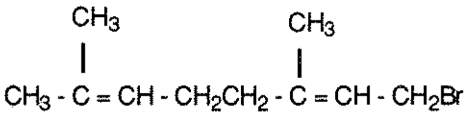
B

4.3



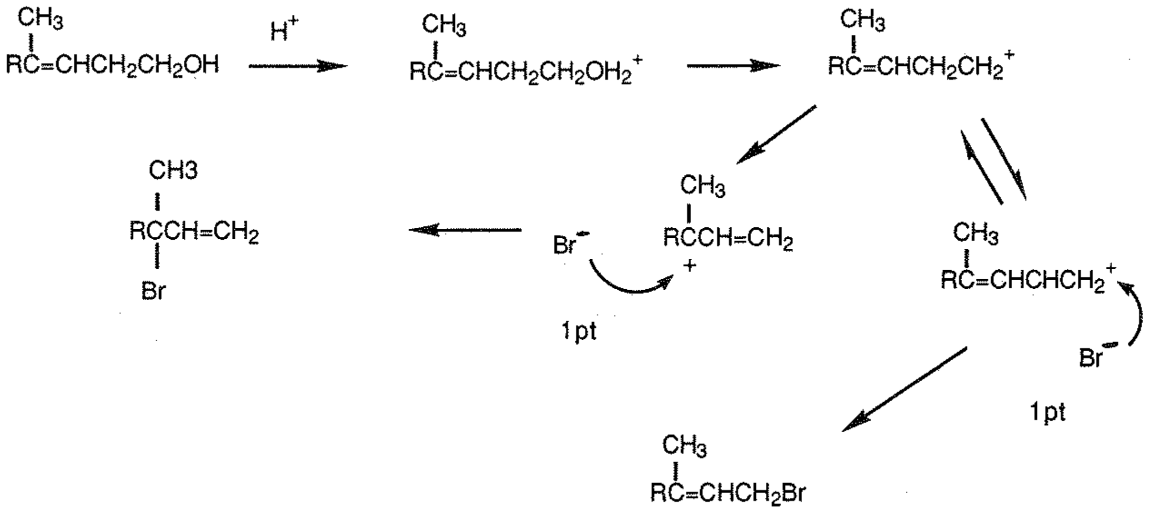
$CH_3 - \overset{CH_3}{C} = CH - CH_2CH_2 - \underset{Br}{\overset{CH_3}{C}} - CH = CH_2$

or



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

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.

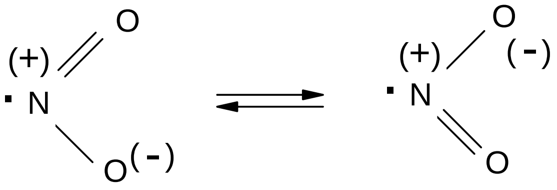
5.4 If ΔH^o for the reaction $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?

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?

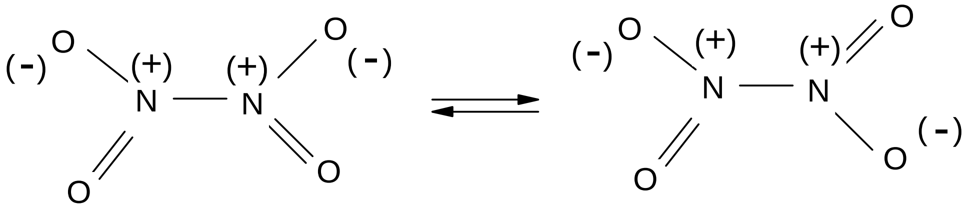
5.6 The association of NO_2(g) to give N_2O_4(g) is a second-order process with a specific rate constant of 9.8×10^6 $dm^3mol^{-1}s^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c, at 298 K for the reaction $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$

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

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

$N_2O_4\,(g) \rightarrow 2\,NO_2\,(g) \qquad \Delta G^o = 5.4$ 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:

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

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

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

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

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

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

T_2 = 318 K

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

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

$$t\ =\ 4.2\times10^{-6}\ \mathrm{s}$$

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

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

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

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 $[H^+] = 2.57\times10^{-6}$; $\underline{pH = 5.59}$

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

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

6.4 Since the reaction is endothermic, the equilibrium constant will increase with temperature. Therefore, $[H^+]$ will also increase and the *pH* will <u>decrease</u>.

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:

$$AgCl(s) \rightarrow Ag(s) + \tfrac{1}{2} Cl_2(g).$$

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 $n(\text{Ag}^+) = n(\text{Cl}^-)$

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

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 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}\downarrow(\text{s})$

7.4 $2\ \text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4\downarrow(\text{s})$ (brick-red colour)

7.5 $K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 4\ x^3$ if $x = [\text{Ag}^+]$ $\Rightarrow$

$[\text{Ag}^+] = 7.07 \times 10^{-6}$; $[\text{CrO}_4^{2-}] = 2 \times 10^{-2}$

$$[\text{Cl}^-] = \frac{K_{sp}(\text{AgCl})}{\left[\text{Ag}^+\right]} = \frac{1.78 \times 10^{-10}}{7.07 \times 10^{-6}} = 2.5 \times 10^{-5}$$

7.6 $2\ \text{CrO}_4^{2-} + 2\ \text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$

either/or

$\text{CrO}_4^{2-} + \text{H}^+ \rightarrow \text{HCrO}_4^- + \text{H}_2\text{O}$

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 $m(\text{NaH}_2\text{PO}_4) = 0.10\ \text{mol dm}^{-3} \times 0.500\ \text{dm}^3 \times 119.98\ \text{g mol}^{-1} = 6.0\ \text{g}$

$m(\text{Na}_2\text{HPO}_4) = 0.10\ \text{mol dm}^{-3} \times 0.500\ \text{dm}^3 \times 141.96\ \text{g mol}^{-1} = 7.1\ \text{g}$

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

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

mol Cl$^-$ in sample:

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

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

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

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

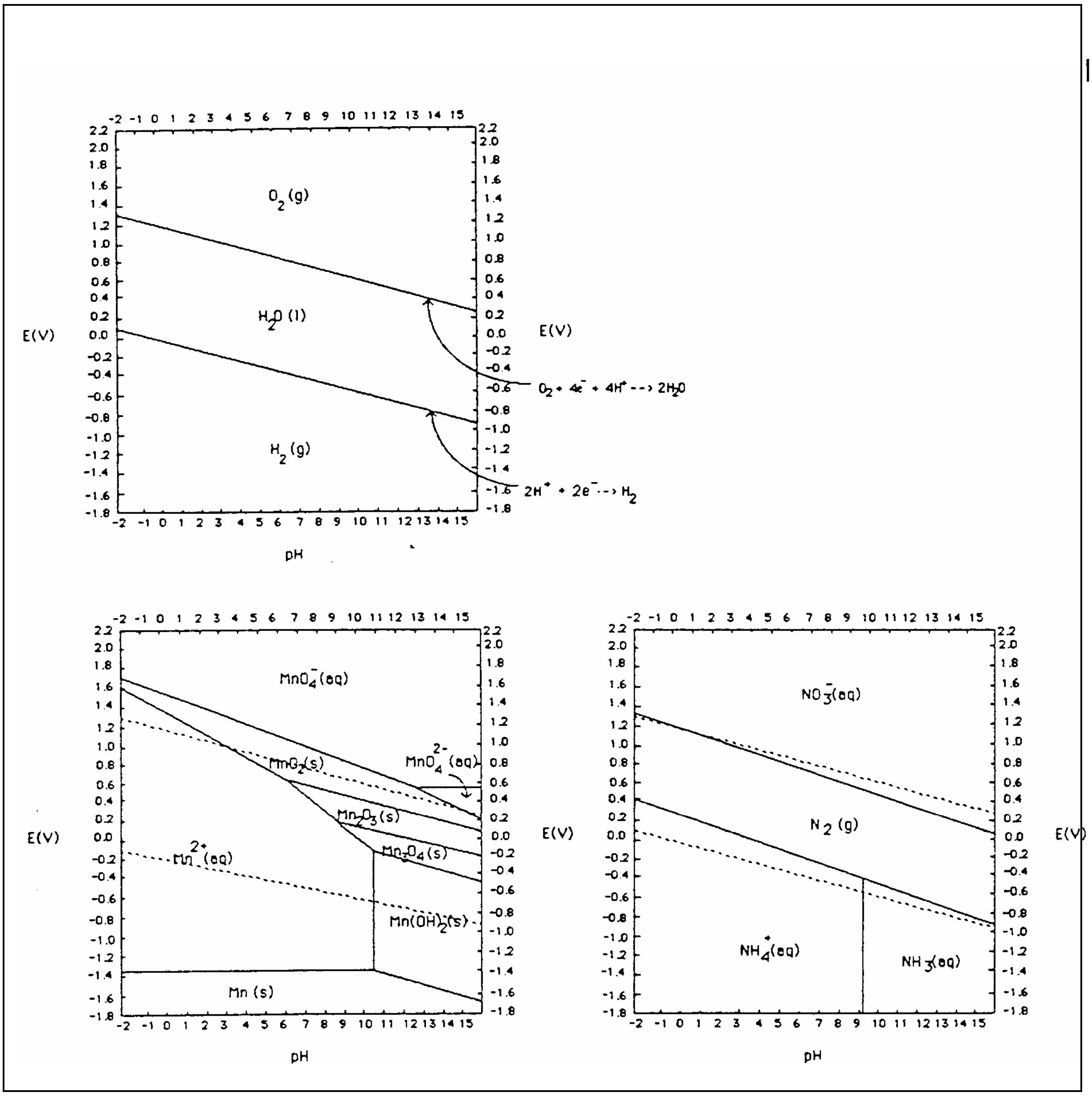
8.7 According to the Pourbaix diagrams, is it dangerous to grind together in a mortar and pestle

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.

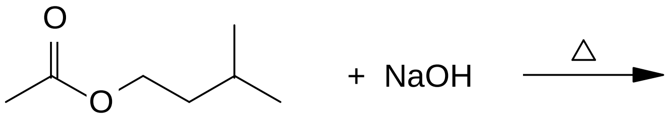
8.8 $$E = E^o + \frac{0.0591}{3}\log[MnO_4^-] + \frac{0.0591}{3}\log[H^+]^4) =$$

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

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.

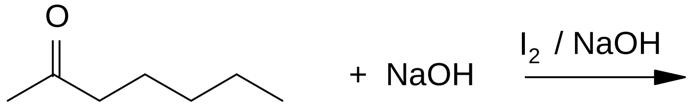
9.1



isoamyl acetate,
bee alarm pheromene

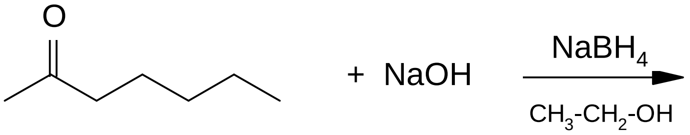
9.2

i)

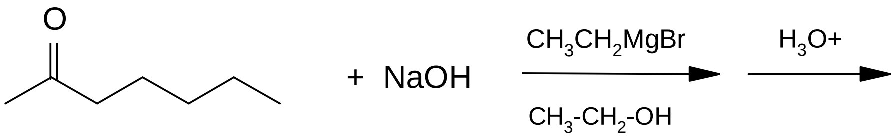


2-heptanone
ant alarm pheromone

ii)

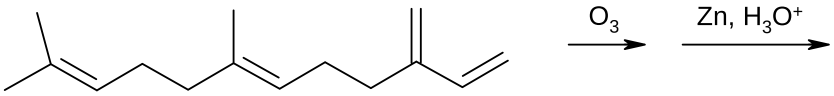


iii)



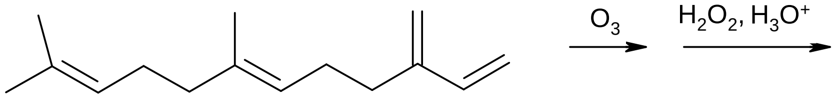
9.3

i)



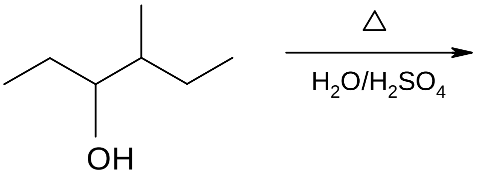
green peach -
aphid pheromone

ii)

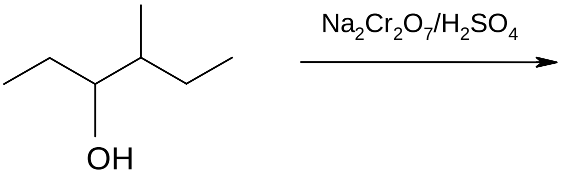


9.4

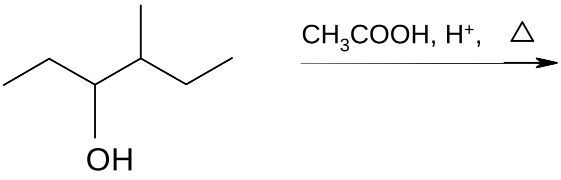
(i)



(ii)

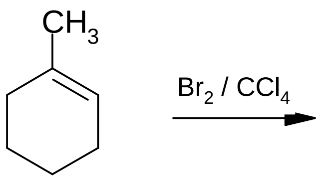


(iii)

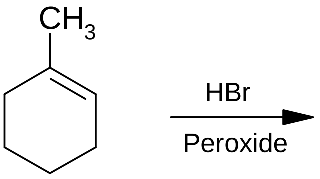


9.5

i)



iv)



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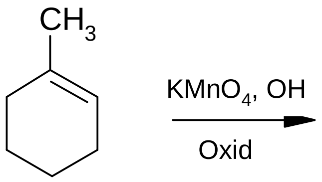
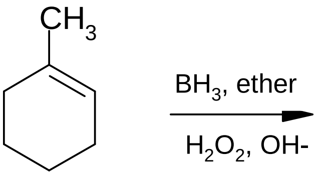
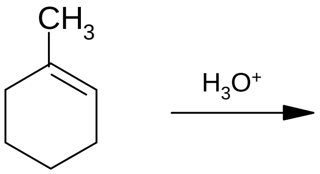


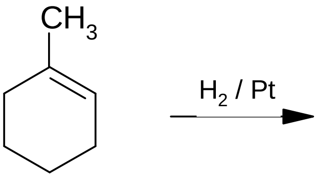
v)



iii)

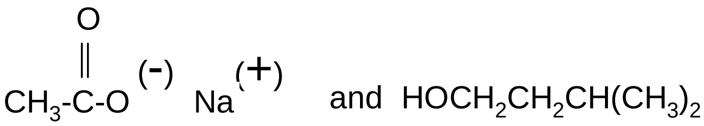


vi)



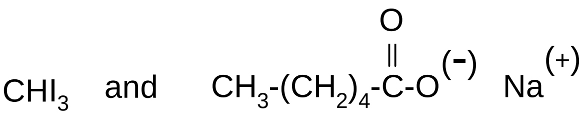
SOLUTION

9.1



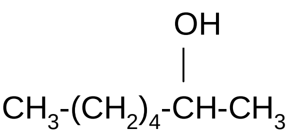
$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^{(-)}\ Na^{(+)}$ and $HOCH_2CH_2CH(CH_3)_2$

9.2 i)



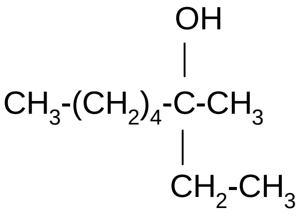
CHI_3 and $CH_3\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^{(-)}\ Na^{(+)}$

ii)



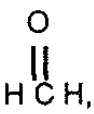
$CH_3\text{-}(CH_2)_4\text{-}\overset{\overset{OH}{|}}{C}H\text{-}CH_3$

iii)

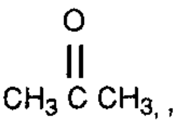


$CH_3\text{-}(CH_2)_4\text{-}\underset{\underset{CH_2\text{-}CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_3$

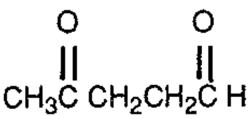
9.3 i)



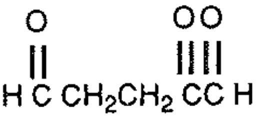
$H\overset{\substack{O\\ \|}}{C}H$,



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

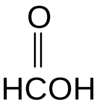


$CH_3\overset{\substack{O\\ \|}}{C}CH_2CH_2\overset{\substack{O\\ \|}}{C}H$,

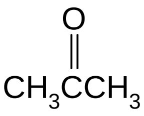


$H\overset{\substack{O\\ \|}}{C}CH_2CH_2\overset{\substack{O\\ \|}}{C}\overset{\substack{O\\ \|}}{C}H$

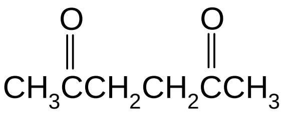
ii)



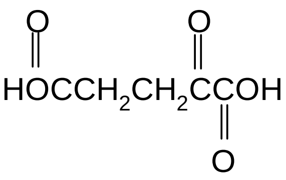
$H\overset{\substack{O\\ \|}}{C}OH$



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

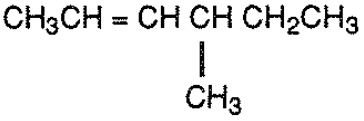


$CH_3\overset{\substack{O\\ \|}}{C}CH_2CH_2\overset{\substack{O\\ \|}}{C}CH_3$

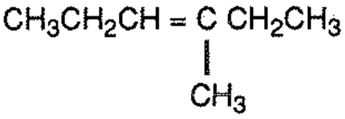


$HO\overset{\substack{O\\ \|}}{C}CH_2CH_2\overset{\substack{O\\ \|}}{C}\underset{\substack{\|\\ O}}{C}OH$

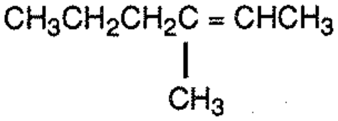
9.4 i)



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

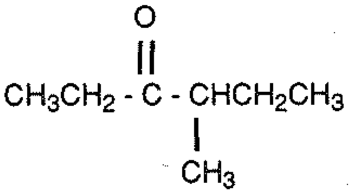


$CH_3CH_2CH=\underset{\substack{|\\ CH_3}}{C}CH_2CH_3$



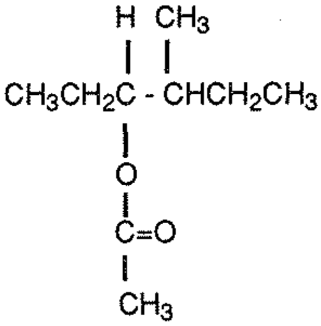
$CH_3CH_2CH_2\underset{\substack{|\\ CH_3}}{C}=CHCH_3$

(ii)



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

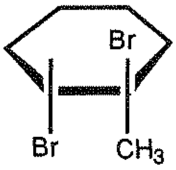
(iii)



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

9.5

(i)



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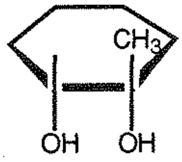

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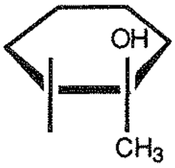

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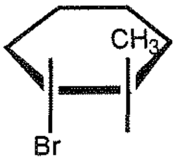

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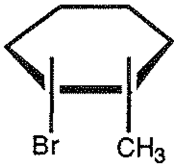

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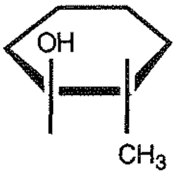
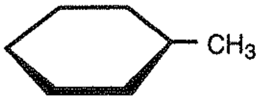


(vi)



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 ^oC 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) <u>Procedure for standardization of EDTA</u>

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

IChO

International Chemistry Olympiad

5 theoretical problems
2 practical problems

THE TWENTY-FIFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
11–22 JULY 1993, PERUGIA, ITALY

THEORETICAL PROBLEMS

PROBLEM 1

^{131}I is a radioactive isotope of iodine (e^- emitter) used in nuclear medicine for analytical procedures to determine thyroid endocrine disorders by scintigraphy. The decay rate constant, k, of ^{131}I is 9.93×10^{-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:

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

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

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:

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

$t_{1/2}$ 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 μcm^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:

$N = 2.56 \times 10^4 \times (25/100) = 64 \times 10^2$

By substituting of α, *K* and *N* values in equation 1, the resolution for each pair of peaks can be found.

For column A:

$$\alpha_{GCA/CA} = \frac{399-120}{380-120} = \frac{279}{260} = 1.07$$

$$K'_{GCA} = \frac{399-120}{120} = 2.32$$

$$R_{GCA/CA} = \frac{\sqrt{64\cdot 10^2}}{4}\times\frac{0.07}{1.07}\times\frac{2.32}{3.32} = 0.91$$

$$\alpha_{i.s./GCA} = \frac{422-120}{399-120} = \frac{322}{279} = 1.15$$

$$K'_{i.s.} = \frac{442-120}{120} = 2.68$$

$$R_{i.s./GCA} = \frac{\sqrt{64\cdot 10^2}}{4}\times\frac{0.15}{1.15}\times\frac{2.68}{3.68} = 1.9$$

For column B:

$$\alpha_{GCA/CA} = \frac{395-130}{350-130} = \frac{265}{220} = 1.20$$

$$K'_{GCA} = \frac{395-130}{130} = 2.04$$

$$R_{GCA/CA} = \frac{\sqrt{64\cdot 10^2}}{4}\times\frac{0.20}{1.20}\times\frac{2.04}{3.04} = 2.2$$

$$\alpha_{i.s./GCA} = \frac{430-130}{395-130} = \frac{300}{265} = 1.13$$

$$K'_{i.s.} = \frac{430-130}{130} = 2.31$$

$$R_{i.s./GCA} = \frac{\sqrt{64\cdot 10^2}}{4}\times\frac{0.13}{1.13}\times\frac{2.31}{3.31} = 1.6$$

For column B the minimum value of *R* is 1.6 (>1.5) so that complete separation is obtained. For column A, *R* = 0.91 (<1.5) for the pair GCA/CA which, then, is not completely separated. Therefore column B should be used.

2.2 The amount of acid in the extract solution (1 cm^3) can be calculated from the relationship:

$$\frac{\text{μmoles}_{\text{acid}}}{\text{μmoles}_{\text{i.s.}}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F}$$

where F is the response factor.

Therefore:

$$\text{μmoles}_{\text{acid}} = \frac{\text{Area}_{\text{acid}}}{\text{Area}_{\text{i.s.}} \times F} \times \text{μmoles}_{\text{i.s.}} \times \frac{1000}{100}$$

$$n(\text{CA}) = \frac{2200}{2304} \times \frac{1}{0.5} \times 2.7 \times 10 = 51.6\ \text{μmol}$$

$$n(\text{GCA}) = \frac{3520}{2304} \times \frac{1}{0.2} \times 2.7 \times 10 = 206\ \text{μmol}$$

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}.

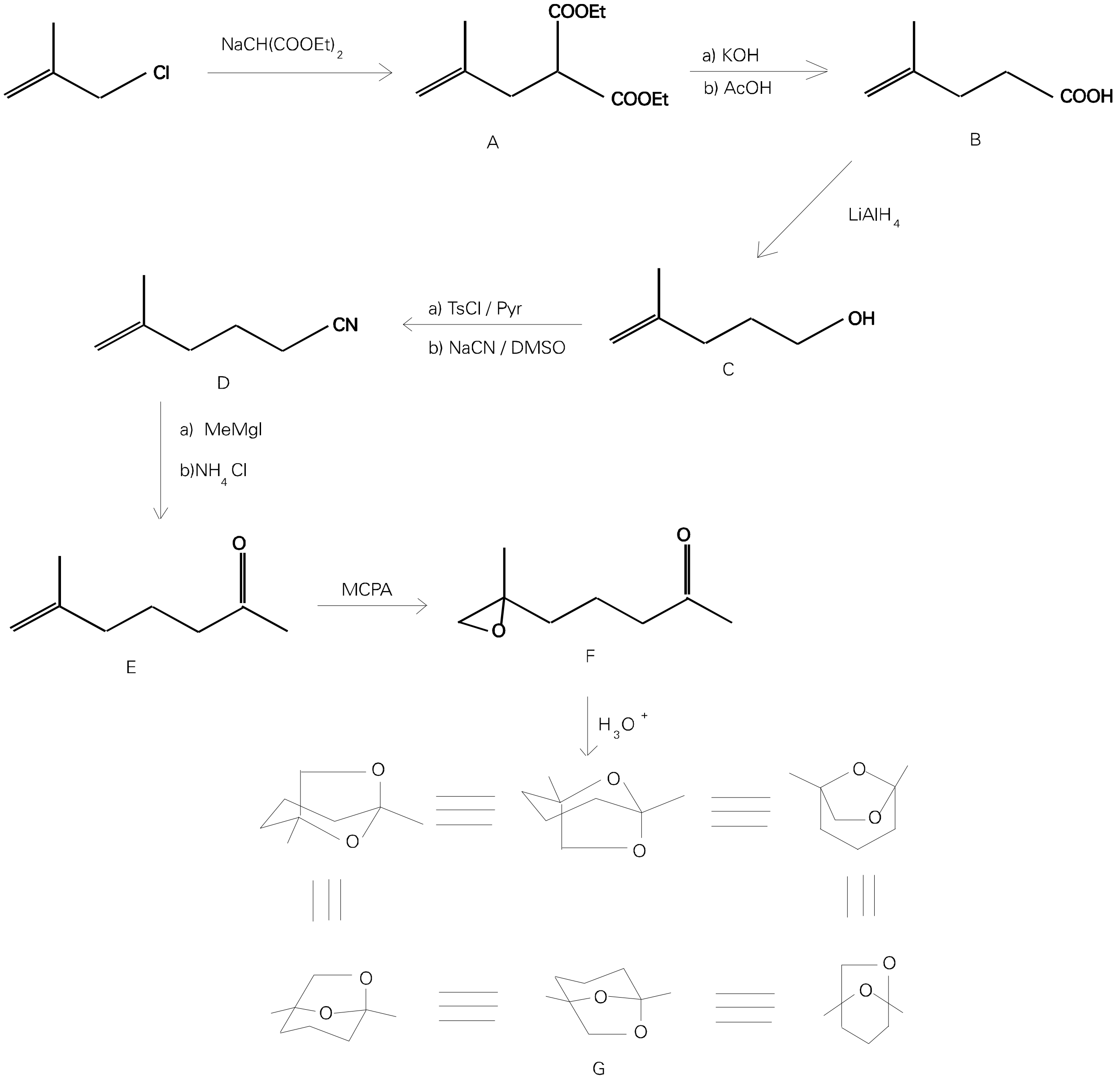
vi) The epoxidation of **E** with metachloroperbenzoic acid then affords **F** ($C_8H_{14}O_2$) which, by treatment with diluted acids is converted to frontalin acetal **G**.

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
LiAlH4
OH
C
a) TsCl / Pyr
b) NaCN / DMSO
CN
D
a) MeMgI
b)NH4Cl
O
E
MCPA
O
O
F
H3O+
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:

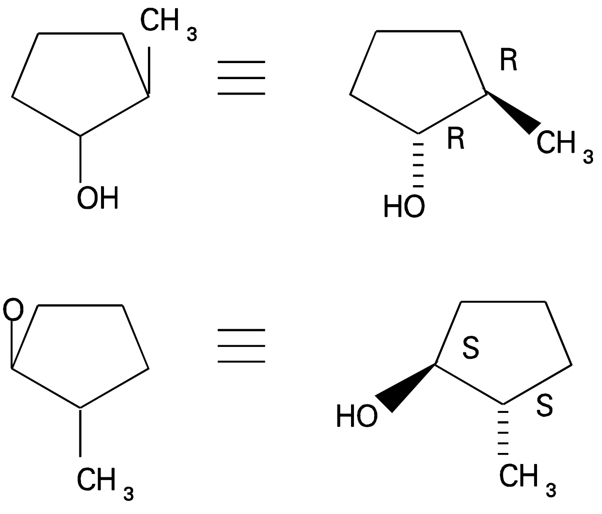
5.1 Write the structures of the alcohols.

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

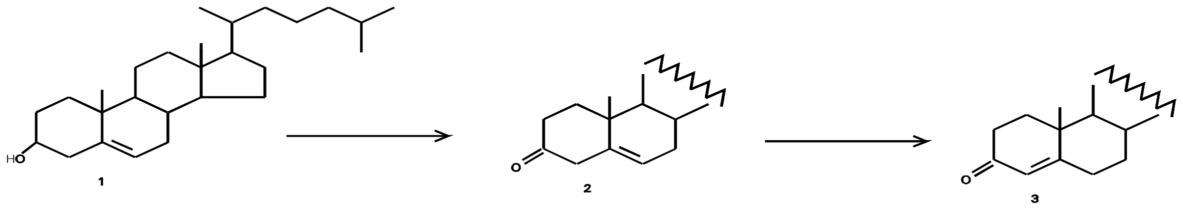
PROBLEM 1 (Practical)

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.

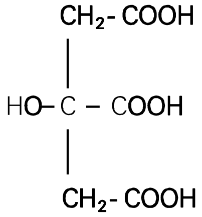
Some additional points were given for melting point measurements.

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*.

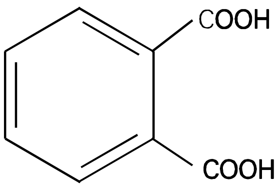
It is utilized as an acidulant and antioxidant in several beverages.



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

MM = 192.12 g/mol

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



MM = 204.23 g/mol

a) Standardization of NaOH solution (ca 0.1 mol dm^{-3}) by potassium hydrogen phthalate

Procedure:

A preweighed quantity (2.050 g) of potassium hydrogen phthalate is in the 100 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

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

$c_0 - x \qquad\qquad x \qquad x$

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

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

Reaction 1 = 2 + 3, $K_1 = K_2 \cdot K_3 = 311 \quad (3.1\times10^2)$

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

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

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

Before: 0.0030 0.024 0 0

After : 0 0.021 0.0030 0.0030

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

(Control: $\dfrac{K_{HL}}{[H_3O^+]} = \dfrac{[L^-]}{[HL]} = 2.2\times10^3$, 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) $[HCO_3^-]_B + [H_2CO_3]_B = 0.0239 \quad (0.024)$

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

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

$c_0 \quad c_0$

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

$c_0 - x \quad x \quad x$

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

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

pH = 1.39

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

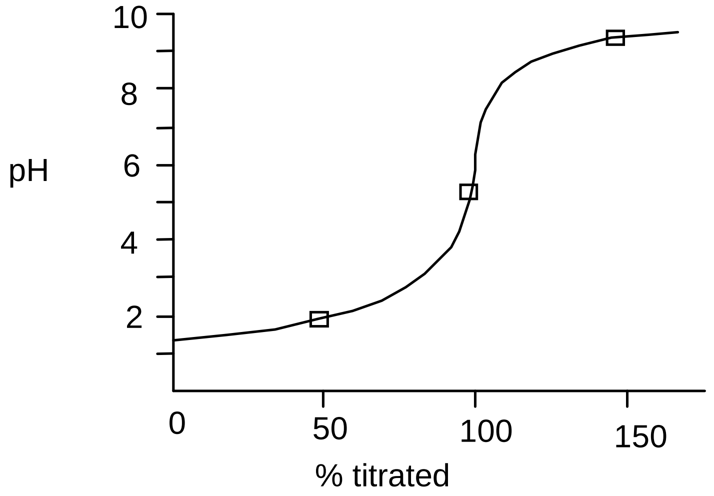
$pH = 1.77$

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

$pH = 5.30$

28.95 cm^3 added: $\boldsymbol{pH} = \mathrm{p}K_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.24 + \log \frac{1.01}{2.01} = 8.94$

2.3



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

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

1 N: $M_r = 73.01$ 2 N: $M_r = 146.02$

PROBLEM 3

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

3.1 Write Lewis structures for molecules SCl_2, SO_3, SO_2ClF, SF_4, and $SBrF_5$.

3.2 Carefully draw the geometries of the 5 molecules. (Disregard small deviations from "ideal" angles.)

3.3 A compound, consisting of sulphur (one atom per molecule), oxygen and one or more atoms of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests?

i) Addition of HNO_3 and $AgNO_3$.

ii) Addition of $Ba(NO_3)_2$.

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.

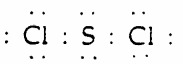
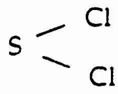
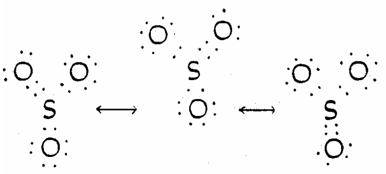
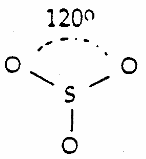
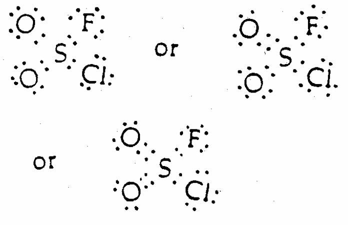
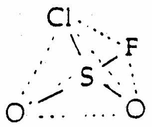
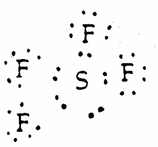
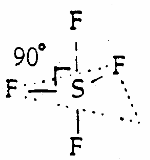
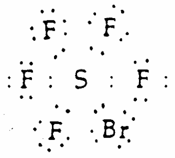
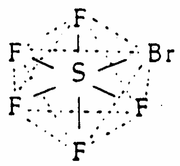
3.5 Finally, a simple quantitative analysis was undertaken:

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

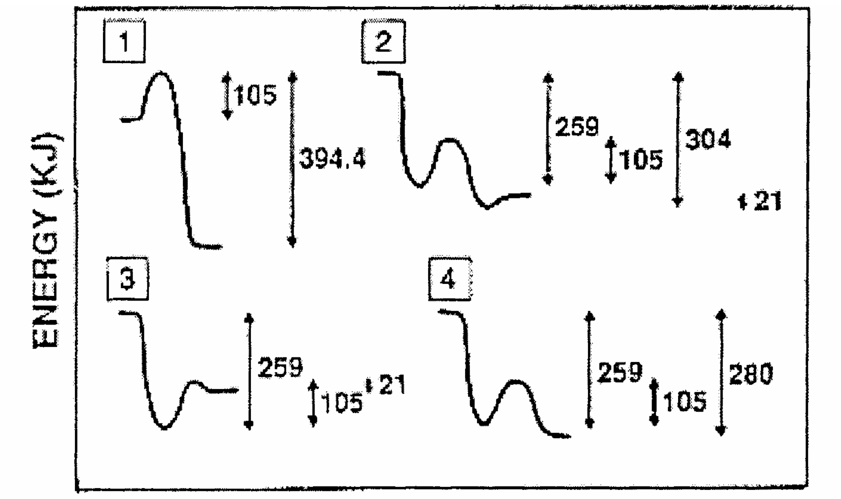
[5] increases, or

[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

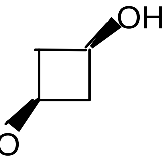
5.1 What is the correct systematic name (IUPAC name) for the compound below?
$(CH_3)_2CHCH(CH_2CH_3)(CH_2CH_2CH_3)$

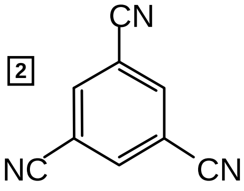
1	3-Isopropylhexane
2	2-Methyl-3-propylpentane
3	Ethyl isopropyl propyl methane
4	3-Hexylpropane
5	3-Ethyl-2-methylhexane

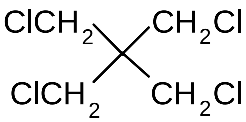
5.2 How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for C_5H_{10}?

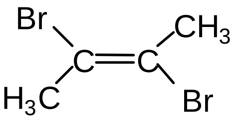
1	4 isomers	2	5 isomers	3	6 isomers
4	7 isomers	5	8 isomers		

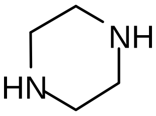
5.3 Which one of the following compounds has a dipole moment significantly different from zero?

1


2


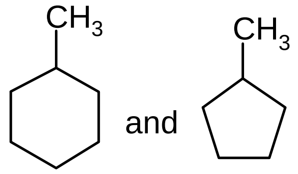
3


4


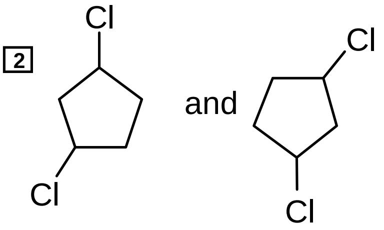
5


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

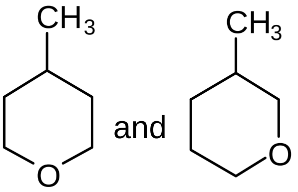
1



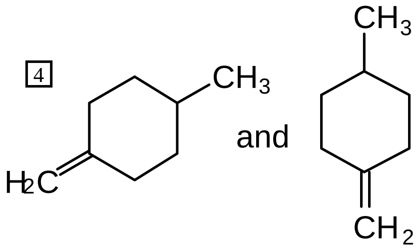
2



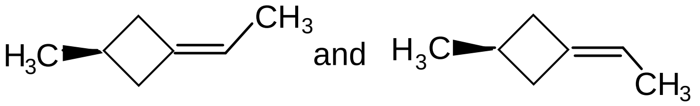
3



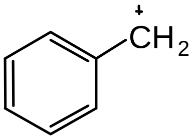
4



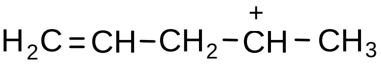
5



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)?

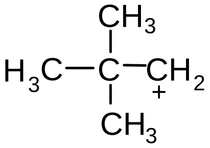


a



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

b

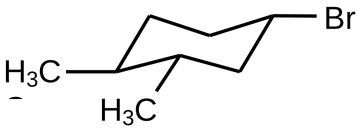


$H_3C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{+}{C}H_2$

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}.

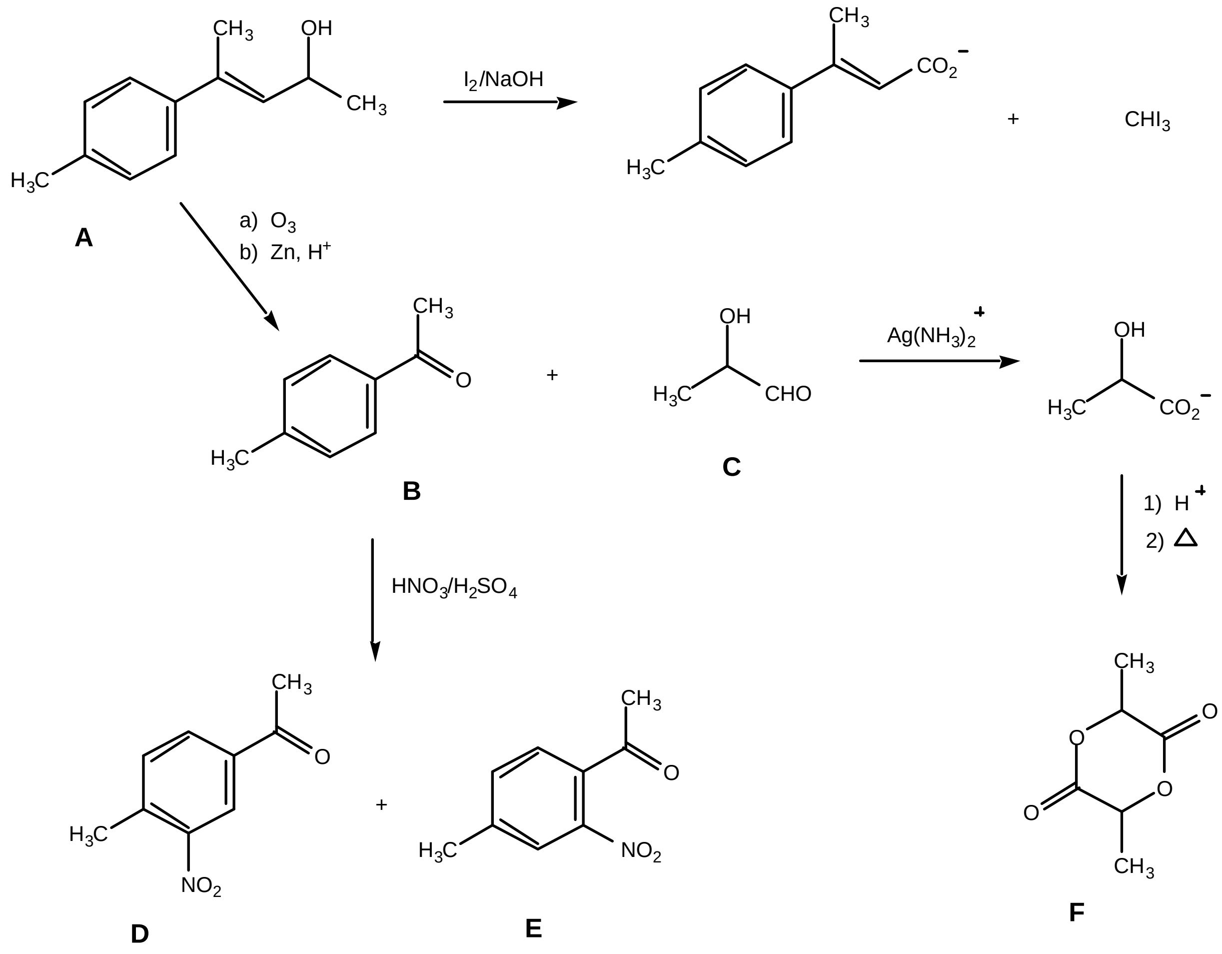
6.1 Based on the above information draw the structure formula(e) for the compounds **A** – **F** and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.

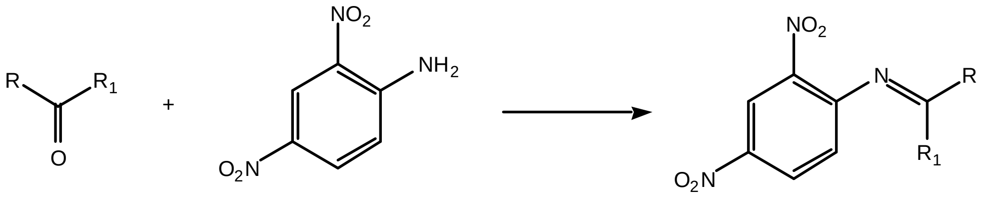
6.2 Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a **D** or L configuration.

SOLUTION

(See the next page.)

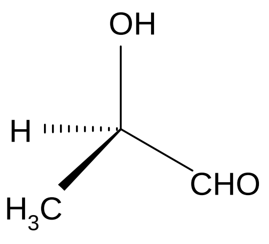
6.1



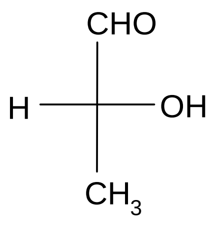


B and **C**

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.

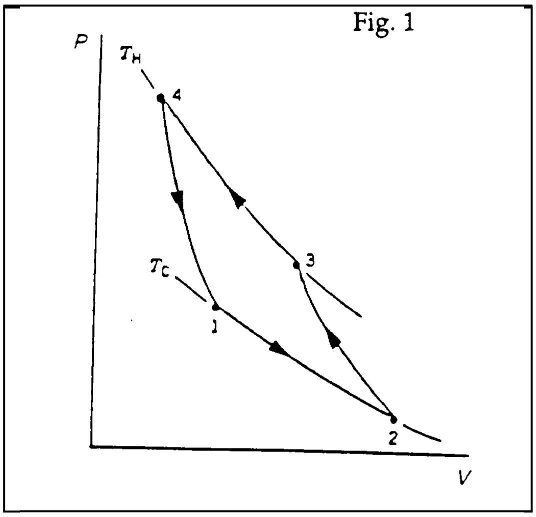


Fig. 1

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

$= 1.26\times10^{24}$

$D = N \ln2 / T_{1/2} = 1.26\times10^{24} \times \ln2 / (4.5\times10^{9}\ (\text{y}) \times 3.16\times10^{7}\ (\text{s/y})) = 6.1\cdot10^{6}$ 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.

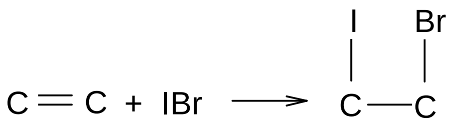
Procedure

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.



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

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.

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$ (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:

$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$ (white)

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

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

$K_{sp}(AgBr) = 5.00 \times 10^{-13}$ $K_{sp}(AgSCN) = 1.00 \times 10^{-12}$

Ignore the effect of *pH* and Fe(III) species.

Note:

On the answer sheet, not only the required final results shall be given, but also examplifications of how the calculations are carried out.

27th

International Chemistry Olympiad

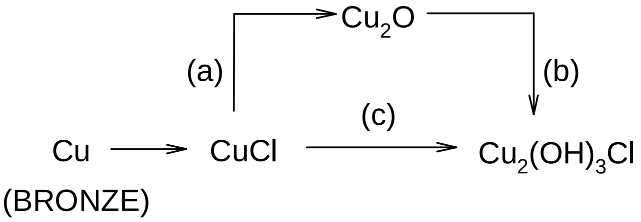
6 theoretical problems
3 practical problems

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)lCuSO$_4$(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: $\ln \dfrac{k_c(T_2)}{k_c(T_1)} = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$E_a = 34.2$ 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: $a = 2\sqrt{2r}$

$$d = \frac{4\left(63.5\times0.75\ +\ 65.4\ \times\ 0.25\right)\times10^{-3}}{a^3\,N_A} = 8.51\times10^{-3}\ \text{kg m}^{-3}$$

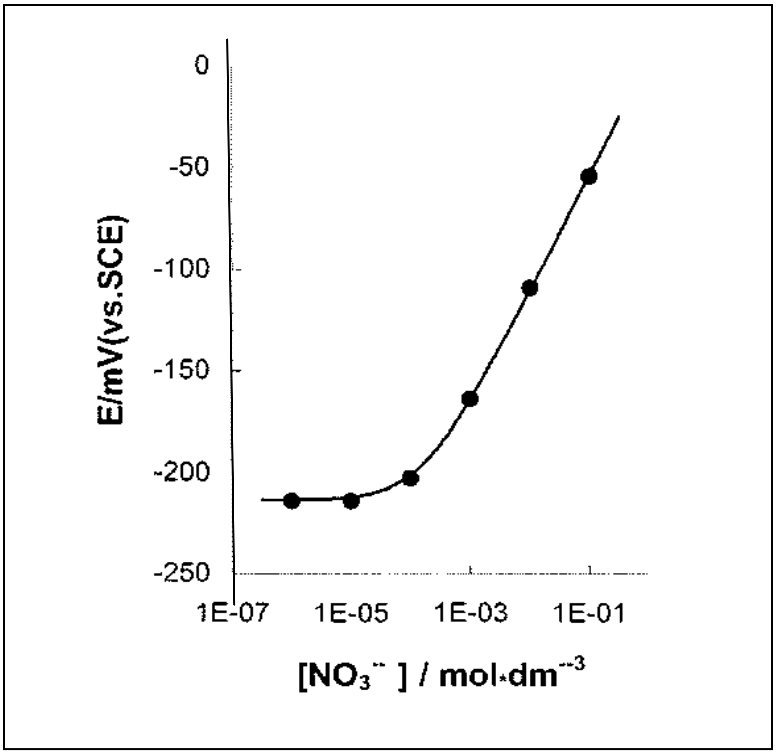
$r^3 = 2.209\times10^{-30}$ m^3

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, $\boldsymbol{E}$ 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}

$p\text{NO}_3 = 2.77$

2.4 $pH = 4.4$

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

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

$(1.4\times10^{-3} \times 0.01) \div [\text{CH}_3\text{COO}^-] = 2.7\times10^{-3}$

$[\text{CH}_3\text{COO}^-] = 5.2\times10^{-3}$ mol dm^{-3}

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

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

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

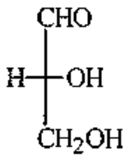
3.3 Write the structural formula for the dimer.

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

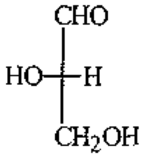
3.5 Denote each chiral carbon atom in the above formulae with *R* or *S*.

SOLUTION

3.1

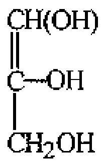


D(+)

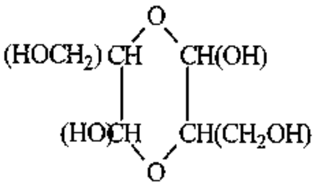


L(-)

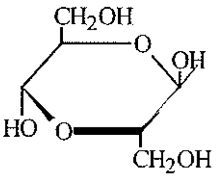
3.2

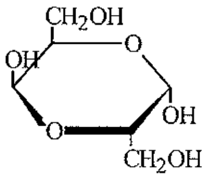


3.3

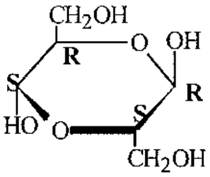

O
(HOCH2) CH
CH(OH)
(HO)CH
CH(CH2OH)
O

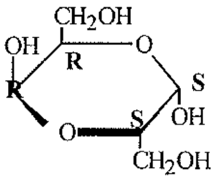
3.4


CH2OH
O
OH
HO
O
CH2OH


CH2OH
O
OH
O
OH
CH2OH

3.5


CH2OH
O
OH
R
S
R
S
HO
O
CH2OH


CH2OH
OH
O
R
R
S
S
O
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.

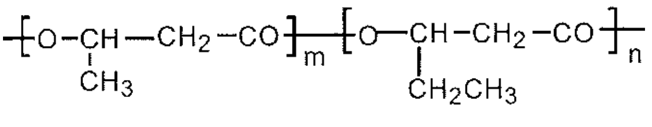
4.1 PHB, Poly(3-hydroxybutanoic acid), produced by bacteria contains only (R)-HB repeating units, while that synthesized by polymer chemists may contain only (R)-HB or only (S)-HB or both (R)-and (S)-HB in an alternating manner or both but in random distributions. Sketch chain structures of the atactic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



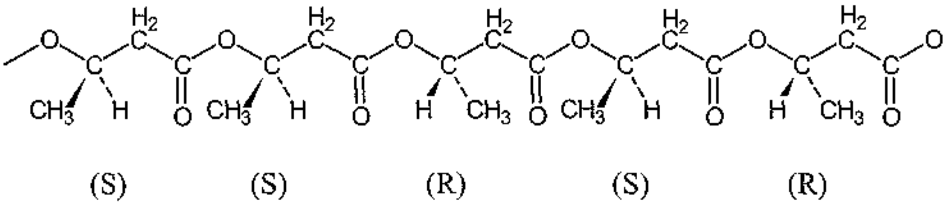
$$\left[O-\underset{CH_3}{CH}-CH_2-CO \right]_m \left[O-\underset{CH_2CH_3}{CH}-CH_2-CO \right]_n$$

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

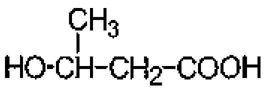


Other arrangements with (*R*) and (*S*) randomly distributed along the chain are correct, e.g. *RSRRS*, *SRSSR*, *RRSRS*, etc.

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*.

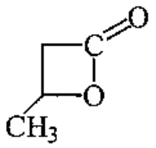
4.2 Monomer 1:



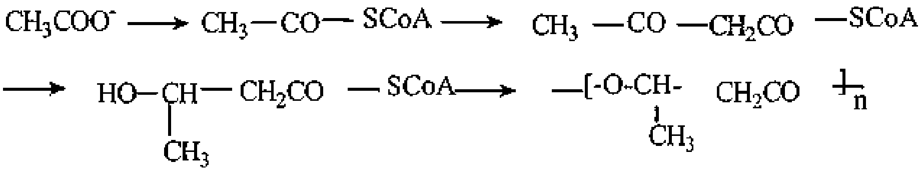
$$HO\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}CH_2\text{-}COOH$$

3-hydroxybutanoic acid

Monomer 2:

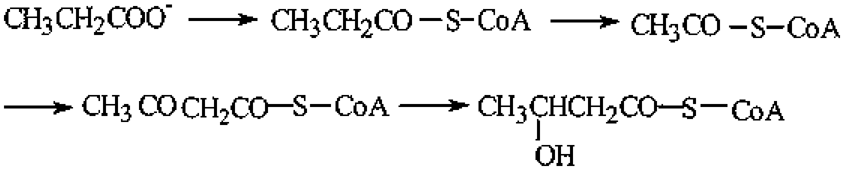


4.3



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

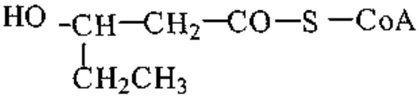
4.4



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

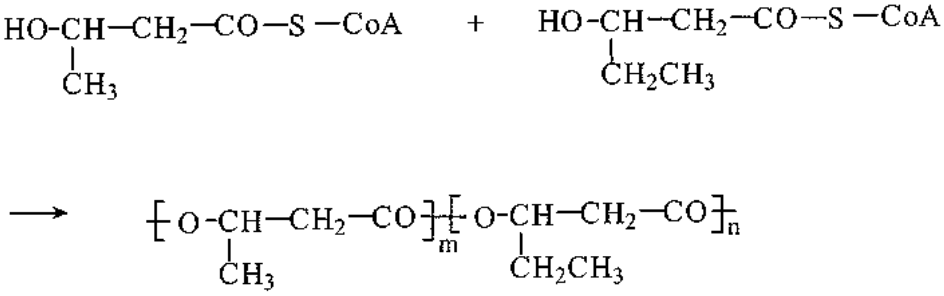
(Coenzyme A activated monomer 3-hydroxypentanoic acid)

This monomer may also be written in the following way:



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

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



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

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

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 ↓.

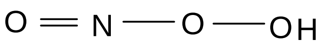
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species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

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

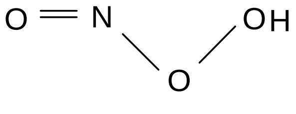
5.3 The cell damage is caused by free radical OH, which is one of the product of reaction between O_2^- and NO:

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

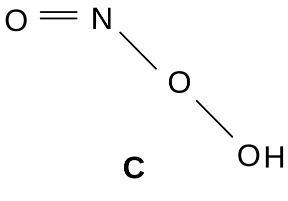
in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.



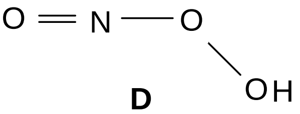
A



B

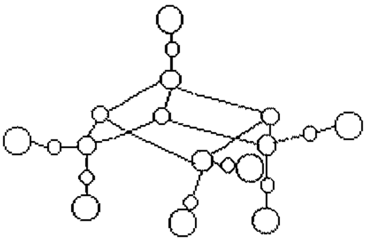


C



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

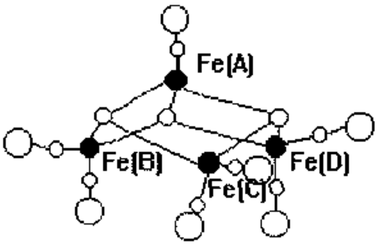
5.1 The HOMO of NO molecule is π*, its electron arrangement ↑;

The LUMO of NO molecule is π*.

5.2 (b)

5.3 B

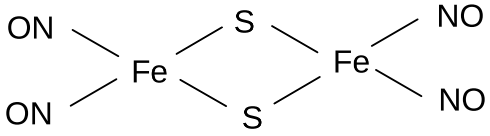
5.4



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.

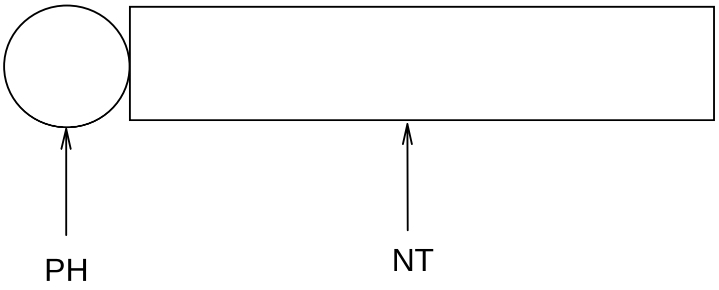


Fig. 1

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)$\times10^4$	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.

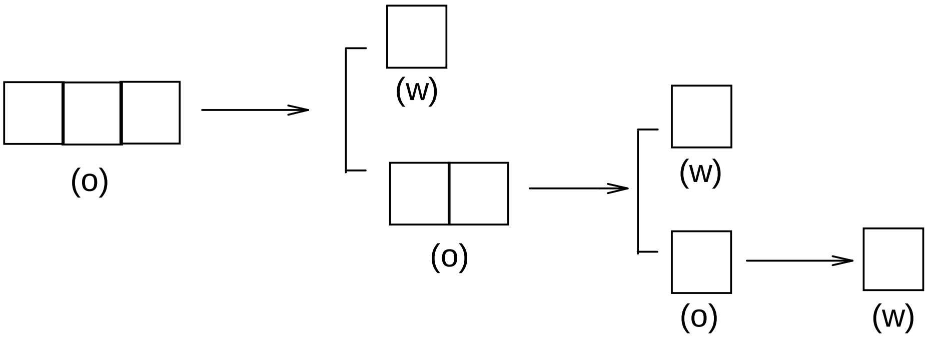


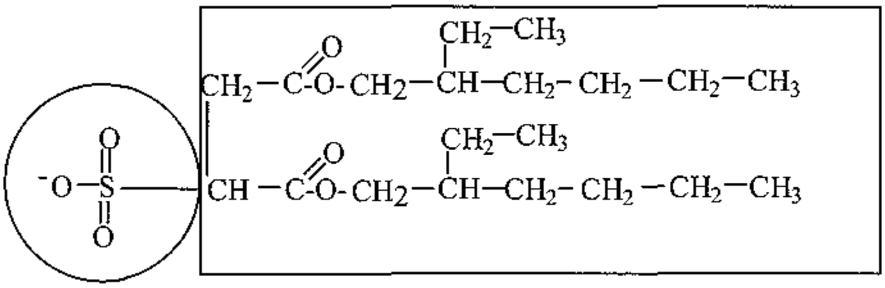
Fig. 2

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.

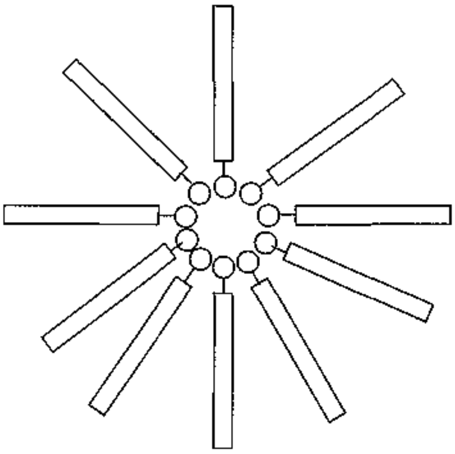
SOLUTION

6.1 i)



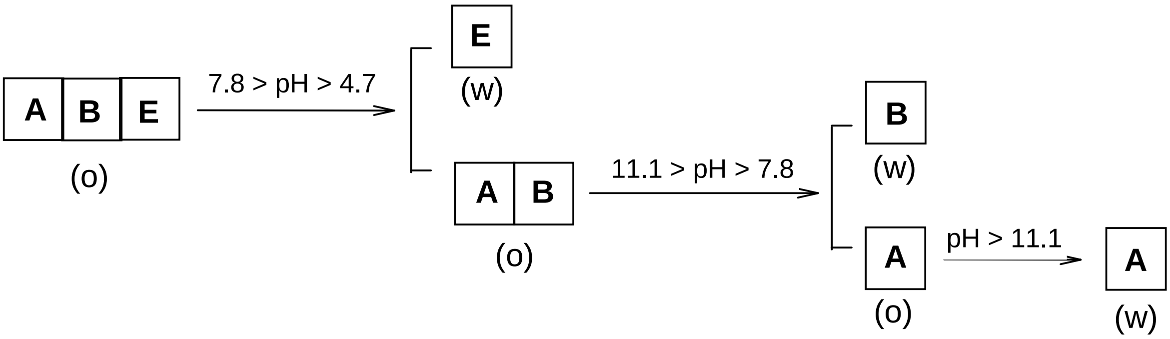
ii) (b)

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 [$Cu(gly)_2 \cdot xH_2O$]

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. *Preparation of cis-Copper-bis-Glycinate Hydrate*

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

28th

IChO

International Chemistry Olympiad

7 theoretical problems
2 practical problems

THE TWENTY-EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
14–23 JULY 1996, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the π-bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like $AlCl_4^-$) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A = Te(cryst.) and B = ($TeCl_4$ + 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.

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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.

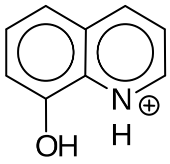
2.10 a) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

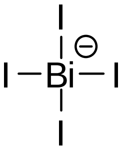
b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm^3 of standard 0.00200 M $Na_2S_2O_3$ solution)?

2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

SOLUTION

2.1 a)





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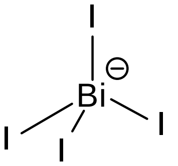


Cation Anion

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 $^{226}_{88}\text{Ra}$) 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$^\text{o}$ 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?

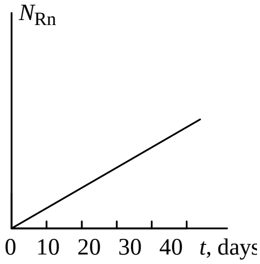
b) How many helium atoms were formed in total during the experiment?

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



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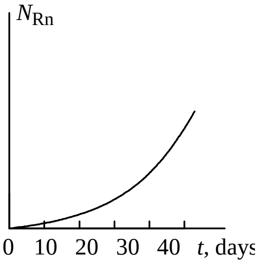

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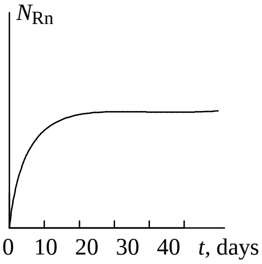

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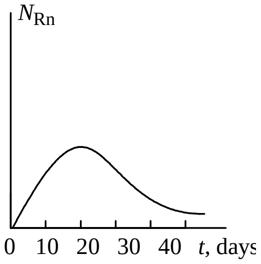
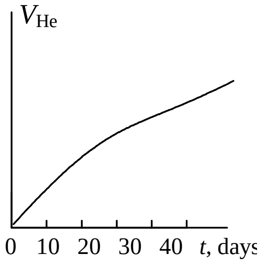
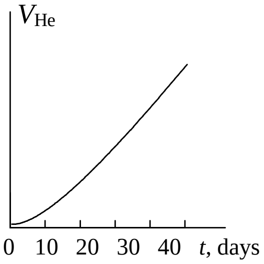


3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.

E



F



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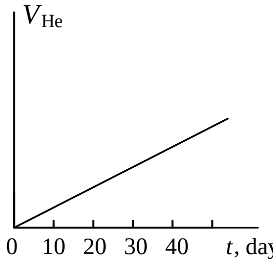
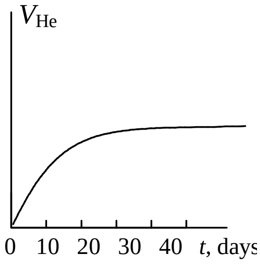


H



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 ($x = 3.42 \times 10^{10}$ α-particles per gram of radium per second).

3.8 How many helium atoms could be formed from radon atoms remaining at the end of experiment N'_{Rn}, if all these atoms had decayed to RaD?

3.9 Using the solutions of the above questions calculate a better approximation to:

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:

$k = 1 / T_{1/2}$	$k = \ln 2 / T_{1/2}$	$k = \ln 2 \cdot T_{1/2}$	$k = \pi / T_{1/2}$

3.7 a) Underline the correct answer:

$N'_{Rn} = k_1 \cdot N_{ra} / k_2$	$N'_{Rn} = k_2 \cdot N_{Ra} / k_1$	$N'_{Rn} = k_1 \cdot N_{Ra} / 2k_2$	$N'_{Rn} = k_1 \cdot N_{Ra} / 3k_2$

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) $N'_{Rn} = 3.14\times10^{15}$

The rate of radium decay is $k_1 N_{Ra} = xm$, whence

$$N'_{Rn} = \frac{xm}{\frac{\ln 2}{T_{1/2(Rn)}}} = \frac{3.42\times10^{10}\times0.192}{\frac{0.693}{3.83\times24\times3600}} = 3.14\times10^{15}$$

3.8 Underline the correct answer:

$4N'_{Rn}$	$2N'_{Rn}$	$5N'_{Rn}$	N'_{Rn}	$3N'_{Rn}$

3.9 a) A more accurate estimate of the number of helium atoms: 1.79×10^{17}

$$N_{He} = 4\,xmt - 3N'_{Rn} = 1.9\times10^{17} - 3\times3.14\times10^{15} = 1.79\times10^{17}$$

b) A more accurate estimate of Avogadro's number (mol^{-1}): 6.09×10^{23}

$$N_{À} = \frac{N_{He}}{n(\text{He})} = \frac{1.79\times10^{17}}{\frac{6.58\times10^{-6}}{22.4}} = 6.09\times10^{23}$$

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) $CrO_4^{2-} + H_2O = HCrO_4^- + OH^- \qquad K = 3.16\times10^{-8}$

$c_{Cr} = [CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] \approx [CrO_4^{2-}]$,

$[HCrO_4^-] \approx [OH^-]$

$[OH^-]^2/c_{Cr}$ = 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 (**) = $[CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] \approx [HCrO_4^-] + 2\,[Cr_2O_7^{2-}]$

$[HCrO_4^-] = x$; $K_2 = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 = (c_{Cr} - x)/2x^2$; $2K_2x^2 + x - c_{Cr} = 0$

hence $[H^+] = (3.16\times10^{-7}\times1.27\times10^{-2})^{1/2} = 6.33\times10^{-5}$; pH = 4.20

c) In 0.10 M CH_3COOH $[H^+] = (K_a\,c)^{1/2/}$ (*) = $(1.8\times10^{-5}\times0.10)^{1/2} = 1.34\times10^{-3}$

$pH = 2.87$

4.4 Equilibrium concentrations

a)	3.0×10^{-6}
b)	3.7×10^{-3}

Calculations:

The different methods can be used.

Method 1.

a)

$[HCrO_4^-] = 1.3\times10^{-2}$ (*)

$[CrO_4^{2-}] = K_1[HCrO_4^-]/[H^+] = 3.16\times10^{-7}\times1.3\times10^{-2}/1.34\times10^{-3} = 3.0\times10^{-6}$

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) $E_\text{I} = E°(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log \dfrac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$

b) $E_\text{I} = E°(\text{Fe(CN)}_6^{3-}/\ \text{Fe(CN)}_6^{4-}) + 0.0590 \log \dfrac{[\text{Fe(CN)}_6^{3-}]}{[\text{Fe(CN)}_6^{4-}]}$

5.2 The units of pre-logarithm factor: V

5.3 The ratio of stability constants

$\beta\{\text{Fe(CN)}_6^{3-}\} / \beta\{\text{Fe(CN)}_6^{4-}\} = 8.90\times10^6$

Calculations:

$$E_{II} = E°(\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}) + 0.0590 \log[\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}] =$$

$$= E°(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log(\beta_1/\beta_2) + 0.0590 \log([\text{CN}^-]^6/[\text{CN}^-]^6) +$$

$$+ 0.0590 \log[\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}] = 0.242$$

(where β_1 and β_2 are stability constants for Fe(CN)_6^{4-} and Fe(CN)_6^{3-}, respectively.)

$[\text{Fe(CN)}_6^{3-}] / [\text{Fe(CN)}_6^{4-}] = [\text{Fe}^{3+}] / [\text{Fe}^{2+}]$, therefore

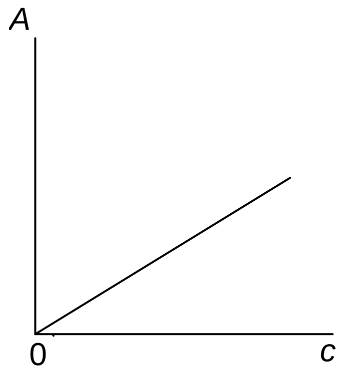
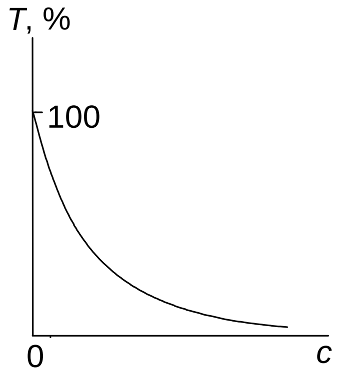
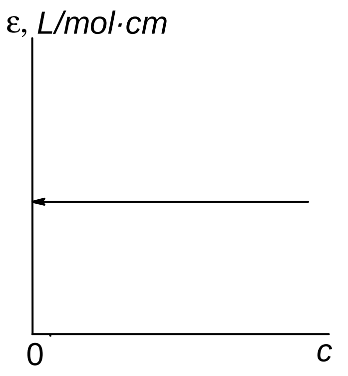
$\Delta E = E_\text{II} - E_\text{I} = 0.0590 \cdot \log(\beta_1/\beta_2)$, and $\beta_2/\beta_1 = 8.90\times10^6$.

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

$$A = \varepsilon l c = \varepsilon l c[\mathrm{Fe(CN)}_6^{3-}] = 0.971;$$

$$c[\mathrm{Fe(CN)}_6^{3-}] = 0.971 / (1100 \times 0.502) = 1.76\times10^{-3}\ \mathrm{M} = c[\mathrm{Fe}^{3+}]$$

b) using Nernst's equation

$E = E°(\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}) + 0.0590 \log[\mathrm{Fe}^{3+}]_\mathrm{I} / [\mathrm{Fe}^{2+}]_\mathrm{I} =$

$= 0.771 + 0.0590 \log [\mathrm{Fe}^{3+}]_\mathrm{I} / [\mathrm{Fe}^{2+}]_\mathrm{I} = 0.652\ V.$

hence,

$[\mathrm{Fe}^{3+}]_\mathrm{I} / [\mathrm{Fe}^{2+}]_\mathrm{I} = 9.62\times10^{-3};$

$[\mathrm{Fe}^{2+}]_\mathrm{I} = 1.76\times10^{-3} / 9.62\times10^{-3} = 0.183$ M.

PROBLEM 6

Two isomeric hydrocarbons A and B contain 85.7 mass % of carbon.

6.1 Write a general formula which satisfies this condition.

The hydrocarbons **A** and **B** possess the following properties. The reaction of each of the compounds with ozone with subsequent treatment of the product with zinc dust in the presence of acid gives a single organic product **C**. The oxidation of compound **C** gives a single product, the carboxylic acid **D**. According to spectral data all hydrogen atoms in this acid except the one in carboxylic group are contained in methyl groups. The density of vapours of **D** corrected to normal conditions (0 °C, 1 atm) is 9. 1 g dm^{-3}.

Compound **A** is more reactive than compound **B** in the reaction with cold neutral potassium permanganate. A single compound **F** is formed from **A**, and a 1 : 1 mixture of isomers **G1** and **G2** is formed from **B**.

6.2 Draw the structural formulae of the compound **D** both in aqueous solution and in vapour phase.

6.3 Write the formula of compound **C**.

6.4 Draw the structures of isomers **A** and **B**.

6.5 a) Write the reactions of the transformation of **A** or **B** into **C** and **D**.

b) Write the reactions of the transformation of **A** and **B** into **F**, **G1** and **G2**.

6.6 Compounds **G1** and **G2** readily react with acetone in the presence of acids and form compounds **H1** and **H2**. Draw the structures of **H1** and **H2**.

6.7 Compounds **A** and **B** react with bromine. One of the products of these reactions is non-polar (dipole moment of this molecule is practically equal to zero) and optically inactive. Draw the stereochemical formula of this product, and write the reaction of its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to *R,S* nomenclature by *R* or *S* letters.

Alkenes react with 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**.

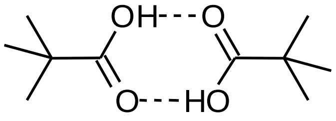
SOLUTION

6.1 The general formula: C_nH_{2n}

6.2 Compound **D**:

In aqueous solution: $(CH_3)_3CCOOH$

In vapours:

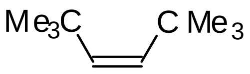


Dimeric structure in vapour phase is guessed using the value of vapour density.

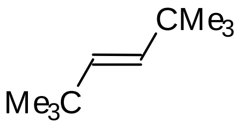
The relative molar weight in vapour phase is $9.1 \times 22.4 = 204$ which is close to double value of the molar weight of $(CH_3)_3CCOOH$. Possibly, as other simple fat acids, this acid is also dimerized in vapours.

6.3 Compound **C**: $(CH_3)_3CCHO$

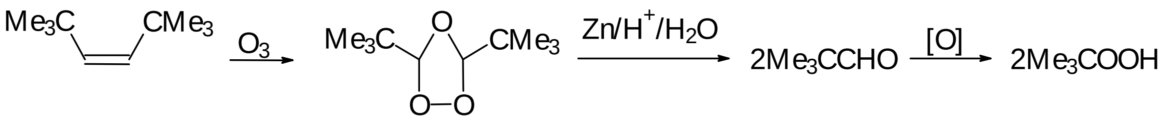
6.4 **A**:



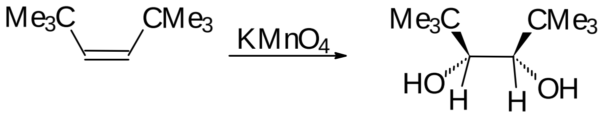
B:



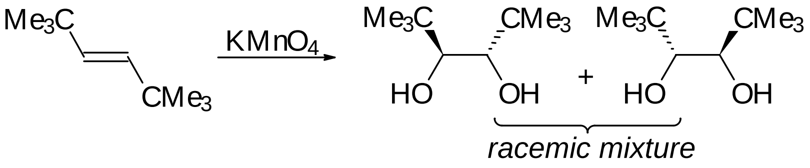
6.5 $\mathbf{A} \longrightarrow \mathbf{C} \longrightarrow \mathbf{D}$



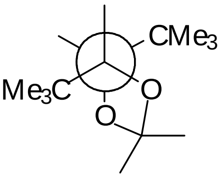
A ⟶ **F**



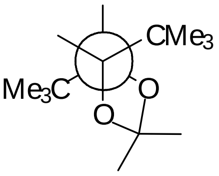
B ⟶ **G1** + **G2**



6.6 **H1**:

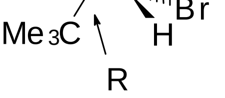


H2:

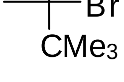


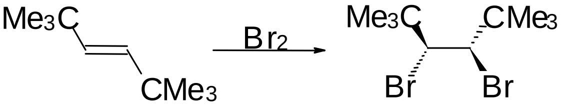
6.7 Non-polar bromination product (either of three types of structures may be given)

or

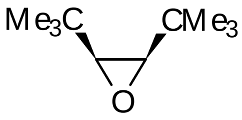


or



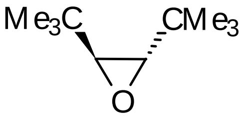


6.8 **K**:



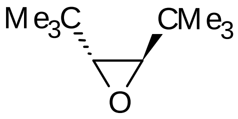
☑ NO; The molecule is not optically active.

L1:



☑ YES; The molecule is optically active.

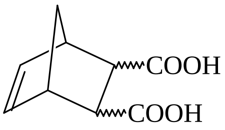
L2:



☑ 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.

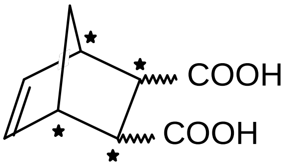
7.6 Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.

7.7 Write the reactions leading from **B** to **A**.

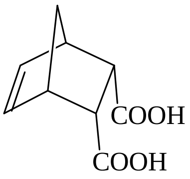
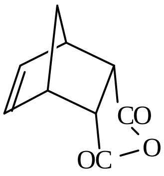
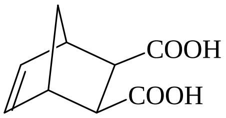
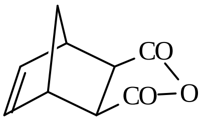
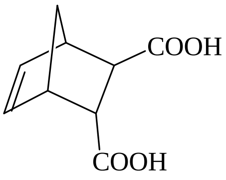
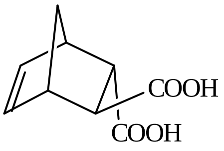
7.8 Are the compounds **A** and **B** diastereomers?

SOLUTION

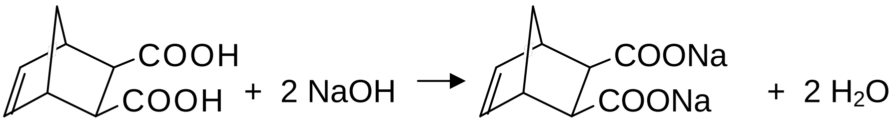
7.1



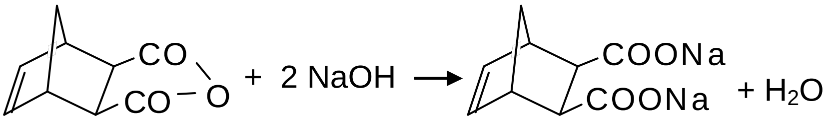
7.2 Fill in left column with the structures of stereoisomers of **X**, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus.

	
	
	—
	—

7.3 The reaction of a stereoisomer of **X** with NaOH:

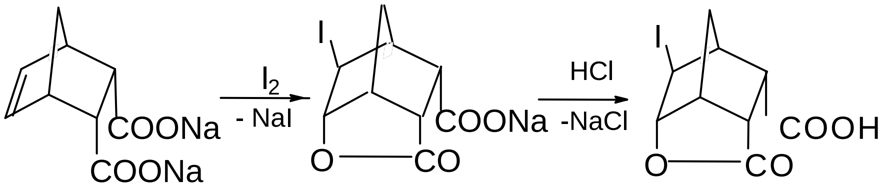


The reaction of a stereoisomer of **Y** with alkali:

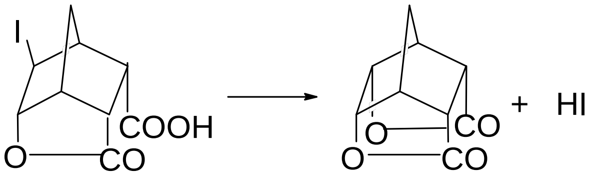


7.4 The molar mass of **A**: 308 g mol^{-1}

The reactions leading from $\mathbf{X_1}$ to **A**

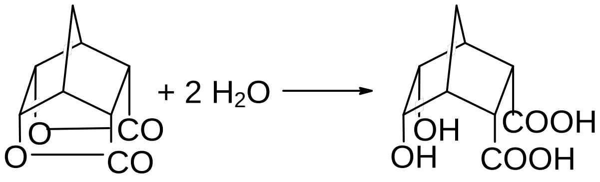


7.5 The transformation of **A** to **C**:

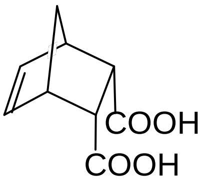


CO

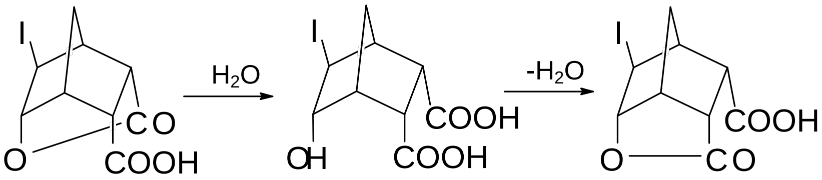
The reaction of **C** with water:



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}.

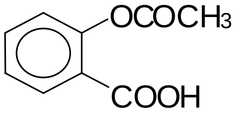
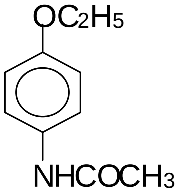
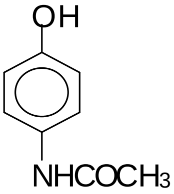
2.3 Calculate the yield of product obtained by you.

2.4 Calculate and compare the values of R_f of unknown drug and your product.

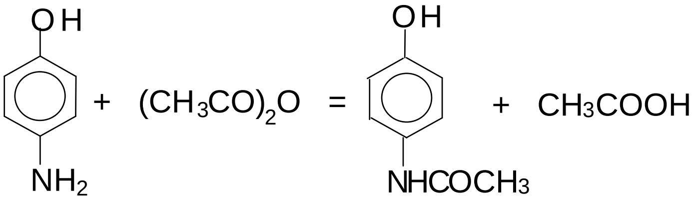
2.5 Is it likely that paracetamol is contained in the sample of drug?

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

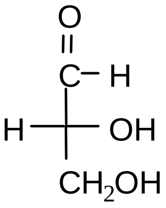
PROBLEM 1

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**).

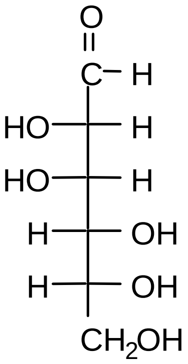
1.1 On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.

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

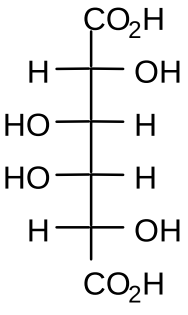


Compound **1**

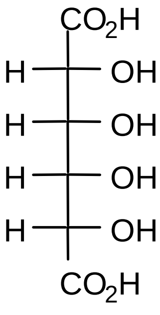
SOLUTION

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:

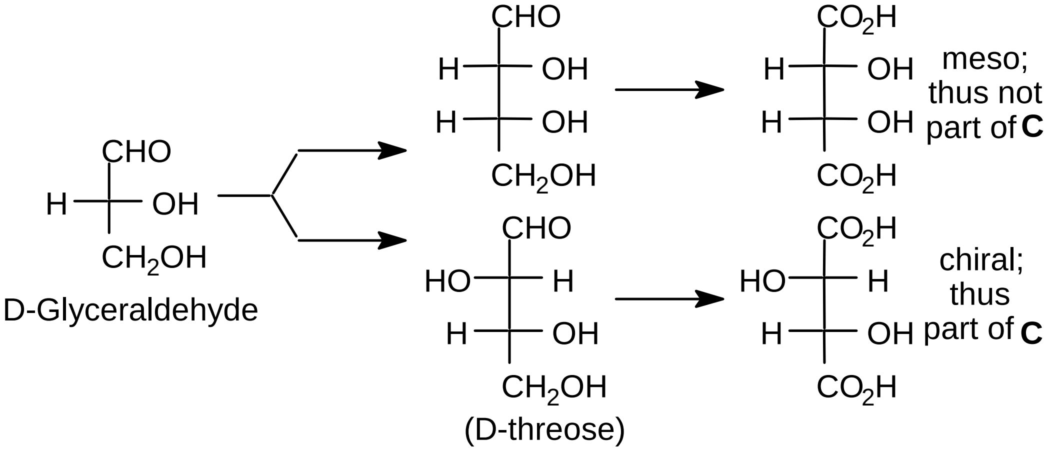


AA1 (=D)



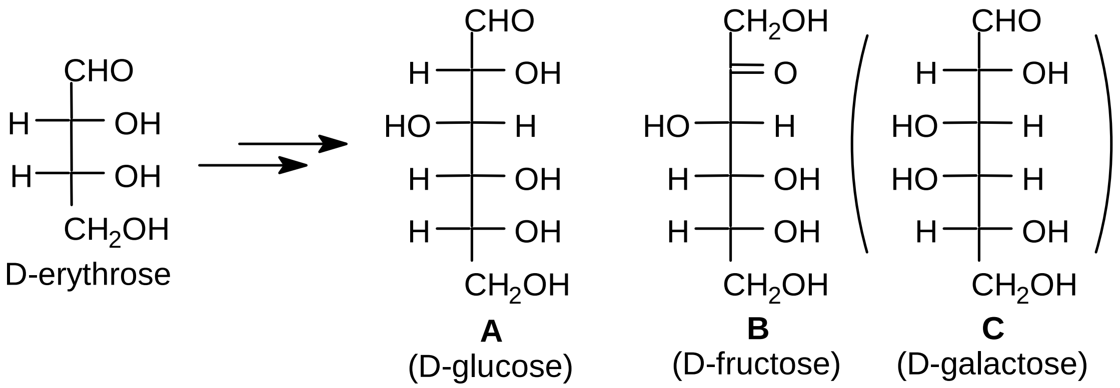
AA2

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:



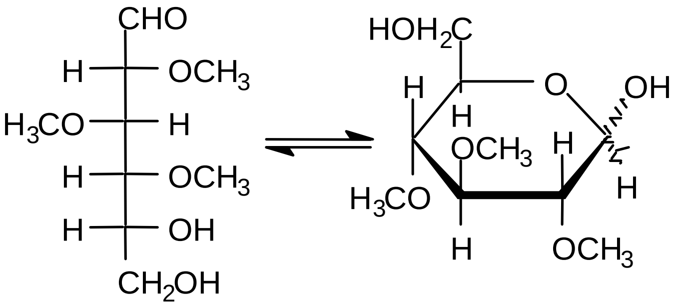
It follows from this that the aldaric acid **D** produced from **C** above is **AA1** and thus that **C** must be D-galactose. Compound **A** reacts with 5 moles of HI to give 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) suggesting that it is an aldohexose while **B** reacts 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.

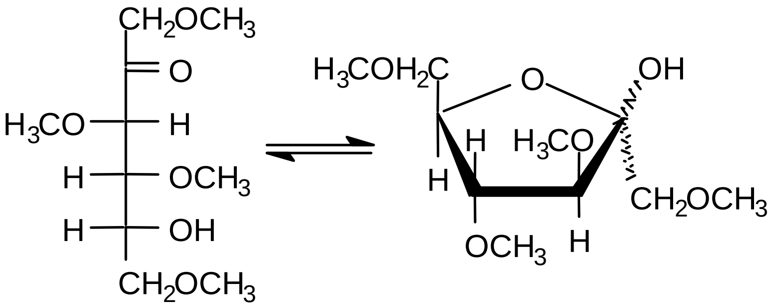


Methylation of **X** followed by hydrolysis yields **E**, **F** and **G** below:

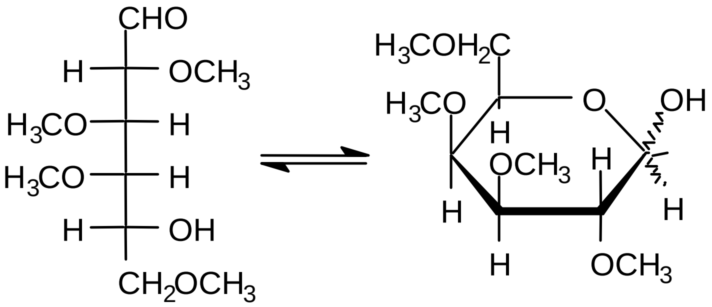
1.2



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.

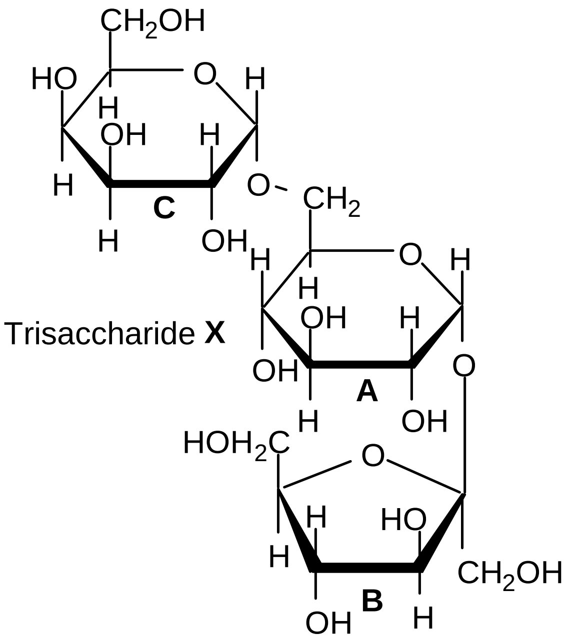
These results indicate that the sequence of monosaccharides in **X** is **C-A-B** (or **B-A-C**).

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 kJ mol^{-1} for Proposal A E_B = – 20 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: $$\frac{d[H_2SO_4]}{dt} = k[H_2O]\,[SO_3]$$

Summing the exponents gives a second order process

Proposal B: $$\frac{d[H_2SO_4]}{dt} = k\,[SO_3][H_2O]^2$$

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: $$[SO_3\cdot 2\,H_2O] = \frac{k_1\,[SO_3][H_2O]^2}{k_{-1} + k_2}$$

Also: $\frac{d[H_2SO_4]}{dt} = k_2\,[SO_3\cdot 2\,H_2O]$ 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 $k_2 << k_{-1}$ 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*.

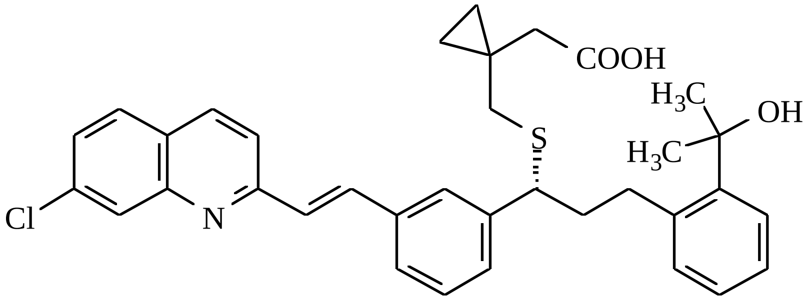
For proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

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

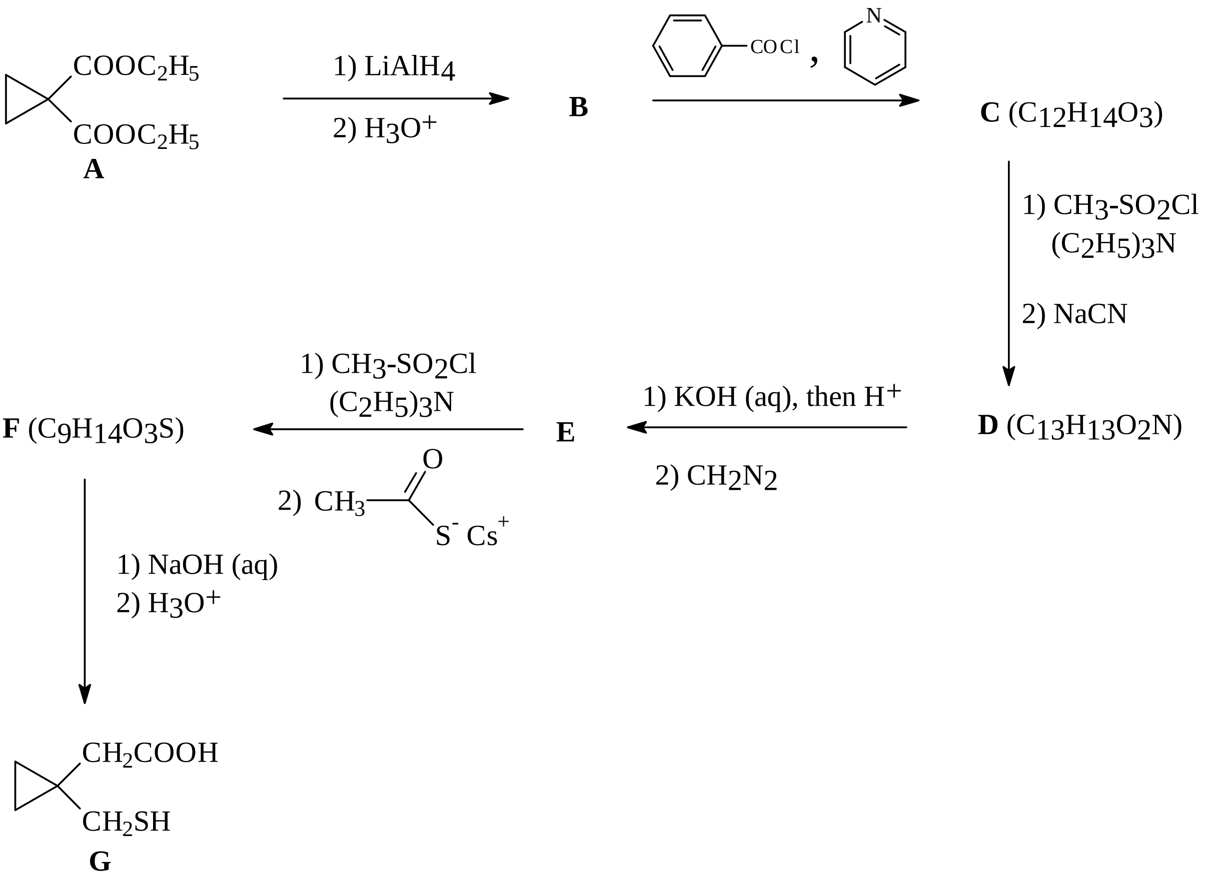
Chemists at Merck Frosst Canada in Montréal have developed a promising drug which is useful against asthma. The structure of MK-0476 is shown below.



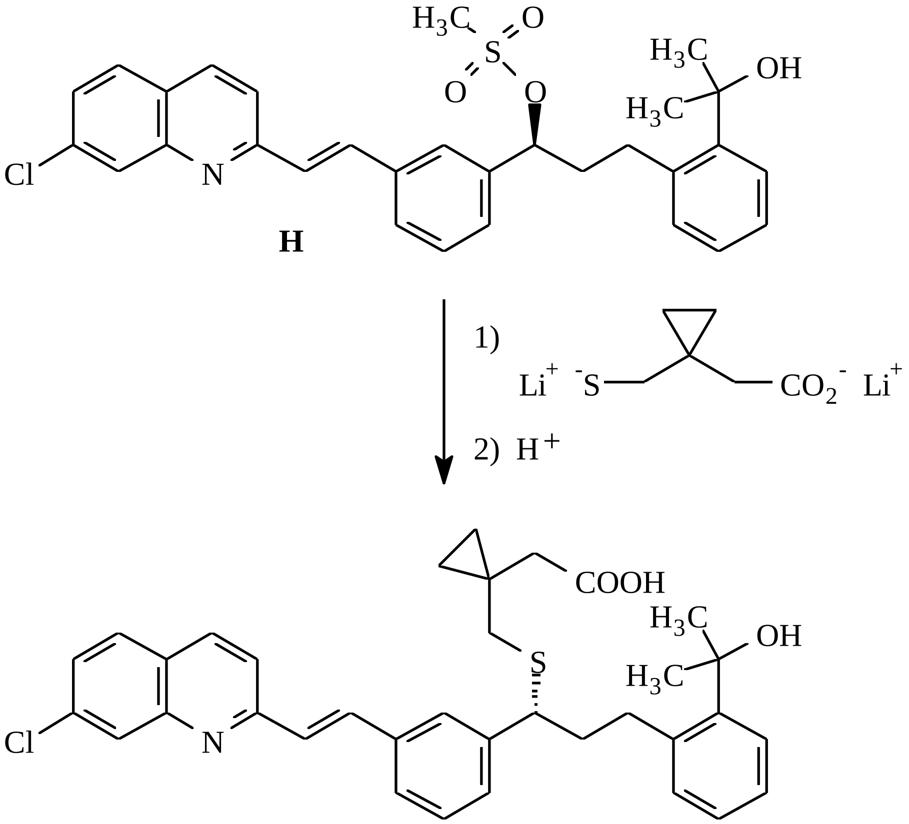
MK-0476

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.



H

MK-0476

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

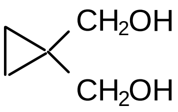
b) **G** plus one molar equivalent of base

3.5 A side reaction of **G** is its oxidative dimerization.

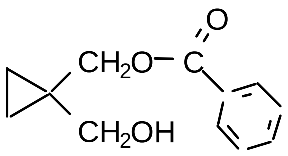
Draw the structure of the dimeric product, showing all non-bonded electrons.

SOLUTION

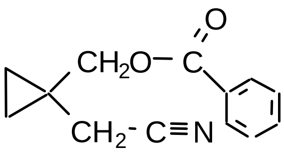
3.1



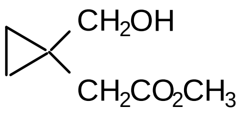
B



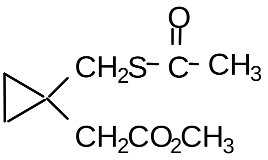
C ($C_{12}H_{14}O_3$)



D ($C_{13}H_{13}O_2N$)



E



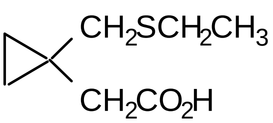
F ($C_9H_{14}O_3S$)

3.2 S_N2 Bimolecular Nucleophilic Substitution

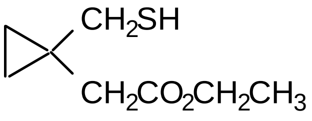
3.3 Rate = k[substrate] [nucleophile]

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

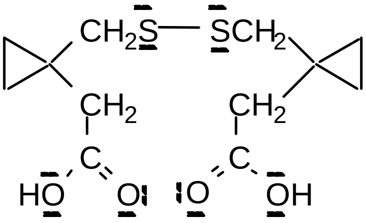


From 2 equiv base



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.

$HIn + Na^+OH^- \rightleftarrows Na^+In^- + H_2O$

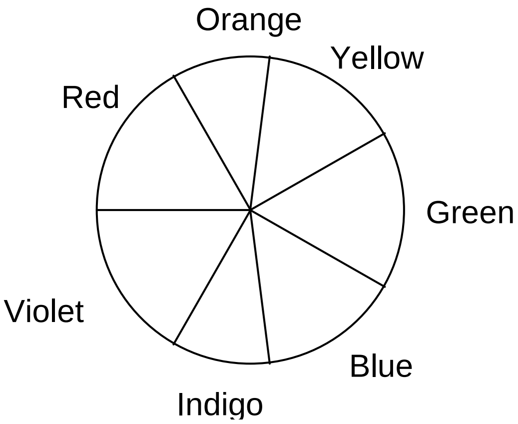
also written as

$HIn \rightleftarrows In^- + H^+$

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)

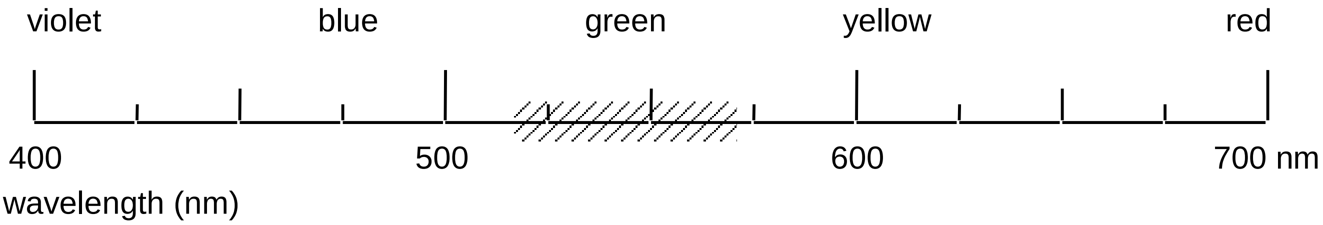
λ, nm	*pH* = 1.00	*pH* = 13.00
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



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.

$$\text{Therefore}\quad \varepsilon = \frac{A}{l\,c} = \frac{0.256}{1.0 \times 5.00\times10^{-4}} = 5.12\times10^{2}\ \text{M}^{-1}\ \text{cm}^{-1}$$

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:

$[HIn] = [H^+] + [In^-]$

accordingly,

[H+] = [In-] (1)

and

[HIn] + [In-] = 1.80×10^{-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-] = 2.15×10^{-4} M

[HIn] = 1.80×10^{-3} M – 2.15×10^{-4} M = 1.58×10^{-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.

<u>Expected steps of the calculation:</u>

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".

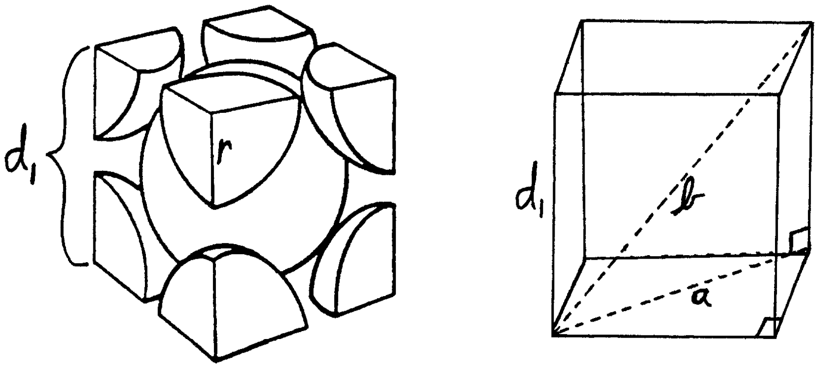
An alternative route to ρ_{fcc} of γ-iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

5'. Calculate the percent space filling ratio of the bcc unit cell.

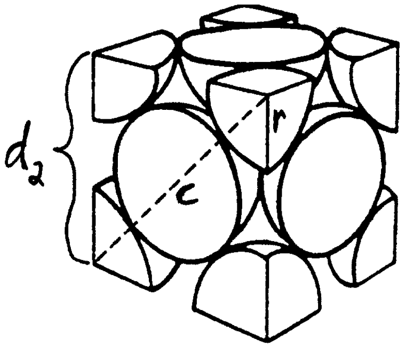
6'. Calculate the percent space filling ratio of the fcc unit cell.

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)

Calculations in details

At 293 K, α-iron has a bcc crystal structure.

Each unit cell possesses 2 atoms and one of them is in the center of the cell.

At 1250 K, γ-iron has a fcc crystal structure.

Each unit cell possesses 4 atoms and each side has one-half an atom at its center.

r = atomic radius of iron.

a = length of the diagonal on one side of the bcc unit cell.

b = length of the diagonal passing through the center of the bcc unit cell.

c = length of the diagonal on one side of the fcc unit cell.

d_1 = length of the edge of the bcc unit cell of α-iron.

d_2 = length of the edge of the fcc unit cell of γ-iron.

V_1 = Volume of the bcc unit cell of α-iron.

V_2 = Volume of the fcc unit cell of γ-iron.

V_a = Volume of one atom.

V_{a1} = Volume occupied by 2 atoms in one bcc unit cell.

V_{a2} = Volume occupied by 4 atoms in one fcc unit cell.

R_1 = Percent space filling ratio in a bcc unit cell.

R_2 = Percent space filling ratio in a fcc unit cell.

$V_a = (4/3)\ \pi\ r^3$ $\qquad V_{a1} = 2\ V_a$ $\qquad V_{a2} = 4\ V_a$

$b = 4\ r;$ $\qquad a^2 = 2\ d_1^2;$ $\qquad b^2 = d_1^2 + a^2 = 3\ d_1^2$

$d_1 = (b^2/3)^{1/2} = (16\ r^2/3)^{½};$ $\qquad V_1 = d_1^3 = [(16\ r^2/3)^{1/2}]^3$

$c = 4\ r;$ $\qquad c^2 = 2\ d_2^2$

$d_2 = (c^2/2)^{1/2} = (16\ r^2/2)^{½};$ $\qquad V_2 = d_2^3 = [(16\ r^2/2)^{½}]^3$

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, $V_1 = 2.356\times10^{-23}$ 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.

$n\ \mathbf{A}_wCl_x + m\ NH_3 \rightarrow p\ NH_4Cl + q\ \mathbf{A} + r\ \mathbf{A}_yN_z$

(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:

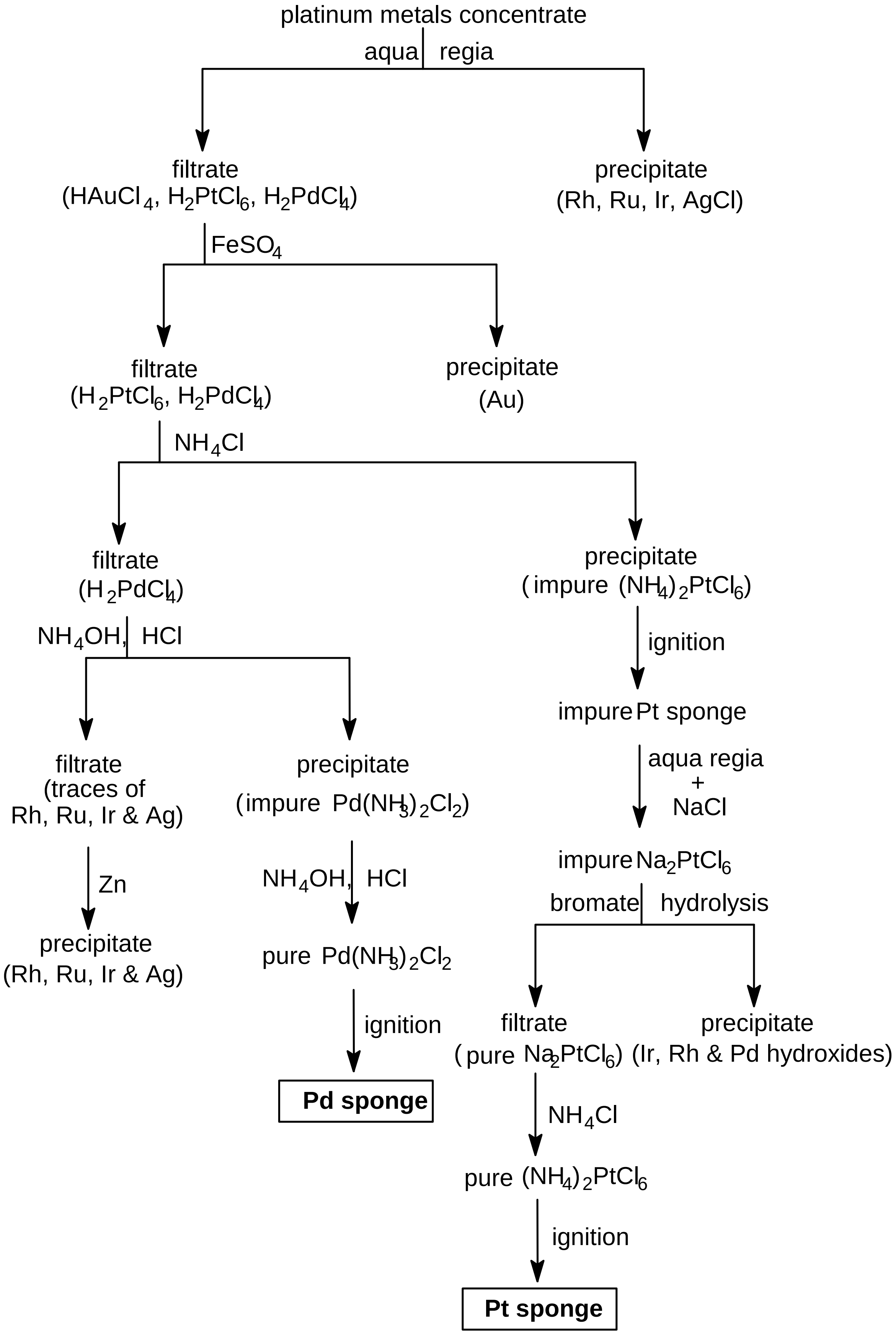
$M(Cl) = 35.453\ g\ mol^{-1}$ $M(N) = 14.007\ g\ mol^{-1}$ $M(H) = 1.008\ g\ mol^{-1}$

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.

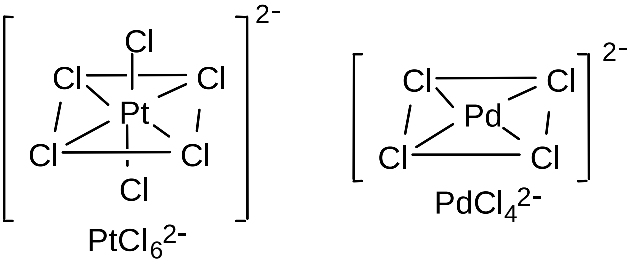
Method of Purification of Platinum and Palladium



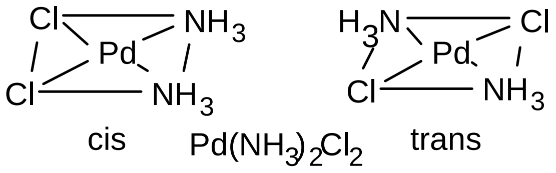
SOLUTION

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

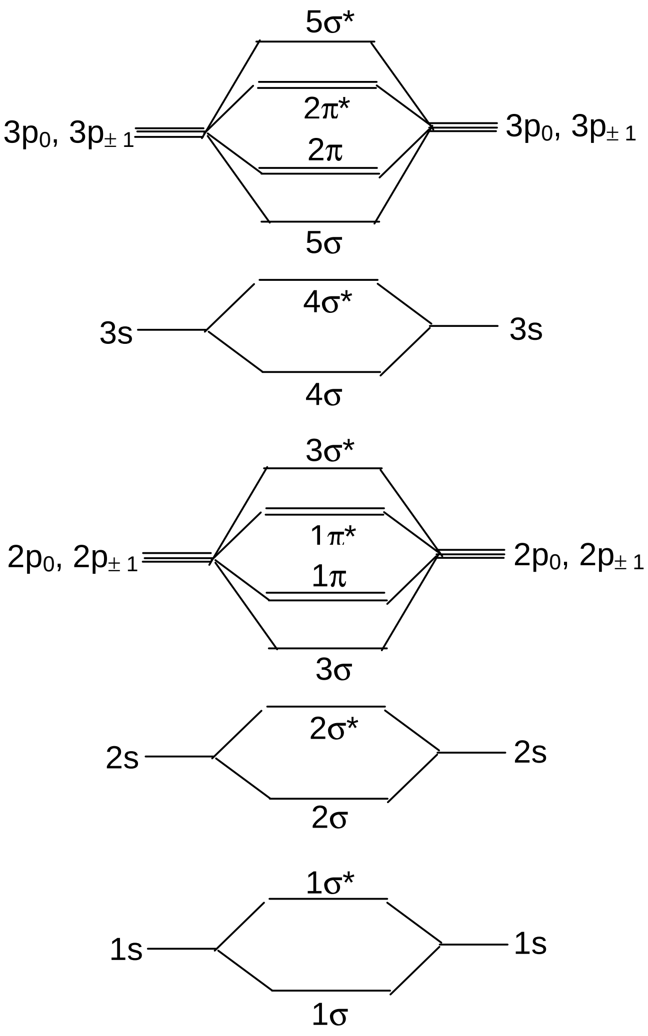
Number of electrons in these AOs: 17

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:

$$\begin{array}{ccccc} Cl_2\ (g) & & Cl_2\ (g) & & Cl_2\ (l) \\ 1\ \text{mol} & \xrightarrow[\text{cooled}]{\Delta E_1} & 1\ \text{mol} & \xrightarrow[1.013\times10^5\ \text{Pa}]{\Delta E_2} & 0.1\ \text{mol} \\ 300\ \text{K} & 1.013\times10^7\ \text{Pa} & 239\ \text{K} & (1\ \text{atm}) & 239\ \text{K} \\ & (100\ \text{atm}) & & & \end{array}$$

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 × 0.0820584 × 239) / 1 = 1.96 dm^3

Volume of liquid Cl_2: (0.1 × 2 × 35.454) / 1.56 = 4.54 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 × (– 20420) + (1 × 1.96 L) × 101.325 J dm^{-3} 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, $Q\,/\,T = Q_p\,/\,T = \Delta H\,/\,T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{0.1 \times (-20420)}{239} = -8.54 \text{ J K}^{-1}$$

ΔS_{sys} = 29.89 – 8.54 = 21.35 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 $K_{c3} = \mathrm{e}^{\frac{15.35}{RT}} = 4.90\times10^2$

Alternatively:
$\Delta G^0_3 = \Delta G^0_2 - \Delta G^0_1 = - 44.05 - (-28.74) = -15.31$ kJ mol^{-1} thus $K = 4.82\times10^2$)
$\Delta S^0 = (\Delta H^0 - \Delta G^0)$ / 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

$$Q_H = 2\times8.9230\times10^{-6}\times N_A\times1.60218\times10^{-19}$$

$$Q_H = 1.7219\ \text{C}$$

(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

$$\frac{96485.3}{1.00795} = \frac{1.0000}{k_H}$$

$$k_H = 1.04467\times10^{-5}\ \text{g C}^{-1}$$

Subsequently

$$Q_H = \frac{m_H}{k_H} = \frac{2\times8.9230\times10^{-6}\times1.00795}{1.04467\times10^{-5}}$$

$$Q_H = 1.7219\ \text{C}$$

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:

$$A_u = a_{Pt}^2 = 1.5395\times10^{-15}\ \text{cm}^2$$

Number of atoms per fundamental (100) unit: $n_u = 2$

Surface atom concentration:

$$s_{Pt(100)} = \frac{n_u}{A_u} = \frac{2}{1.5395\times10^{-15}\,\text{cm}^2} = 1.2991\times10^{15}\,\text{cm}^{-2}$$

The number of Cu atoms per 1 cm^2 equals the number of Pt atoms - epitaxial growth

$$\sigma_{Cu(100)} = \sigma_{Pt(100)} = 1.2991\times10^{15}\,\text{cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{ML} = 2\times e\times1.2991\times10^{15}$$

$$q_{ML} = 4.1628\times10^{-4}\,\text{C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{ML} = \frac{0.2780\text{C}}{4.1628\times10^{-4}\,\text{C}}$$

$$n_{ML} = 668\text{ ML}$$

One can also calculate the number of Cu atoms (8.6802×10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991×10^{15}) on the exposed Pt surface to also arrive at 668 monolayers.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Mg^{2+} and Ca^{2+} in Bottled Water

- The K_{sp} for calcium oxalate is 2.3×10^{-9} and the K_{sp} for magnesium oxalate is 8.6×10^{-5}.
- In a solution buffered to maintain *pH* 10, Calmagite indicator is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Calcium ions are not bound by Calmagite.
- EDTA binds to Mg^{2+} and Ca^{2+} even in the presence of Calmagite. The stoichiometry of the EDTA-metal complex formed with both Mg^{2+} and Ca^{2+} is 1:1.
- Molar masses: $M(\text{Ca}) = 40.08\ \text{g mol}^{-1}$ $M(\text{Mg}) = 24.31\ \text{g mol}^{-1}$

Chemicals Available

500 cm^3 sample of “Bottled Water”
aqueous buffer (pH 10)
Calmagite indicator
aqueous saturated ammonium oxalate
aqueous ethylenediaminetetraacetic acid
aqueous standardized* Mg^{2+}
distilled water
*0.928 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.

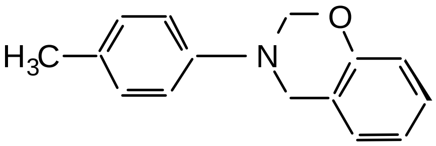
Chemicals Available
litmus paper, red and blue
aqueous ceric ammonium nitrate
aqueous chromic-sulfuric acid
aqueous 2,4-dinitrophenylhydrazine
aqueous 0.2% KMnO4
acetone (2-propanone)

Possible Unknowns*
2-butanone
1-decene
2,3-diamino-2,3-dimethylbutane
hexane
3-methyl-1-butanol
2-methyl-2-butanol
nonanal
propanoic acid

*Several of the unknowns are present as dilute aqueous solutions.
This will not interfere with the test results.

PROBLEM 3 (Practical)

Synthesis of the Substituted Dihydro-1,3-benzoxazine (C)



C

Benzoxazines have long been recognized as useful biologically-active compounds. One such compound (**C**) will be prepared using the three-step synthesis described below. All of the product obtained in Step I should be used in Step II and similarly all of the product from Step II should be used in Step III. You will be evaluated on both the yield and purity of the final product.

Chemicals available

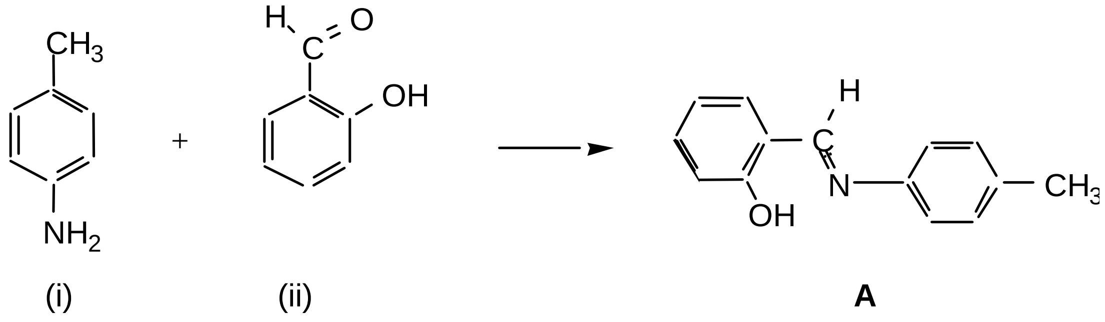
5 cm^3 reaction vial containing 2.5 cm^3 of ethanolic 1-amino-4-methylbenzene (0.22 g),
vial containing 0.25 g of 2-hydroxybenzaldehyde,
vial containing 0.1 g of sodium borohydride,
vial containing 0.042 g of paraformaldehyde,
test tube containing dilute ethanolic KOH,
(50 mg of KOH dissolved in 10 cm^3 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}

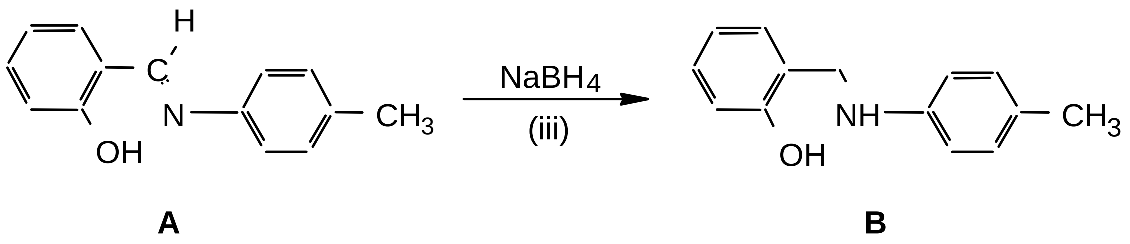
Procedure

STEP I



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

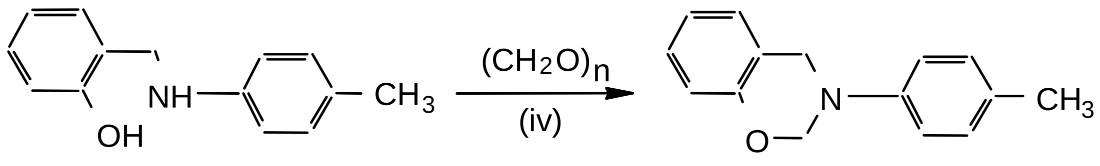


1. Add the impure Product A from Step I to a 5 cm^3 reaction vial containing approximately 1.5 cm^3 of ethanol.
2. Surround the vial with ice/water, and stir the reaction vigorously with the spatula while carefully adding small amounts of sodium borohydride (iii) over a period of about

   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

7 theoretical problems
2 practical problems

THE THIRTIETH
INTERNATIONAL CHEMISTRY OLYMPIAD
5–14 JULY 1998, MELBOURNE, AUSTRALIA

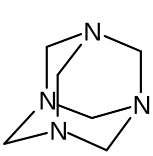
THEORETICAL PROBLEMS

PROBLEM 1

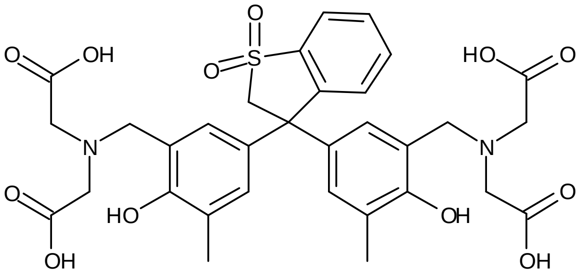
The following 8 steps describe the procedure for analysing a sample of alloy that contains both tin and lead.

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.



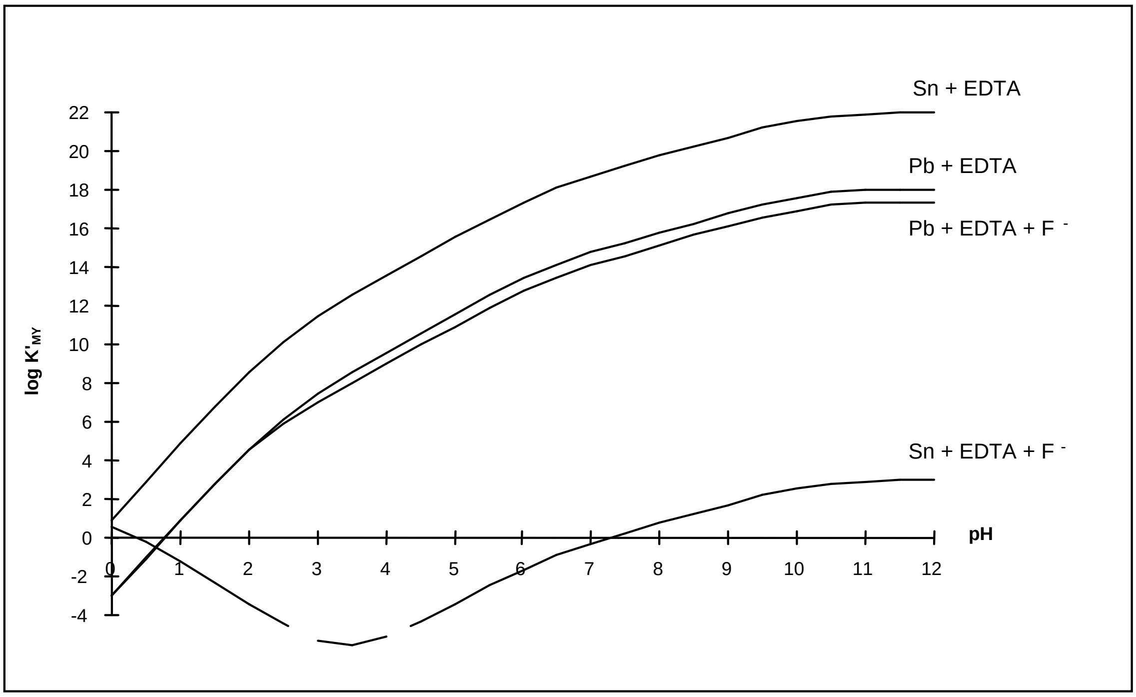
Hexamine



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:

$n(\text{EDTA}) = n(Pb^{2+}) = 0.02405\ dm^3 \times 0.009970\ mol\ dm^{-3} = 2.398\times10^{-4}$ 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.

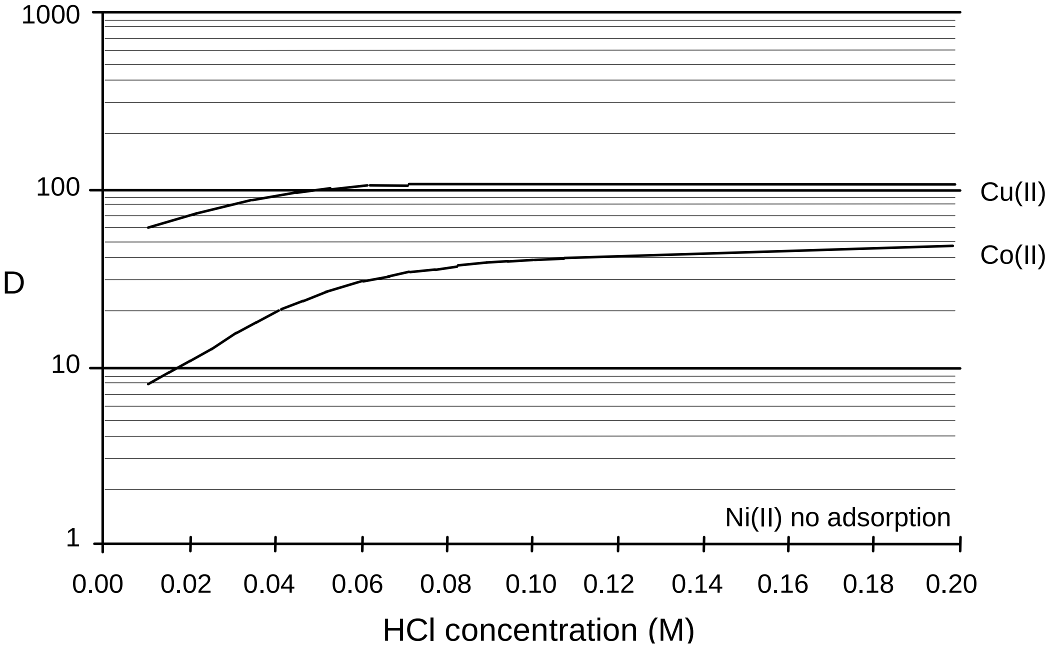


Figure 1. Distribution coefficients, *D* of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note *D* value for Zn > 1000)

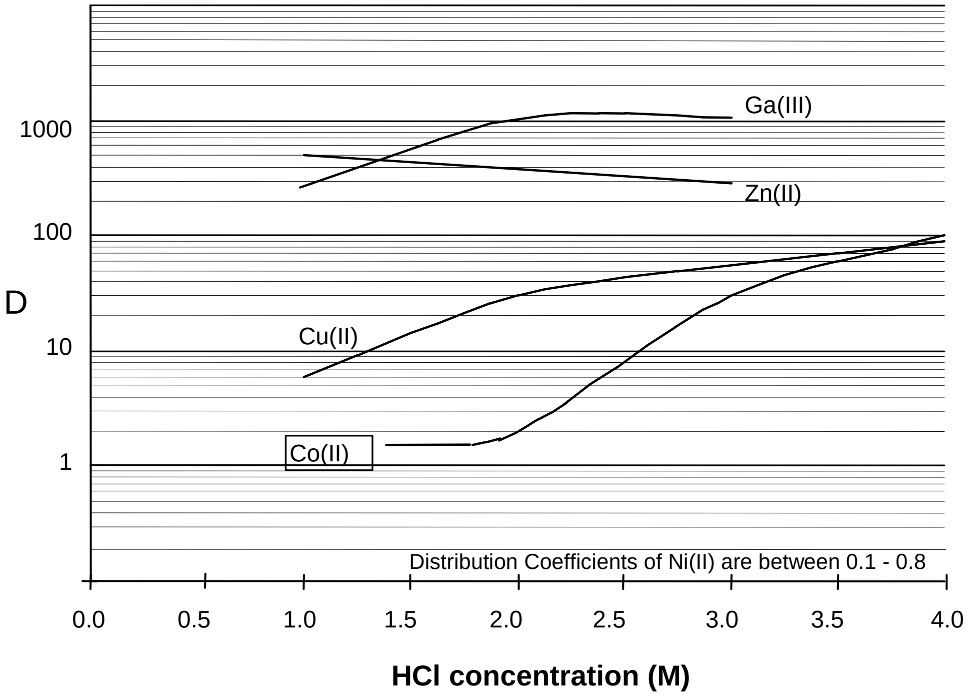


Figure 2. Distribution coefficients, *D* of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

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

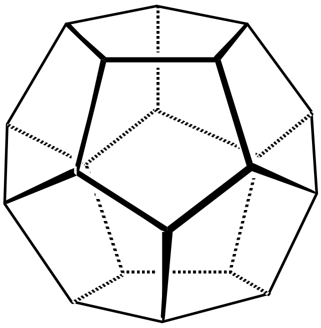
b) True

c) False

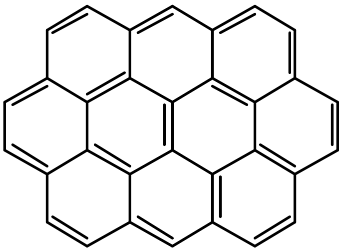
d) True

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, $C_{32}H_{14}$.

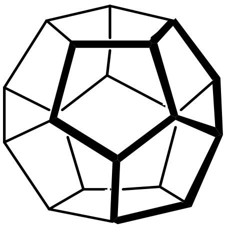
Each C_5 ring of dodecahedrane is a regular pentagon, while each C_6 ring of ovalene can be regarded as a regular hexagon.

3.1 What are the ∠(CCC) angles for each of these rings?

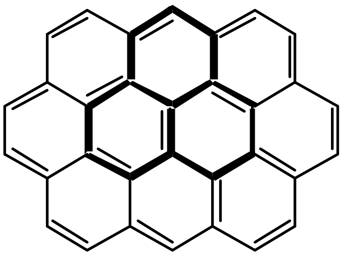
3.2 Which configuration (trigonal planar, 120°; tetrahedral, 109.5°; or octahedral, 90°) do the above ∠ (CCC) angles most closely match?

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?

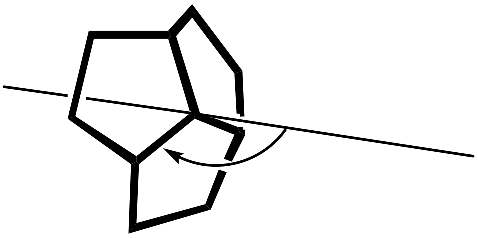
A "<u>juncture</u>" is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctures (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:



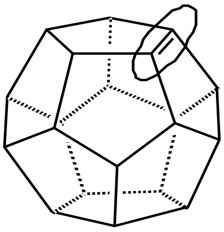
Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.



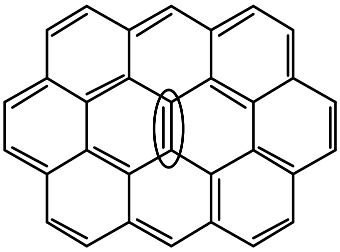
3.4 What is the value of this angle for dodecahedrane (make an "educated guess", to the nearest three degrees), and for ovalene?

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 ($C_{20}H_{18}$):



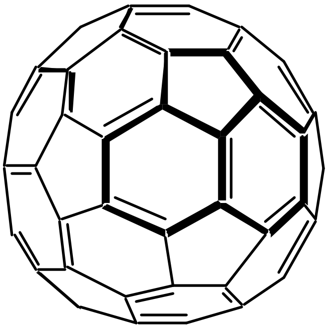
and ovalene:



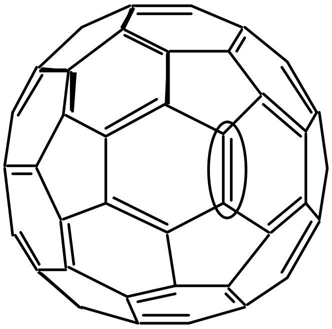
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

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.



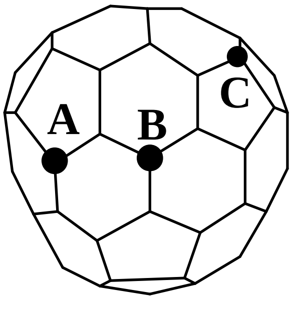
For C_{60}, all junctures are entirely equivalent. Now consider H_2 addition at a C=C bond of C_{60}:



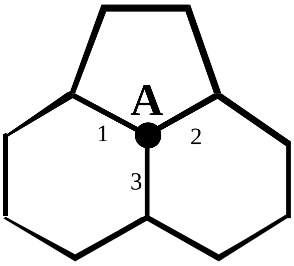
3.7 For which of C_{60}, dodecahedrene, or ovalene is H_2 addition <u>most</u> exothermic? (Again, assume localization of double bonds.)

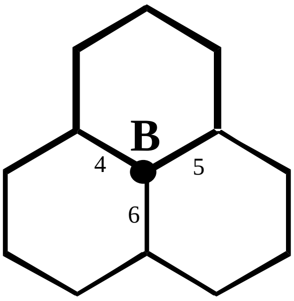
3.8 For which of C_{60}, dodecahedrene, or ovalene is H_2 addition <u>least</u> exothermic?

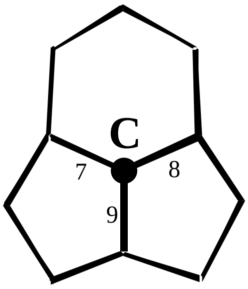
There is evidence for fullerenes smaller than C_{60}, such as C_{58}. The C_{58} structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:



The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:





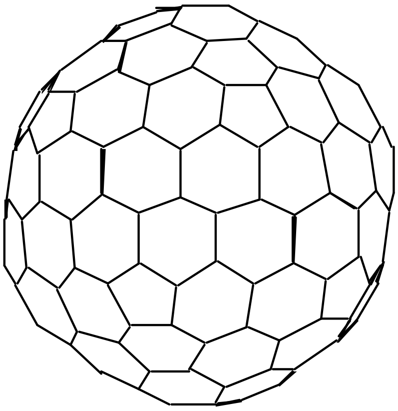


3.9 Which juncture has the least deviation from planarity ?

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).

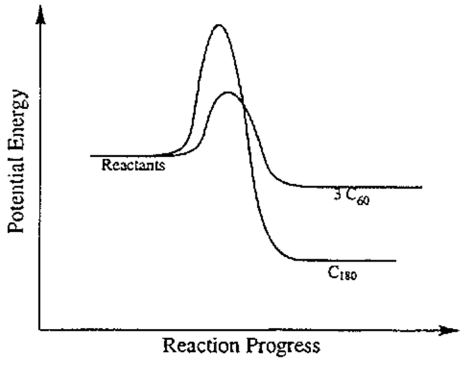
3.14 Which of graphs best represents the dependence of potential energy upon reaction progress for the two processes:

$$\text{reactants} \rightleftharpoons 3\ C_{60}$$

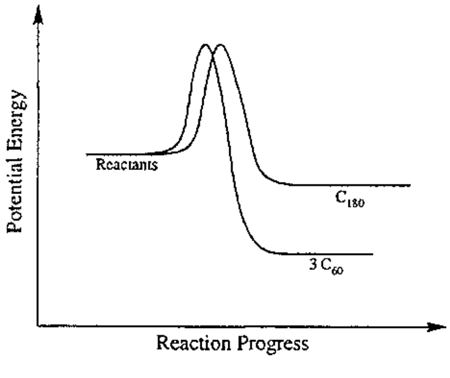
and

$$\text{reactants} \rightleftharpoons C_{180}$$

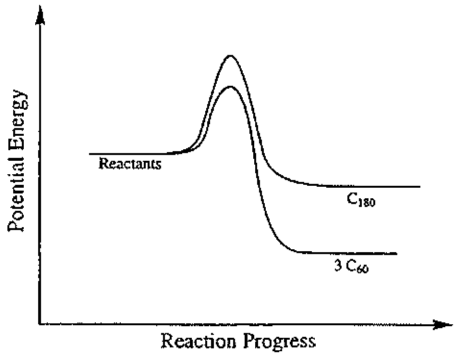
a).



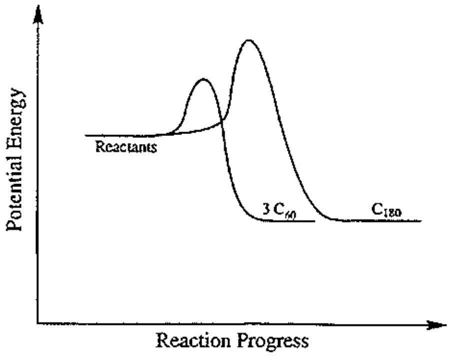
b).



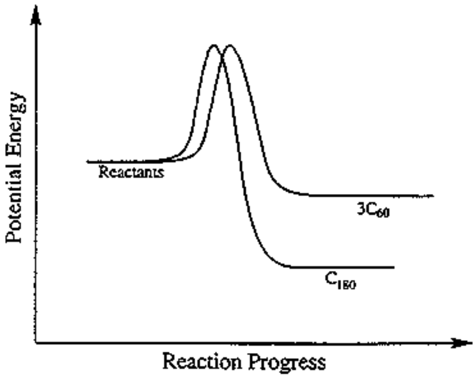
c).



d).



e).



The best graph is: a)

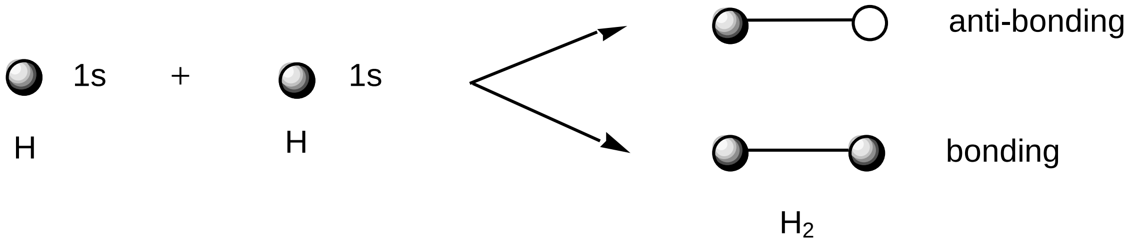
Reasoning: The equilibrium reaction

$$C_{60} \rightleftharpoons \text{reactants} \rightleftharpoons 3\ C_{60}$$

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.

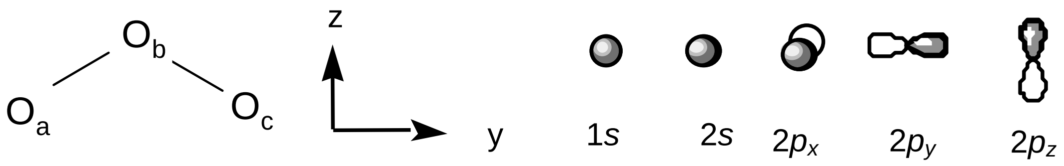
PROBLEM 4

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.

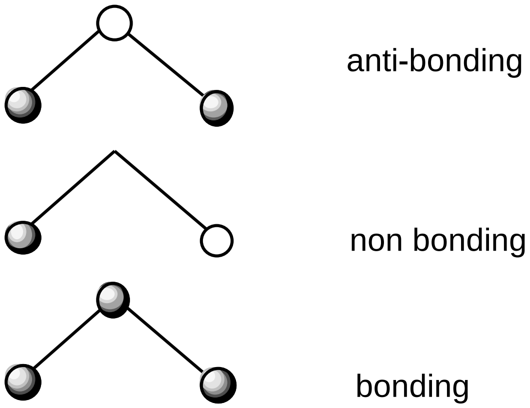
Consider the ozone molecule, O_3, which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the *yz* plane) and assume that there are 1*s*, 2*s*, 2p_x, 2p_y and 2p_z orbitals on each atom.



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:

Symmetric Anti-symmetric

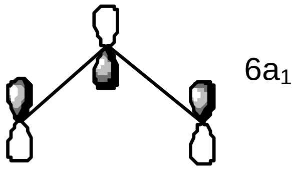
In this molecule the 1*s* atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final 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).

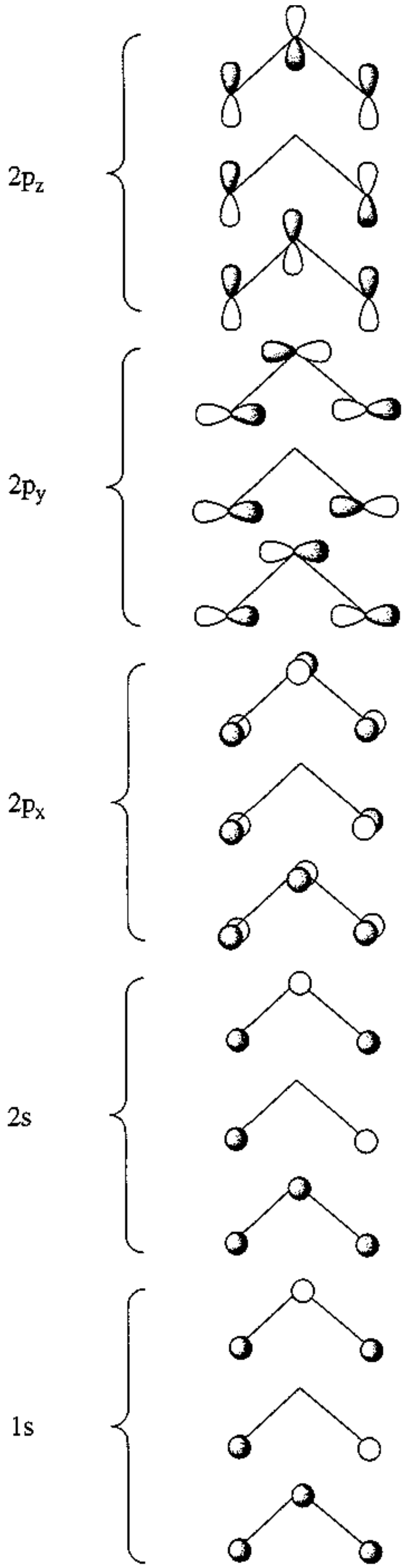
<u>Reasoning</u>: The energy changes so rapidly because the overlap is bonding between all three atoms in the bent molecule, but becomes more and more anti-bonding as the molecule approaches linearity:

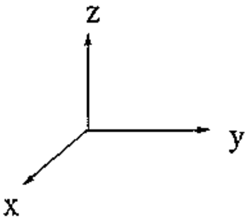
4.3

O_3	BO_2	CO_2	NO_2	FO_2
$\boxed{6a_x\ (24e-)}$	$\boxed{4b_2\ (21e-)}$	$\boxed{4b_2\ (22e-)}$	$\boxed{6a_1\ (23e-)}$	$\boxed{2bx\ (25e-)}$

4.4 The correct answer is (d): NO_2 is less bent than O_3, and FO_2 is more bent than O_3.

Atomic orbitals Molecular orbitals





PROBLEM 5

Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[Au(CN)_2]^-$, 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.

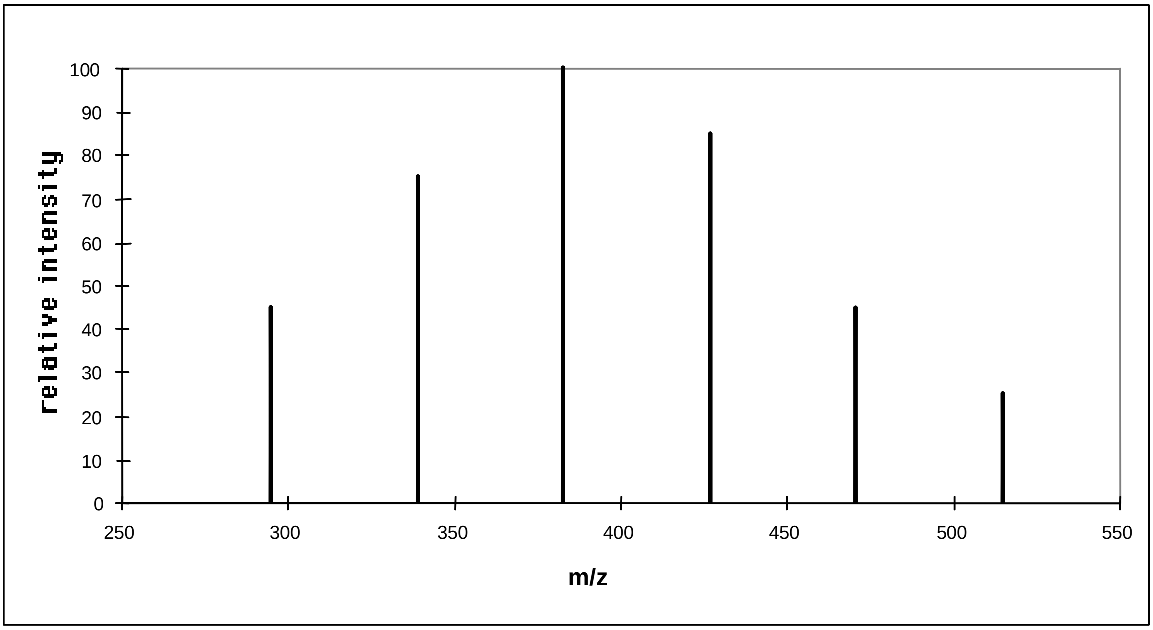
A solution containing $SnBr_6^{2-}$ (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at m/z=515.

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



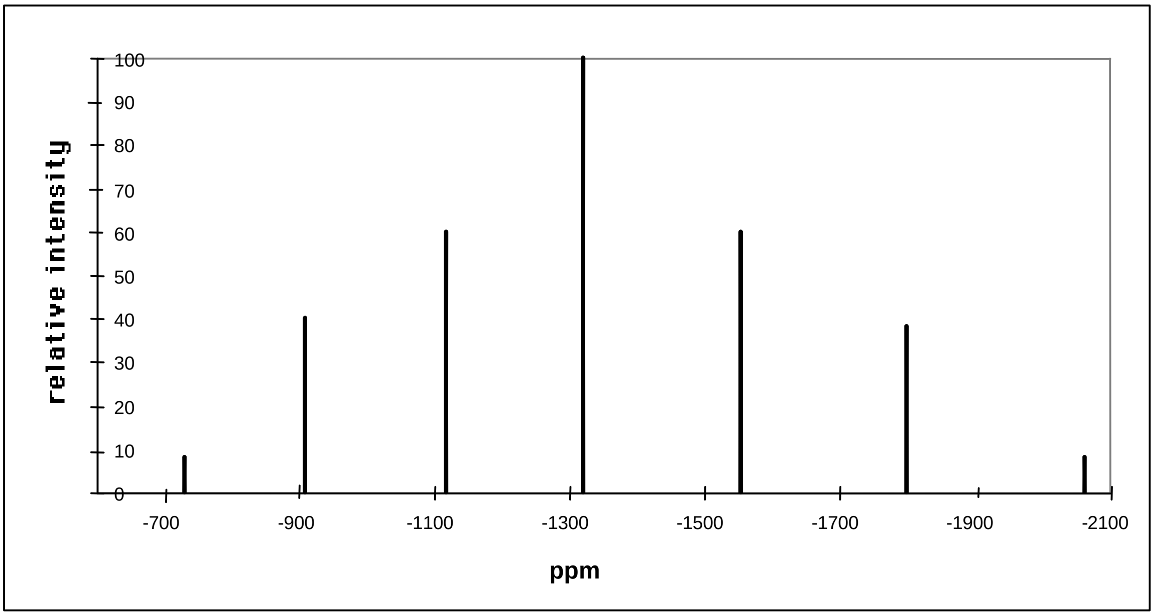
6.8 Write the empirical formula for each of the four new species.

^1H and ^{13}C NMR spectroscopy of molecules enable detection of a separate signal for each proton and ^{13}C nucleus which is in a different environment. These signals are recorded on dimensionless parts per million (ppm) scale relative to some agreed standard reference compound. Similarly, ^{119}Sn NMR gives a signal for each tin atom which is in a different environment.

The ^{119}Sn NMR spectrum of a solution of $SnCl_6^{2-}$ (as the tetrabutylammonium salt) contains only one signal which occurs at –732 ppm (relative to tetramethyltin, Me_4Sn). The ^{119}Sn NMR spectrum of a solution of $SnBr_6^{2-}$ (as the tetrabutylammonium salt) occurs at 2064 ppm. The ^{119}Sn NMR spectrum at 60 °C of a solution formed by mixing equimolar amounts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ contains seven peaks (Fig. 2).

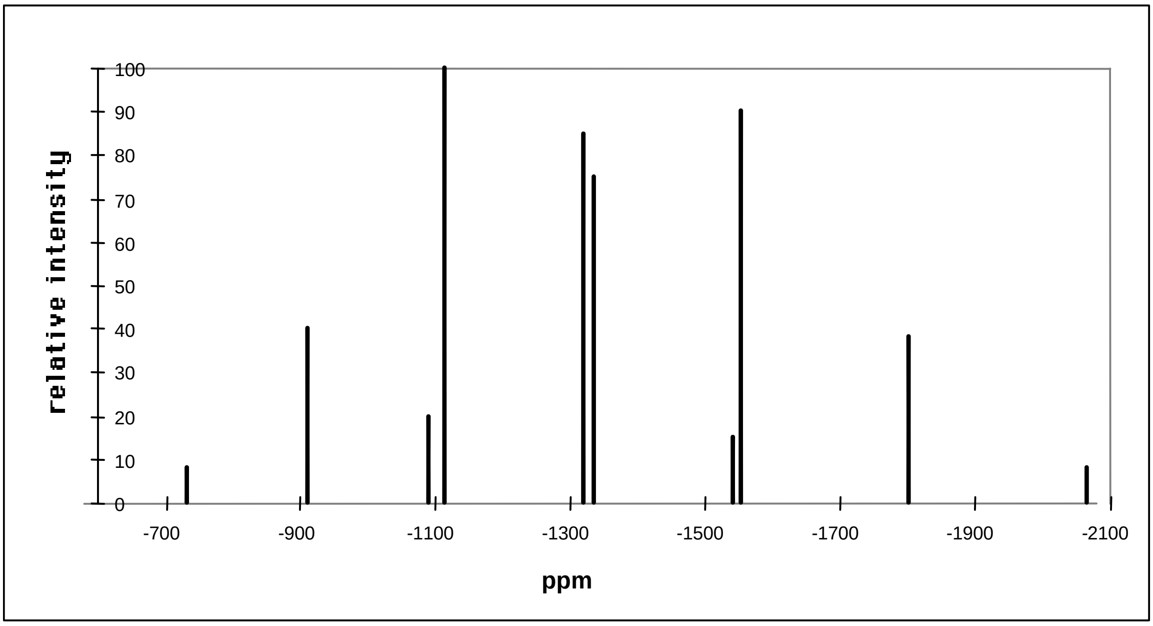
6.9 Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed on the answer template.

Fig. 2



Cooling the solution causes a change to this ^{119}Sn NMR spectrum and at -30 °C ten peaks are observed (Fig. 3).

Fig. 3

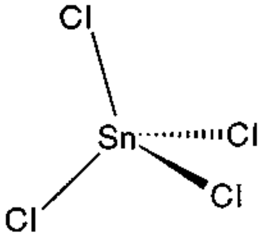


6.10 Draw the geometry for the four tin-containing species present in this solution at –30 °C that give rise to the peaks at –1092 and –1115, –1322 and –1336 ppm.

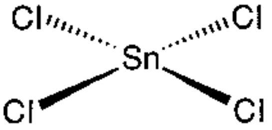
SOLUTION

6.1

A

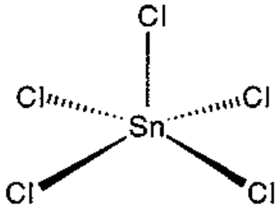


B

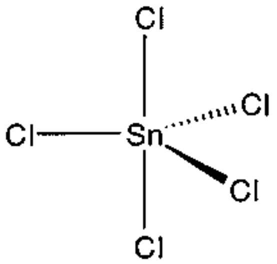


6.2

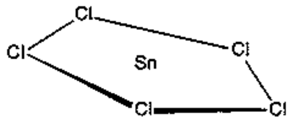
C



D



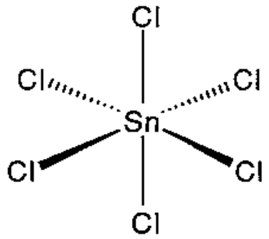
E



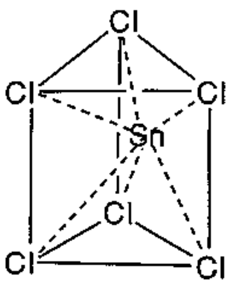
6.3 In accordance with VSEPR theory geometry D is likely to be preferred for $SnCl_5^-$.

6.4

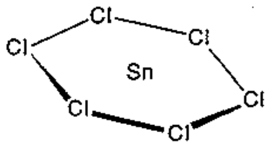
F



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

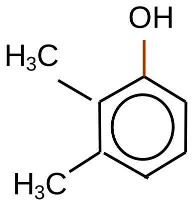
-1092 ppm and -1115 ppm (2 compounds)

-1322 ppm and -1336 ppm (2 compounds)

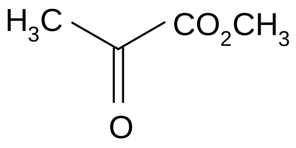
PROBLEM 7

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

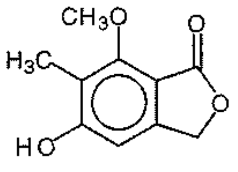
Compound **D** was synthesised as follows: The phenol **E** was methylated (MeI/K_2CO_3) to afford **F** ($C_9H_{12}O_2$) which in turn was reduced with lithium metal in liquid ammonia and 2-methyl-propan-2-ol to give the symmetrical unconjugated diene **G**. Conjugation of this diene was achieved by 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**.

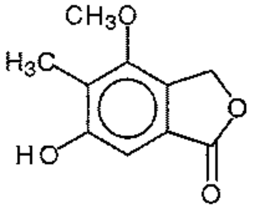
7.2 Using the last space on the answer template provide a second structure for **B**.

SOLUTION

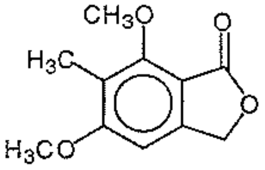
7.1 and **7.2**



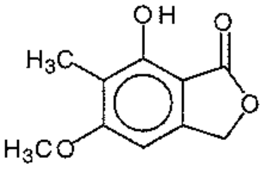
A



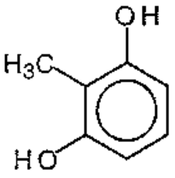
B



C



D



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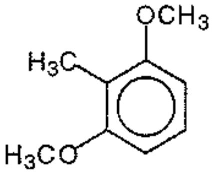
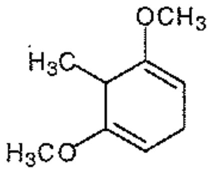
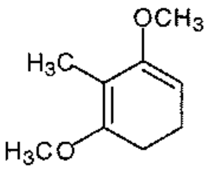


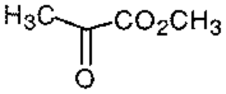
F



G



H



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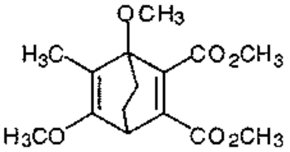

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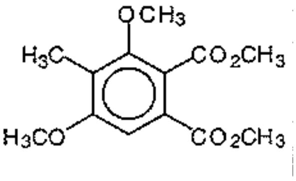

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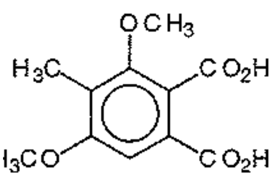

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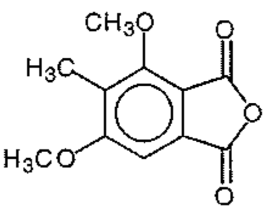

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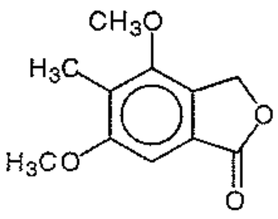

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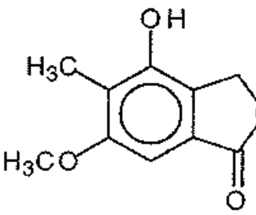


Other structure for **B**

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.

$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4 \text{ (s)}$$

The precipitate must then be re-dissolved in acid:

$$CaC_2O_4 \text{ (s)} + 2\ H^+ \rightarrow Ca^{2+} + H_2C_2O_4$$

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 °C, then when all the calcium oxalate precipitate is dissolved, carefully titrate the hot solution with standard potassium permanganate solution.

    CARE! It is not necessary to measure the temperature of the solution with a thermometer. 60 °C is uncomfortably hot to touch.
17. Discard the titrated solution into the residue bottle labelled "**Permanganate/Oxalate residues**".

Calculate the average concentration of calcium ion in the <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 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! $dm^{-3} \times 0.02412\ dm^3 = 0.01206$ 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:

$c(H^+) = 0.01206\ mol\ dm^{-3} \times (25.00\ cm^3) / (22.32\ cm^3) = 0.01351\ mol\ dm^{-3}$

total $n(H^+)$ collected from column:

$n(H^+) = 0.01351\ mol\ dm^{-3} \times 0.100\ dm^3 = 1.351 \times 10^{-3}\ mol$

$n(H^+)$ from aliquot put onto column:

$n(H^+) = 0.00500\ mol\ dm^{-3} \times 0.02500\ dm^3 = 1.250 \times 10^{-4}\ mol$

$n(H^+)$ ion-exchanged from complexes in aliquot put onto column:

$n(H^+) = 1.351 \times 10^{-3}\ mol - 1.250 \times 10^{-4}\ mol = 1.226 \times 10^{-3}\ mol$

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 = $(25.00\ cm^3 / 40\ cm^3) \times 0.2000\ g = 0.1250\ g$

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} = 0.007663x 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 %

31st

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE THIRTY-FIRST
INTERNATIONAL CHEMISTRY OLYMPIAD
3–12 July 1999, BANGKOK, THAILAND

THEORETICAL PROBLEMS

PROBLEM 1

A compound **Q** (molar mass 122.0 g mol^{-1}) consists of carbon, hydrogen and oxygen.

PART A

The standard enthalpy of formation of CO_2(g) and H_2O(l) at 25.00 °C are –393.51 and –285.83 kJ mol^{-1}, respectively. The gas constant, R = 8.314 J K^{-1} mol^{-1}.
(Relative atomic masses : H = 1.0; C = 12.0; O = 16.0)

A sample of solid **Q** that weighs 0.6000 g, is combusted in an excess of oxygen in a bomb calorimeter, which initially contains 710.0 g of water at 25.000 °C. After the reaction is completed, the temperature is observed to be 27.250 °C, and 1.5144 g of CO_2 (g) and 0.2656 g of H_2O(l) are produced.

1.1 Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of **Q**.

If the specific heat of water is 4.184 J g^{-1} K^{-1} and the internal energy change of the reaction (ΔU^0) –3079 kJ mol^{-1}.

1.2 Calculate the heat capacity of the calorimeter (excluding the water).

1.3 Calculate the standard enthalpy of formation ($\Delta H_f^{\,0}$) of **Q**.

PART B

The following data refer to the distribution of **Q** between benzene and water at 6 °C, C_B and C_W being equilibrium concentrations of the species of **Q** in the benzene and water layers, respectively:

Assume that there is only one species of **Q** in benzene independent of concentration and temperature.

Concentration (mol dm^{-3})	
c_B	c_W
0.0118	0.00281
0.0478	0.00566
0.0981	0.00812
0.156	0.0102

1.4 Show by calculation whether **Q** is monomer or dimer in benzene. Assume that **Q** is a monomer in water.

The freezing point depression, for an ideal dilute solution, is given by

$$T_f^0 - T_f = \frac{R(T_f^0)^2\ X_s}{\Delta H_f}$$

where T_f is the freezing point of the solution, T_f^0 the freezing point of solvent, ΔH_f the heat of fusion of the solvent, and X_s the mole fraction of solute. The molar mass of benzene is 78.0 g mol^{-1}. At 1 atm pure benzene freezes at 5.40 °C. The heat of fusion of benzene is 9.89 kJ mol^{-1}.

1.5 Calculate the freezing point (T_f) of a solution containing 0.244 g of **Q** in 5.85 g of benzene at 1 atm.

SOLUTION

PART A

1.1 Mole C : H : O = $\dfrac{\dfrac{15144 \times 12.0}{44.0}}{12.0} : \dfrac{\dfrac{0.2656 \times 2.0}{18.0}}{1.0} : \dfrac{0.1575}{16.0}$

= 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2

The formula mass of $C_7H_6O_2$ = 122 which is the same as the molar mass given.

$C_7H_6O_2(s) + 15/2\ O_2(g) \rightarrow 7\ CO_2(g) + 3\ H_2O(l)$ or

$2\ C_7H_6O_2(s) + 15\ O_2(g) \rightarrow 14\ CO_2(g) + 6\ H_2O(l)$

1.2 $n(\text{Q}) = \dfrac{0.6000}{122.0} = 4.919\times10^{-3}$ mol

$q_v = n\,\Delta U^0 = \dfrac{0.6000}{122.0} \times (-3079) = -15.14$ kJ

Total heat capacity = $\dfrac{-q_v}{\Delta T} = \dfrac{15.14}{2.250} = 6.730$ kJ K^{-1}

Heat capacity of water = 710.0 × 4.184 = 2971 J K^{-1}

Heat capacity of calorimeter = 6730 – 2971 = 3759 J K^{-1}

1.3 $\Delta n_g = 7 - 15/2 = -0.5$ mol

$\Delta H° = \Delta U° + \text{RT}\,\Delta n_g = -3079 + (8.314\times10^{-3}) \times (298) \times (-0.5) = -3079 - 1 = -3080$

$\Delta H° = (7\,\Delta_f H°, \text{CO}_2(\text{g}) + 3\,\Delta_f H°, \text{H}_2\text{O(l)}) - (\Delta_f H°, \text{Q})$

$\Delta_f H°$ of Q = $7 \times (-393.51) + 3 \times (-285.83) - (-3080)$ $\underline{= -532 \text{ kJ mol}^{-1}}$

PART B

1.4

c_B (mol dm^{-3})	0.0118	0.0478	0.0981	0.156
c_W (mol dm^{-3})	0.00281	0.00566	0.00812	0.0102
either c_B/c_W	4.20	8.44	12.1	15.3
or c_B/c_W^2	1.49×10^3	1.49×10^3	1.49×10^3	1.50×10^3
(or $\sqrt{c_B}\,/\,c_W$	38.6	38.6	38.6	38.7)

From the results show that the ratio c_B/c_W varies considerably, whereas the ratio c_B/c_W^2 or $\sqrt{c_B}\,/\,c_W$ is almost constant, showing that in benzene, Q is associated into double molecule. Q in benzene is dimer.

1.5 If Q is completely dimerized in benzene, the apparent molecular mass should be 244.

Mole fraction of $\text{Q}_2 = \dfrac{\dfrac{0.244}{244}}{\dfrac{0.244}{244} + \dfrac{5.85}{78.0}} = 1.32\times10^{-2}$ (0.01316)

$$\Delta T_f = \frac{8.314 \times 278.55^2}{9.89\times10^3} \times 1.32\times10^{-2} = 0.861$$

$T_f = 5.40 - 0.861 = 4.54$ ℃

PROBLEM 2

PART A

A diprotic acid , H_2A , undergoes the following dissociation reactions :

$$H_2A \rightleftharpoons HA^- + H^+; \qquad K_1 = 4.50\times10^{-7}$$

$$HA^- \rightleftharpoons A^{2-} + H^+; \qquad K_2 = 4.70\times10^{-11}$$

A 20.00 cm^3 aliquot of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode *pH* meter. Two points on the titration curve are as follows :

cm^3 HCl added	*pH*
1.00	10.33
10.00	8.34

2.1 On adding 1.00 cm^3 of HCl, which species reacts first and what would be the product?

2.2 What is the amount (mmol) of the product formed in (2.1)?

2.3 Write down the main equilibrium of the product from (2.1) reacting with the solvent?

2.4 What are the amounts (mmol) of Na_2A and NaHA initially present?

2.5 Calculate the total volume of HCl required to reach the second equivalence point.

PART B

Solutions I, II and III contain a *pH* indicator HIn ($K_{In} = 4.19\times10^{-4}$) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cell, are also given in the table. K_a of CH_3COOH is 1.75×10^{-5}.

Table:

	Solution I	Solution II	Solution III
Total concentration of indicator HIn	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400	0.000	0.300	?

2.6 Calculate the absorbance at 400 nm of solution III.

2.7 Apart from H_2O, H^+ and OH^-, what are all the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio?

2.8 What is the absorbance at 400 nm of the solution in (2.7)?

2.9 What is the transmittance at 400 nm of the solution in (2.7)?

SOLUTION

PART A

2.1 Species which reacts first is A^{2-}.

The product is HA^-.

2.2 n(product) = 1.00 × 0.300 = 0.300 mmol

2.3 $HA^- + H_2O \rightleftharpoons H_2A + OH^-$

2.4 At pH 8.34 which is equal to (pK_{a1} + pK_{a2}) / 2 all A^- are protonated as HA^- .

Therefore $n(A^{2-})$ initially present in the solution = 0.300 × 10.00 = 3.00 mmol

At pH = 10.33, the system is a buffer in which the ratio of $[A^{2-}]$ and $[HA^-]$ is equal to 1.

Thus

$[HA^-]_{initial} + [HA^-]_{formed} = [A^{2-}]_{jnitial} - [HA^-]_{formed}$

$n(HA^-)_{initial}$ = 3.00 – 0.300 – 0.300 mmol = 2.40 mmol

$n(Na_2A)$ = <u>3.00 mmol</u>

n(NaHA) = <u>2.40 mmol</u>

2.5 Total volume of HCl required = [(2 × 3.00) + 2.40] / 0.300 = 28.00 cm^3

PART B

2.6 Solution III is the indicator solution at 1×10^{-5} M in a solution containing 1.0 M CH_3COOH.

To obtain the absorbance of the solution, it is necessary to calculate the concentration of the basic form of the indicator which is dependent on the [H$^+$] of the solution.

[H$^+$] of solution III = $\sqrt{K_a\,c} = \sqrt{1.75\times10^{-5}\times1.0} = 4.18\times10^{-3}$

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{1\times10^{-3.38}}{1\times10^{-2.38}} = 0.100$$

Since $\quad [\text{HIn}] + [\text{In}^-] = 1\times10^{-5}$

$10\,[\text{In}^-] + [\text{In}^-] = 1\times10^{-5}$

$[\text{In}^-] = 0.091\times10^{-5}$

Absorbance of solution III = $\dfrac{0.091\times10^{-5}}{1.00\times10^{-5}}\times0.300 = 0.027$

2.7 All the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio (apart from H^+, OH^- and H_2O) are the following: CH_3COOH , CH_3COO^-, Na^+ , HIn , In^-.

2.8 When solutions II and III are mixed at 1 : 1 volume ratio, a buffer solution of 0.05 M CH_3COO^- / 0.45 M CH_3COOH is obtained.

[H$^+$] of the mixture solution = $K_a\dfrac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.75\times10^{-5}\times\dfrac{0.45}{0.05} = 15.75\times10^{-5}$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{1\times10^{-3.38}}{15.75\times10^{-5}} = 2.65$$

Since $\quad [\text{HIn}] + [\text{In}^-] = 1\times10^{-5}$

$\dfrac{[\text{In}^-]}{2.65} + [\text{In}^-] = 1\times10^{-5}$

$[\text{In}^-] = 0.726\times10^{-5}$

Absorbance of solution = $\dfrac{0.726\times10^{-5}}{1.00\times10^{-5}}\times0.300 = 0.218$

2-9 Transmittance of solution = $10^{-0.218}$ = 0.605 ⇒ 60.5%

PROBLEM 3

One of naturally occurring radioactive decay series begins with $^{232}_{90}\mathrm{Th}$ and ends with a stable $^{208}_{82}\mathrm{Pb}$.

3.1 How many beta (β^-) decays are there in this series? Show by calculation.

3.2 How much energy in MeV is released in the complete chain?

3.3 Calculate the rate of production of energy (power) in watts (1 W = J s^{-1}) produced by 1.00 kilogram of $^{232}\mathrm{Th}$ ($t_{½} = 1.40\times10^{10}$ years).

3.4 $^{228}\mathrm{Th}$ is a member of the thorium series. What volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of $^{228}\mathrm{Th}$ ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years. The half-lives of all intermediate nuclides are short compared to the half-life of $^{228}\mathrm{Th}$.

3.5 One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic masses are :

$^{4}_{2}\mathrm{He}$ = 4.00260 u, $^{208}_{82}\mathrm{Pb}$ = 207.97664 u, $^{232}_{90}\mathrm{Th}$ = 232.03805 u; and 1u = 931.5 MeV

1 MeV = 1.602×10^{-13} J

$N_A = 6.022\times10^{23}$ mol^{-1}

The molar volume of an ideal gas at 0 °C and 1 atm is 22.4 dm^3 mol^{-1}.

SOLUTION

3.1 A = 232 – 208 = 24; 24/4 = 6 alpha particles

The nuclear charge is therefore reduced by 2 × 6 = 12 units, however, the difference in nuclear charges is only 90 – 82 = 8 units. Therefore there must be

12 – 8 = 4 β^- emitted.

Number of beta decays = 4

3.2 $^{232}_{90}\mathrm{Th} \rightarrow {}^{208}_{82}\mathrm{Pb} + 6\,{}^{4}_{2}\mathrm{He} + 4\beta^-$

Energy released is Q value

$Q = [m(^{232}Th) – m(^{208}Pb) – 6\, m(^{4}He)]\, c^2$

(the mass of 4e$^-$ are included in daughters)

$= [232.03805\ u – 207.97664\ u – 6 \times 4.00260\ u] \times 931.5\ MeV\ u^{-1} =$

$= (0.04581u) \times (931.5\ MeV) = 42.67\ MeV$

3.3 The rate of production of energy (power) in watts (1 W = J s$^{–1}$) produced by 1.00 kilogram of ^{232}Th ($t_{tl/2} = 1.40\times10^{10}$ years).

1.00 kg contains = $\dfrac{1000\ g \times 6.022\times10^{23}\ mol^{-1}}{232\ g\ mol^{-1}}$ = 2.60×10^{24} atoms

Decay constant for ^{232}Th:

$$\lambda = \frac{0.693}{1.40\times10^{10}\ y \times 3.154\times10^{7}\ \ s\,y^{-1}} = 1.57\times10^{-18}\ s^{-1}$$

For activity: $A = N\,\lambda = 2.60\times10^{24} \times 1.57\times10^{-18} = 4.08\times10^{6}$ dis s$^{–1}$

(disintegrations s$^{–1}$)

Each decay liberates 42.67 MeV

Rate of production of energy (power):

4.08×10^{6} dis s^{-1} × 42.67 MeV dis^{-1} × 1.602×10^{-13} J MeV^{-1} =

= 2.79×10^{-5} J s^{-1} = 2.79×10^{-5} W

3.4 The volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years.

$^{228}Th \rightarrow {}^{208}Pb + 5\ {}^{4}He$

The half-lives of various intermediates are relatively short compared with that of ^{228}Th.

$$A = \lambda N = \frac{0.693}{1.91\,y} \times \frac{1.000\ g \times 6.022\times10^{23}\ mol^{-1}}{228\ g\,mol^{-1}} = 9.58\times10^{20}\ y^{-1}$$

Number of He collected:

$N_{He} = 9.58\times10^{20}\ y^{-1} \times 20.0\ y \times 5$ particles = 9.58×10^{22} particles of He

$$V_{He} = \frac{9.58\times10^{22} \times 22{,}4\ dm^3\,mol^{-1}}{6.022\times10^{23}\ mol^{-1}} = 3.56\ dm^3 = 3.56\times10^{3}\ cm^3$$

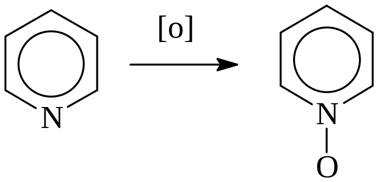
3.5 The half-life:

$A = \lambda N$

$$t_{½} = \frac{0.693}{\lambda} = \frac{0.693\,N}{A} = \frac{0.693 \times 510 \times 10^{10}\text{ atoms}}{3440\text{ atoms min}^{-1}} = 3.02 \times 10^{6}\text{ min} = 5.75\text{ years}$$

PROBLEM 4

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70 – 80 °C for 3 hrs. The final product **L** crystallizes out as fine needles and its molecular mass is 188. An analogous reaction with pyridine is ;



Complexes of **L** with Fe and Cr have the formulae of $FeL_m(ClO_4)_n$. 3 H_2O (**A**) and $CrL_xCl_y(ClO_4)_z.H_2O$ (**B**), respectively. Their elemental analyses and physical properties are given in Tables 4a and 4b. The relationship of colour and wavelength is given in Table 4c.

Table 4a: Elemental analyses.

Complex	Elemental analyses , (wt. %)
A	Fe 5.740, C 37.030, H 3.090 , Cl 10.940, N 8.640
B	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080

Use the following data:

Atomic number: Cr = 24, Fe = 26

Relative atomic mass: H = 1, C = 12, N = 14, O = 16, Cl = 35.45, Cr = 52, Fe = 55.8

Table 4b: Physical properties

Complex	Magnetic moment , μ B.M.	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

4.1 Write down the molecular formula of **L**.

4.2 If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L** .

4.3 Does the ligand **L** have any charge, i. e. net charge?

4.4 Draw the structure when one molecule of **L** binds to metal ion (M).

4.5 From the data in Table 4a, determine the empirical formula of **A**. What are the values of m and n in $FeL_m(ClO_4)_n$ .3 H_2O? Write the complete formula of **A** in the usual IUPAC notation. What is the ratio of cation to anion when **A** dissolves in water?

4.6 What is the oxidation number of Fe in **A**? How many d-electrons are present in Fe ion in the complex? Write the high spin and the low spin configurations that may exist for this complex. Which configuration, high or low spin, is the correct one? What is the best evidence to support your answer?

4.7 From Table 4c, estimate λ_{max} (nm) of **A**.

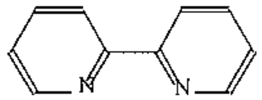
4.8 Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the 'spin-only' magnetic moment of this compound.

4.9 Compound **B** is a 1 : 1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in $CrL_xCl_y(ClO_4)_z$. H_2O.

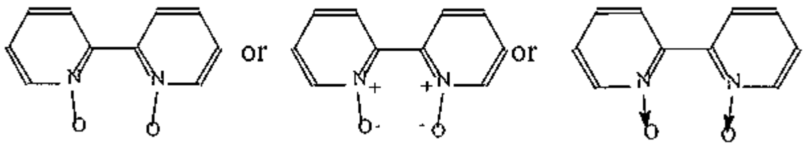
SOLUTION

4.1 Knowing that L was synthesized from bipyridine and during the reaction bipyridine was simply oxidized to bipyridine oxide. The molecular mass of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of **L** is 188. The difference of 32 is due to 2 atoms of oxygen. Therefore, the molecular formula of **L** is $C_{10}H_8N_2O_2$.

4.2 The structures of bipyridine and **L**:



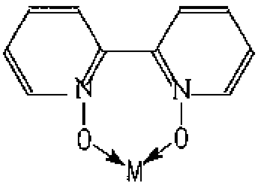
Structure of bipyridine



structure of L

4.3 The ligand **L** has no charge.

4.4 The structure when one molecule of **L** binds to metal ion (M):



4.5 The empirical formula of **A**. Calculation:

	Fe	C	H	Cl	N	O
%	5.740	37.030	3.090	10.940	8.640	34.560*
mol	0.103	3.085	3.090	0.309	0.617	2.160
mol ratio	1.000	29.959	30.00	2.996	5.992	20.971
atom ratio	1	30	30	3	6	21

*) Percentage of O is obtained by difference.)

The empirical formula of **A** is $FeC_{30}H_{30}Cl_3N_6C_{21}$

The values of m and n in $FeL_m(C104)_n$. 3 H_2O:

Since the molecular formula contains one atom of Fe, so in this case the empirical formula is equivalent to the molecular formula. The molecular formula of **L** has been obtained previously in (4a) and (4b), therefore we can work to find m = 3. Having obtained the value of m , one can work out for n and find that n = 3.

The complete formula of **A** is $[FeL_3](ClO_4)_3 \cdot 3\,H_2O$

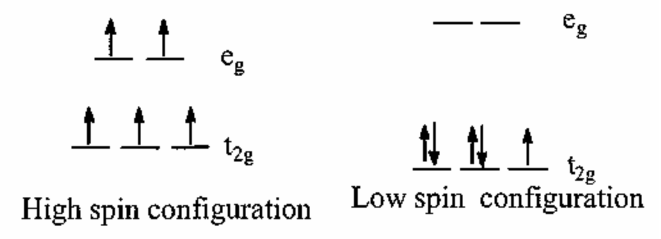
The ratio of cation to anion is equal to 1 : 3.

The three ClO_4^- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as $[FeL_3]^{3+}$ and 3 ClO_4^- in solution.

4.6 The oxidation number of Fe in complex **A** is +3 or III.

The number of *d*-electrons in Fe^{3+} ion in the complex = 5.

The high spin and the low spin configuration that may exist for this complex:



The correct answer is high spin configuration.

The best evidence to support your answer for this high/low spin selection is magnetic moment.

There exist a simple relation between number of unpaired electrons and the magnetic moment as follows:

$$\mu = \sqrt{n(n+2)}$$

where μ is the so-called 'spin-only' magnetic moment and n is the number of unpaired electrons. Thus, for high spin configuration in the given case,

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M.}$$

For low spin case:

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ B.M.}$$

The measured magnetic moment, for **A** is 6.13 B.M. (Table 4b) which is in the range for high spin configuration. Therefore, we can conclude that **A** can exist as a high spin complex.

4.7 From Table 4c, the color absorbed is complementary to the color seen. Thus, λ_{max} for complex A is 450 nm.

4.8 The 'spin-only' magnetic moment of complex **B**.

For Cr^{3+}: n = 3

Therefore, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M.

4.9 The empirical formula of B is $Cr_{20}H_{18}N_4Cl_3O_9$, i.e. x = 2, y = 2, z = 1.

PROBLEM 5

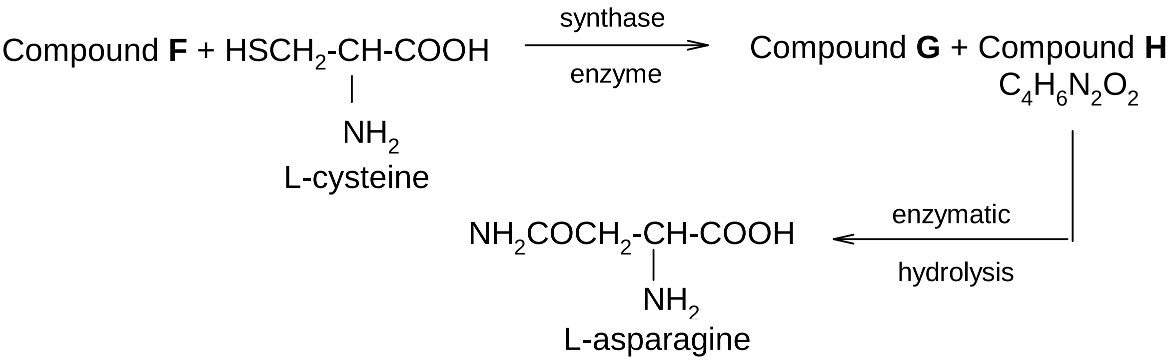
Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedicts' or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$ and (-) **E**, $C_8H_8O_3$.

C has a β-glycosidic linkage and gives positive test with Benedicts' or Fehling's solution. Methylation of **C** with MeI/Ag_2O gives $C_{20}H_{38}O_{11}$, which upon acidic hydrolysis gives 2,3,4-tri-*O*-methyl-D-glucopyranose and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose.

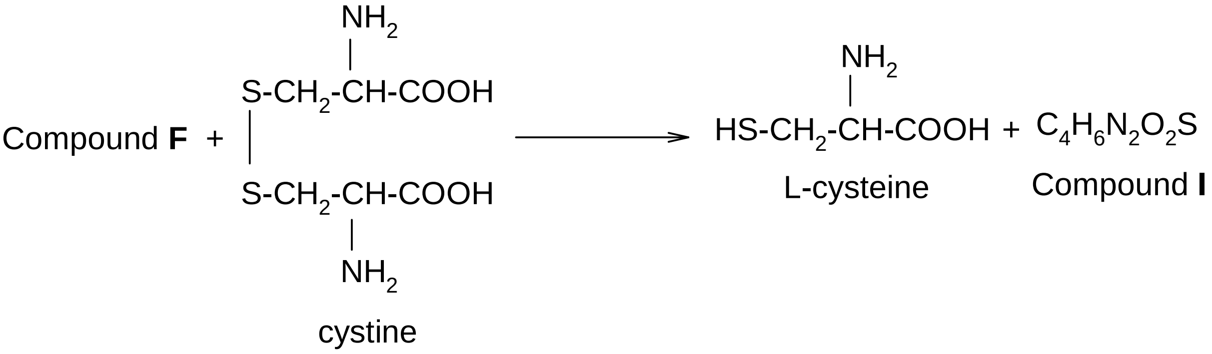
(±)**B** can be prepared from benzaldehyde and $NaHSO_3$ followed by NaCN. Acidic hydrolysis of (±)**B** gives (±)**E**, $C_8H_8O_3$.

5.1 Write structures of **A** – **D** with appropriate stereochemistry in Haworth projection, except for **B**.

Glycoside **A** is found to be toxic and believed to be due to extremely toxic compound **F**, liberated under the hydrolytic conditions. Detoxification of compound **F** in plant may be accompanied by the reactions (stereochemistry not shown).



A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).



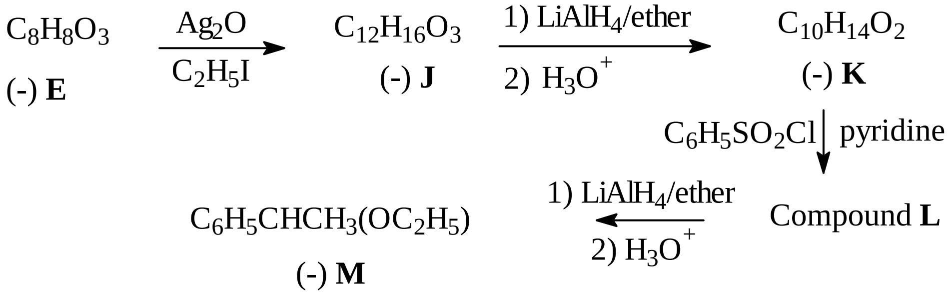
Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

5.2 Write molecular formula for compounds **F** and **G,** and structural formula for compounds **H** and **I** and indicate stereochemistry of **H**. (Table 5.1 may be useful for structure identification.)

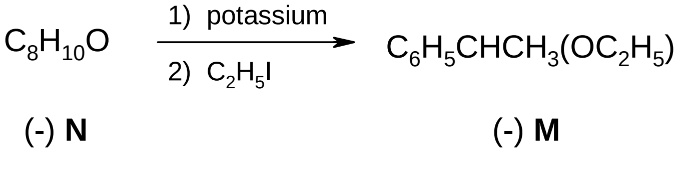
(-)1-Phenylethane-1-*d*, $C_6H_5CHDCH_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_D$ is equal to -0.6.

(-) 1-phenylethane-1-*d*

The absolute configuration of (-)1-phenylethane-1-*d* is related to (-) **E** according to the following reactions.



Compound (-) **M** can also be obtained from compound **N** as follows.



5.3 Deduce the absolute configuration of (-) **E** and the structure with configuration of each intermediate (**J – O**) in the sequence with the proper *R*,*S*-assignment as indicated in the answer sheet.

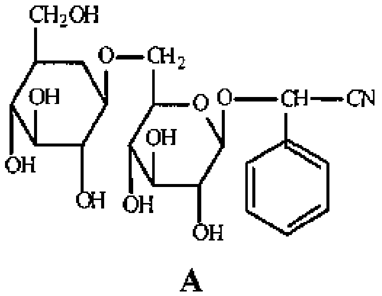
5.4 Choose the mechanism involved in the conversion of compound **O** to 1-phenylethane-*1-d*.

Table 5.1 Characteristic Infrared Absorption

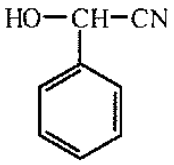
Stretching Vibration	Region (cm^{-1})	Stretching Vibration	Region (cm^{-1})
C-H (alkane)	2850-2960	O-H (free alcohol)	3400-3600
C-H (alkene)	3020-3100	O-H (H-bonded alcohol)	3300-3500
C=C	1650-1670	O-H (acid)	2500-3100
C-H (alkyne)	3300	C-O	1030-1150
C≡C	2100-2260	NH, NH_2	3310-3550
C-H (aromatics)	3030	C-N	1030, 1230
C=C (aromatics)	1500-1600	C=N	1600-1700
C-H (aldehyde)	2700-2775, 2820-2900	C≡N	2210-2260
C=O	1670-1780		

SOLUTION

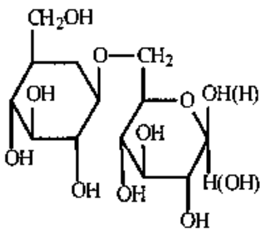
5.1



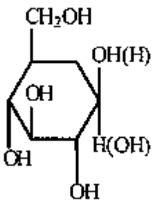
A



B



C

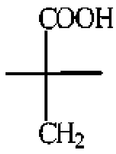


D

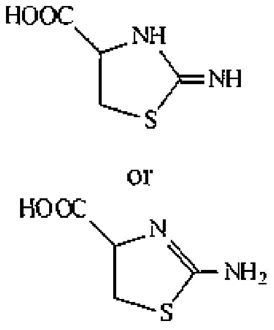
5.2

Molecular formula of compound **F** = HCN

Molecular formula of compound **G** = H_2S

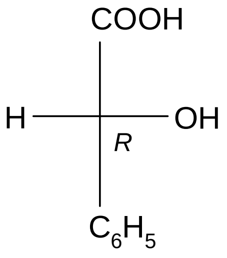


Compound **H**

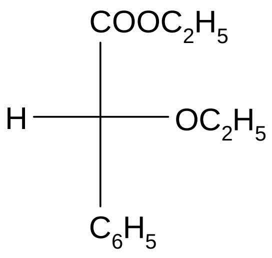


Compound **I**

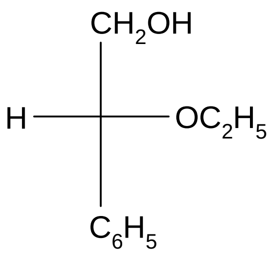
5.3



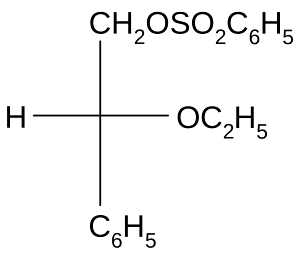
(-) **E**



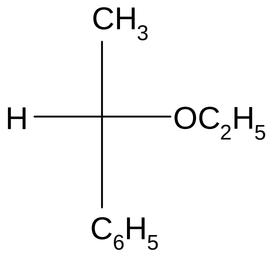
(-) **J**



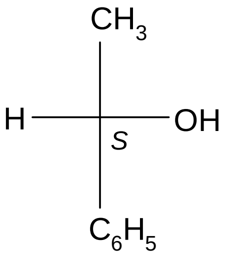
(-) **K**



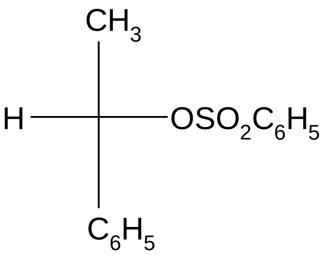
Compound **L**



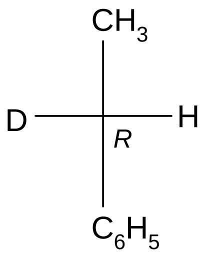
(-) **M**



(-) **N**



Compound **O**



(-) 1-phenylethane-*1-d*

5.4 The mechanism involved in the conversion of compound **O** to (-) 1-phenylethane-*1-d* is S_N2.

PROBLEM 6

Peptide **A** has a molecular weight of 1007. Complete acid hydrolysis gives the following amino acids in equimolar amounts: Asp, Cystine, Glu, Gly, Ile, Leu, Pro, and Tyr (see Table 1). Oxidation of **A** with HCO_2OH gives only **B** which carries two residues of cysteic acid (**Cya** which is a cysteine derivative with its thiol group oxidized to sulfonic acid).

6.1 How many sulphonic acid groups are formed from oxidation of a disulfide bond ?

Partial hydrolysis of **B** gives a number of di and tri-peptides (B1-B6). The sequence of each hydrolysis product is determined in the following ways.

The N-terminal amino acid is identified by treating the peptide with 2,4-dinitrofluorobenzene (DNFB) to give DNP-peptide. After complete acid hydrolysis of the DNP-peptide, a DNP-amino acid is obtained which can be identified readily by comparison with standard DNP-amino acids.

6.2 B1, on treatment with DNFB followed by acid hydrolysis gives a product, DNP-Asp. This suggests that B1 has aspartic acid at the N-terminus. Write down the complete structure of DNP-Asp at its isoelectric point (no stereochemistry required).

Next, the C-terminal amino acid is identified by heating the peptide at 100 °C with hydrazine, which cleave all the peptide bonds and convert all except C-terminal amino acids into amino acid hydrazides, leaving the C-terminal carboxyl group intact.

In this way N- and C-terminal amino acids are identified and the complete sequences of B1-B6 are as shown :

B1	Asp-Cya	B4	Ile-Glu
B2	Cya-Tyr	B5	Cya-Pro-Leu
B3	Leu-Gly	B6	Tyr-Ile-Glu

Hydrolysis of **B** with an enzyme from *Bacillus subtilis* gives B7-B9 with the following compositions:

B7	Gly-NH_2 (Glycinamide)
B8	Cya, Glu, Ile, Tyr
B9	Asp, Cya, Leu, Pro

6.3 Write down the sequence of B8, if DNP-Cya is obtained on treatment of B8 with DNFB followed by complete acid hydrolysis.

6.4 If the N- and C-terminal amino acids of B9 are identified as Asp and Leu respectively, write down the sequence of B9.

6.5 Write down the complete structure of **A** using abbreviation in Table 1, indicating the position of the disulfide bond.

However, the calculated molecular weight of **A** based on the above sequence is 2 mass units higher than the experimental value. On careful observation of the mixture from complete acid hydrolysis of **A**, 3 molar equivalents of ammonia are also produced in addition to the amino acids detected initially.

6.6 Suggest the revised structure of **A** and circle the site(s) of the structure to indicate all the possible source of ammonia.

6.7 Using the information in Table 2, calculate the isoelectric point of **A**.

Table 1**:** Formulae and symbols of common amino acids at isoelectric point

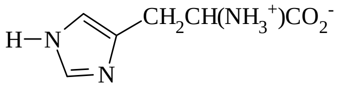
Name	Formula	Three-letter symbol
Alanine	$CH_3CH(NH_3^+)CO_2^-$	Ala
Arginine	$H_2NC(=NH)NH(CH_2)_3CH(NH_3^+)CO_2^-$	Arg
Asparagine	$H_2NCOCH_2CH(NH_3^+)CO_2^-$	Asn
Aspartic Acid	$HO_2CCH_2CH(NH_3^+)CO_2^-$	Asp
Cysteine	$HSCH_2CH(NH_3^+)CO_2^-$	Cys
Cystine	$[SCH_2CH(NH_3^+)CO_2^-]_2$	-
Glutamic Acid	$HO_2CCH_2CH_2CH(NH_3^+)CO_2^-$	Glu
Glutamine	$H_2NCOCH_2CH_2CH(NH_3^+)CO_2^-$	Gln
Glycine	$^+H_3NCH_2CO_2^-$	Gly
Histidine		His
Isoleucine	$CH_3CH_2CH(CH_3)CH(NH_3^+)CO_2^-$	Ile
Leucine	$(CH_3)_2CHCH_2CH(NH_3^+)CO_2^-$	Leu
Lysine	$H_2N(CH_2)_4CH(NH_3^+)CO_2^-$	Lys

Table 1 (continued)

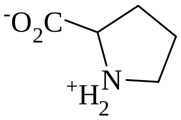
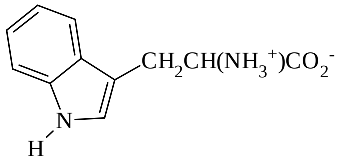
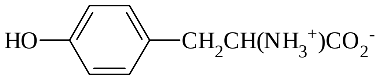
Methionine	$CH_3SCH_2CH_2CH(NH_3^+)CO_2^-$	Met
Phenylalanine	$PhCH_2CH(NH_3^+)CO_2^-$	Phe
Proline		Pro
Serine	$HOCH_2CH(NH_3^+)CO_2^-$	Ser
Threonine	$CH_3CH(OH)CH(NH_3^+)CO_2^-$	Thr
Tryptophan		Trp
Tyrosine		Tyr
Valine	$(CH_3)_2CHCH(NH_3^+)CO_2^-$	Val

Table 2: pK_a of some important groups in amino acids

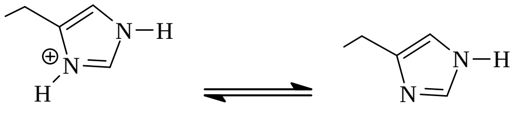
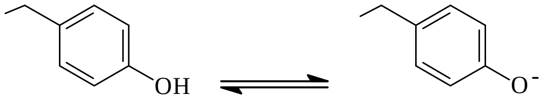
Groups	**Equilibrium**	**pK_a**
Terminal carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	3.1
Asp /or Glu side- chain carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	4.4
His side-chain	 + H^+	6.5
Terminal amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	8.0
Cys side-chain	$-SH \rightleftharpoons -S^- + H^+$	8.5

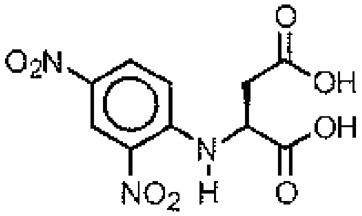
Table 2 (continued)

Tyr side-chain	 + H^+	10.0
Lys side-chain amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	10.0
Arg side-chain	$-NH(NH_2)C=NH_2^+ \rightleftharpoons -NH(NH_2)C=NH + H^+$	12.0

SOLUTION

6.1 Two sulphonic acid groups are formed from oxidation of a disulfide bond.

6.2 Complete structure of DNP-Asp at its isoelectric point is



6.3 The sequence of B8 is: Cya-Tyr-Ile-Glu

6.4 The sequence of B9 is: Asp-Cya-Pro-Leu

6.5 The *complete* structure of A is

Cys-Tyr-Ile-Glu-Asp-Cys-Pro-Leu-Gly-NH₂

6.6 Write the revised structure of A below and circle the site(s) to indicate all the possible source of ammonia

Cys-Tyr-Ile-Gln-Asn-Cys-Pro-Leu-Gly-NH₂

6.7 The isoelectric point of A is 9.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

The reaction between acetone and iodine in aqueous solution is catalyzed by H$^+$.

$$CH_3\text{-}CO\text{-}CH_3\,(aq) + I_2\,(aq) \xrightarrow{H^+} CH_3\text{-}CO\text{-}CH_2I\,(aq) + H^+(aq) + I^-(aq)$$

In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of I_2(aq) has been shown to have the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

where H$^+$ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x, y and z, the initial rate of reaction is measured.

$$\text{Initial rate} = k\,[CH_3COCH_3]_0^x\,[I_2]_0^y\,[H^+]_0^z$$

where $[\ ]_0$ are the initial concentrations of acetone, I_2 and H$^+$, respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the I_2(aq) concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H$^+$ to produce acetic acid and so reducing the concentration of H$^+$. The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution should be titrated immediately after the addition of the sodium acetate solution.

The remaining iodine I_2 (aq) is determined by titration with sodium thiosulphate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour disappears.

Chemicals

1.	Aqueous iodine solution in 0.4 M KI	80 cm^3
2.	0.100 M aq. HCl	50 cm^3
3.	0.50 M aq. CH_3COONa	80 cm^3
4.	Standard 0.02 M $Na_2S_2O_3$(aq) solution (the exact concentration will be announced at the beginning of practical part)	200 cm^3
5.	Aqueous acetone (50% by volume) (Density of pure acetone; 0.787 g cm^{-3}, MW. = 58.08)	50 cm^3
6.	Starch indicator	7 cm^3

Procedure

A. Standardization of Iodine Solution

1. Pipet 5.00 cm^3 of aqueous iodine into a clean 125 cm^3 Erlenmeyer flask.
2. Add 10 cm^3 of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02 M sodium thiosulphate solution until the colour of the solution is pale yellow.
4. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulphate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5).
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution

1. Label the stoppered flasks as follows: Flask I, II, III and IV.
2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50 % acetone:

Flask No.	Volume (cm^3)		
	water	0.100 M HCl	50 % acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

Stopper each flask immediately after addition of the solutions.

3. Measure out 10 cm^3 of 0.50 M aq. CH_3COONa into the graduated cylinder.
4. Set the stop-watch to 0.0000 display.
5. Pipet 5.00 cm^3 of iodine solution into the stoppered Flask No. I.
   Start the stop-watch as soon as the first drop of iodine solution is added.
6. Stopper the flask and swirl continuously.
7. Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm^3 of sodium acetate solution (from step 3) into the reaction flask. Shake well.
8. Titrate the remaining iodine with standard thiosulphate solution.
9. Record the volume of the thiosulphate solution.
10. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I_2(aq) solution to each flask as indicated:

Flask II: 10.00 cm^3 I_2 solution
Flask III: 5.00 cm^3 I_2 solution
Flask IV: 5.00 cm^3 I_2 solution

Calculations

B-1. Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.

B-2. Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.

B-3. Calculate the initial reaction rate for Flasks I to IV in M s^{-1}.

B-4. The rate of reaction has the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

Calculate the reaction orders x, y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x, y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k, for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

SOLUTION

The competitors were required to perform the following tasks:

In part A: Using the concentration of standard $Na_2S_2O_3$ solution (in bottle) and titration results it was required to calculate the concentration of iodine in the solution. Results were expected to be shown in a table in the answer sheet.

In part B: The following calculations B1 – B5 were required to be shown in the answer sheet:

B-1. *Calculation for initial concentrations (M) in the solution mixtures.*

B-2. *Calculation of the concentration (M) of iodine remaining in flasks I to IV at 7 minutes.*

B-3. *Calculation of initial rate of disappearance of I_2 at 7 minutes in flasks I to IV*.

Rate of disappearance of iodine (M s^{-1}) = $-\dfrac{d[I_2]}{dt} = \dfrac{c(I_2)_{\text{initial}} - c(I_2)_{7\text{ min}}}{7 \times 60\ s}$

B-4. *Calculation of x, y, and z in the rate equation*:

rate = $-\dfrac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$

In comparing the rates in solutions **II** : **I**, **III** : **I**, and **IV** : **I** one can calculate the following values:

$x = 1$; $y = 0$; $z = 1$

The rate equation has the form: rate = $k\,[CH_3COCH_3]\,[H^+]$

B-5. *Calculation of the rate constants for solution mixtures **I** to **IV** and the mean value of the rate constant.*

PROBLEM 2 (Practical)

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)

Unknown **Y** (in a vial)

Anhydrous Na_2SO_4 (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH_3, 5 % aq. $AgNO_3$, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. $NaHCO_3$, 1 % $FeCl_3$ in EtOH, 0.2 % aq. $KMnO_4$, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm^3 round bottomed flask for distillation and a 10 cm^3 round bottomed flask to collect the distillate. Heat the sand bath to approximately 150 °C before proceeding the next step.

Simplified Steam Distillation: Mix 1 g of ground sample with 15 cm^3 of water in the 25 cm^3 round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170 °C) to provide a steady rate of distillation. At least 5 cm^3 of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. Be sure that the condenser is dry before using in the next step

Extraction of the Essential Oil: Transfer the distillate to a 15 cm^3 capped centrifuge tube and add 1 cm^3 of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 cm^3 test tube. Repeat this extraction with fresh 1 cm^3 dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na_2SO_4 and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm^3 conical vial. Use approximately 1 cm^3 of clean dichloromethane to wash Na_2SO_4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na_2SO_4 into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm^3. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 cm^3) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. $AgNO_3$ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH_3 to the tube until all the precipitate dissolved. The solution is ready for the test.

2. Structure elucidation of the main essential oil (S)

Reaction of the main essential oil (**S**) with CH_3I in the presence of K_2CO_3 gives compound **X** ($C_{11}H_{14}O_2$). Oxidation of **X** gives unknown **Y** ($C_{10}H_{12}O_4$) as the main product and CO_2.

3. Structure elucidation of the unknown Y:

Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.

Hand in your copy of answer sheet PART I (Demonstrator copy) of functional group analysis and ask for ^{1}H NMR spectra. ^{1}H NMR spectra will be given only when the functional group analysis is completed.

4. Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^{1}H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.

5. Draw the structures of compound X and unknown Y. Assign each proton of unknown **Y** from the provided ^{1}H NMR spectra in the same manner as in (4).

SOLUTION

1. It was expected to obtain at least 5 cm^3 of distillate.
2. Functional group analysis of the distilled essential oil:

Reagents	Positive test	Negative test
0.2 % $KMnO_4$	✓	
1 % $FeCl_3$	✓	
2,4-DNP		✓
Ceric ammonium nitrate	✓	
Tollen's Reagent		✓

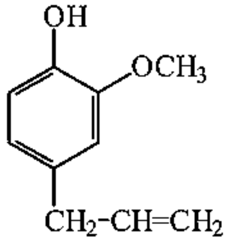
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

3. Funcional group analysis of the unknown compound Y:

Reagents	Positive test	Negative test
5 % HCl		✓
5 % NaOH	✓	
5 % $NaHCO_3$	✓	
0.2 % $KMnO_4$		✓
1 % $FeCl_3$		✓
2,4-DNP		✓
Ceric ammonium nitrate		✓
Tollen's Reagent		✓

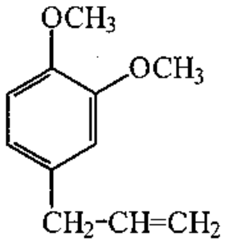
Functional groups in **Unknown Y**	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

4. The structure which represents the main essential oil (S):

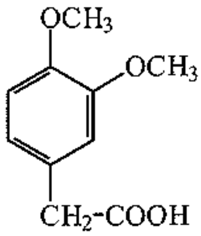


5. The structure of compound **X** and unknown **Y**:

Compound **X**



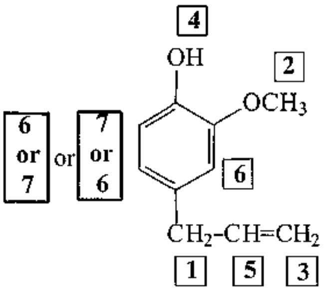
Compound **Y**



NMR spectrum of the main essential oil (S):
(See peak number in the given 'H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.31	2H	d
2	3.84	3H	S
3 4	5.0 – 5.1	2H	m
5	5.6	1H	S
	5.9 – 6.0	1H	m
6	6.7	2H	S d or m
7	6.87	1H	d

NMR assignment of the main essential oil (S):

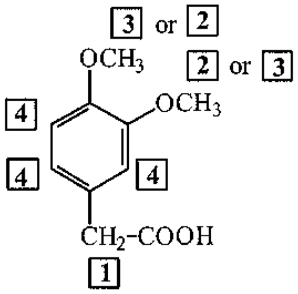


NMR spectrum of the unknown **Y**:

(See peak number in the given 'H NMR spectrum. Labile proton does not appear in the spectrum.)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.59	2H	s
2	3.86	3H	s
3	3.88	3H	s
4	6.81	3H	s

NMR assignment of the main essential oil (S):



32nd

International Chemistry Olympiad

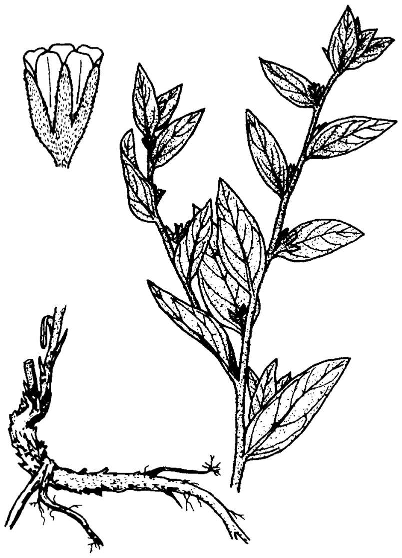
6 theoretical problems
2 practical problems

THE THIRTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 2000, COPENHAGEN, DENMARK

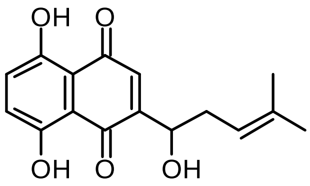
THEORETICAL PROBLEMS

PROBLEM 1

Synthesis of Compounds with Wound Healing Properties



Shikonin is a red compound found in the roots of the plant *Lithospermum erythrorhizon* which grows in Asia. Extracts of the root have been used for centuries in folk medicine and are used today in ointments for healing of wounds.



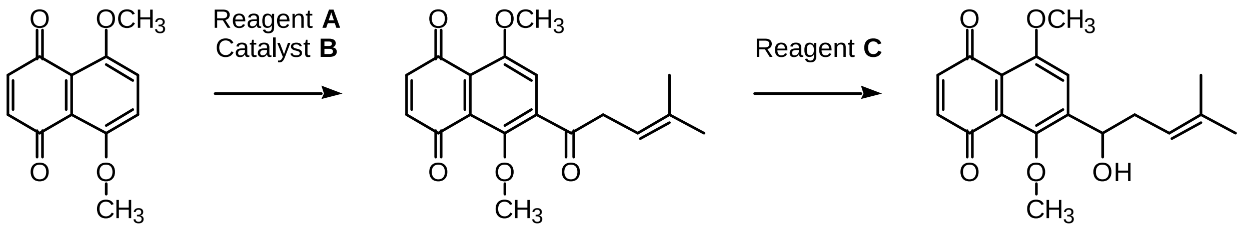
Shikonin

1.1 How many stereoisomers of Shikonin are possible ?

1.2 Do all stereoisomers of Shikonin have the same melting point? Mark with an X.

yes	no

The following sequence is part of a synthetic route to Shikonin:



1.3 Draw the structural formula of reagent **A**.

1.4 Indicate (by means of an X in the appropriate check-box) the correct IUPAC name for reagent **A**.

2-Methyl-2-pentenoyl chloride ☐
1-Chloro-4-methyl-3-pentene ☐
4-Methyl-3-pentenoyl chloride ☐
4-Methyl-3-pentene-1-ol ☐
4,4-Dimethyl-3-butenoyl chloride ☐

1.5 Write the molecular formula of reagent **C**.

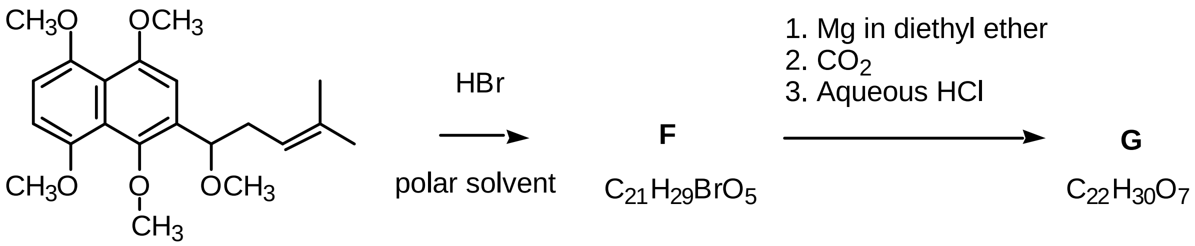
Numerous Shikonin analogues have been synthesized with a view to obtaining more potent compounds. One reaction sequence is shown below:

$$\text{Shikonin} \xrightarrow{SOCl_2} \underset{\mathbf{D}}{C_{16}H_{15}ClO_4} \xrightarrow[70\ ℃]{\text{KOH in ethanol}} \underset{\mathbf{E}}{C_{16}H_{14}O_4}$$

1.6 Draw the structural formula of compound **E**.

1.7 How many stereoisomers of compound **E,** if any, are possible

Another route to useful Shikonin analogues is the following:



1.8 Draw the structural formula of compound **F**.

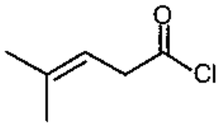
1.9 Draw the structural formula of compound **G**.

SOLUTION

1.1 2 stereoisomers.

1.2 Stereoisomers of Shikonin have the same melting point.

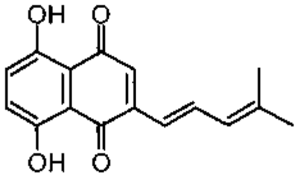
1.3 The structural formula of reagent **A**:



1.4 The correct IUPAC name for reagent **A** is 4-Methyl-3-pentenoyl chloride.

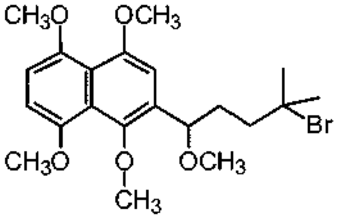
1.5 $NaBH_4$ (LiAlH4 will be acccepted)

1.6 The structural formula of compound **E**:

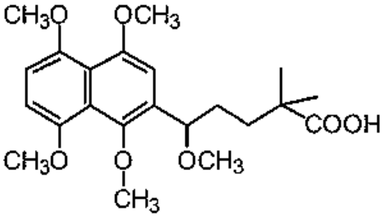


1.7 **2** stereoisomers

1.8 The structural formula of compound **F**:



1.9 The structural formula of compound **G**:



PROBLEM 2

Bridge between Denmark and Sweden

On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $CaSO_4 \cdot 2\ H_2O$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot ½\ H_2O$. Consider the following reaction:

$$CaSO_4 \cdot 2\ H_2O(s) \rightarrow CaSO_4 \cdot ½\ H_2O(s) + 1½\ H_2O(g)$$

The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar:

Compound	$\Delta_f H$ (kJ mol^{-1})	S (J K^{-1} mol^{-1})
$CaSO_4 \cdot 2\ H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot ½\ H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant: R = 8.314 J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

0 °C = 273.15 K.

2.1 Calculate ΔH (in kJ) for transformation of 1.00 kg of $CaSO_4 \cdot 2\ H_2O(s)$ to hemihydrate $CaSO_4 .\ ½\ H_2O(s)$. Is this reaction endothermic or is it exothermic?

2.2 Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \cdot 2\ H_2O(s)$, $CaSO_4 \cdot ½\ H_2O(s)$ and $H_2O(g)$ at 25 °C.

2.3 Calculate the temperature at which the equilibrium water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH and ΔS are temperature independent.

Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:

(1) $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$

(2) $O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$

An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 ºC. The cell is represented by the following cell diagram:

$Fe(s)\ |\ Fe^{2+}(aq)\ ||\ OH^-(aq), O_2(g)\ |\ Pt(s)$

Standard electrode potentials (at 25 ºC):

$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$ E = – 0.44 V

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$ E = 0.40 V

Nernst factor: $RT \ln 10 / F$ = 0.05916 volt (at 25 ºC)

Faraday constant: F = 96485 C mol^{-1}

2.4 Calculate the standard electromotive force (the standard cell voltage), E, at 25 ºC.

2.5 Write down the overall reaction which takes place during discharge of the cell under standard conditions.

2.6 Calculate the equilibrium constant at 25 °C for the overall cell reaction.

2.7 The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe^{2+} after 24 hours. Oxygen and water may be assumed to be present in excess.

2.8 Calculate E for the cell at 25 °C for the following conditions:

$[Fe^{2+}]$ = 0.015 M, $pH_{\text{right-hand half-cell}}$ = 9.00, $p(O_2)$ = 0.700 bar.

SOLUTION

2.1 ΔH^0 = –1575.0 kJ mol^{-1} + 1.5× (–241.8) kJ mol^{-1} – (–2021.0 kJ mol^{-1}) = 83.3 kJ mol^{-1}

$n = m / M$ = 1000g / 172.18 g mol^{-1} = 5.808 mol

ΔH^0 = 484 kJ

The reaction is endothermic.

2.2 ΔS^0 = 130.5 J K^{-1} mol^{-1} + 3/2 × 188.6 J K^{-1} mol^{-1} – 194.0 J K^{-1} mol^{-1}

= 219.4 J K^{-1} mol^{-1}

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ = 17886 J mol^{-1}

$\Delta G^0 = - RT \ln K$

$K = (p(H_2O))^{3/2} = 7.35 \times 10^{-4}$ (pressure in bar)

$p(H_2O) = 8.15 \times 10^{-3}$ bar

2.3 $p(H_2O)$ = 1.00 bar implies K = 1.00 and $\Delta G^0 = - RT \ln K = 0$

$\Delta G = \Delta H - T\Delta S$

0 = 83300 J K^{-1} – T 219.4 J K^{-1} mol^{-1}

T = 380 K or 107 °C

2.4 E^0(cell) = E^0(right) – E^0(left) = 0.40 V – (– 0.44 V) = 0.84 V

2.5 Oxidation takes place at the negative, left half-cell.

Left half: $2\ Fe \rightarrow 2\ Fe^{2+} + 4\ e^-$ (multiplied by 2)

Right half: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Overall: $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ OH^-$

2.6 $K = [Fe^{2+}]^2\ [OH^-]^4 / p(O_2)$ (conc. in M and pressure in bar)

$\Delta G = - n\ F\ E\ (\text{cell}) = - RT \ln K$

$K = 6.2 \times 10^{56}$

2.7 $Q = I\ t = 0.12\ \text{A} \times 24 \times 60 \times 60\ \text{s} = 10\ 368\ \text{C}$

$n(e^-) = Q / F = 10\ 368\ \text{C} / 96485\ \text{C mol}^{-1} = 0.1075\ \text{mol}$

$m(Fe) = n(Fe)\ M(Fe) = 1/2 \times 0.1075\ \text{mol} \times 55.85\ \text{g mol}^{-1} = 3.0\ \text{g}$

2.8 $$E(\text{cell}) = E^0(\text{cell}) - \frac{0.05916\ \text{V}}{n} \log \frac{[Fe^{2+}]^2\ [OH^-]^4}{p(O_2)}$$

$pH = 9.00$ implies $[H^+] = 1 \times 10^{-9}$ and $[OH^-] = 1 \times 10^{-5}$

$$E(\text{cell}) = 0.84\ \text{V} - \frac{0.05916\ \text{V}}{4} \log \frac{0.015^2\ [1 \times 10^{-5}]^4}{0.700} = 1.19\ \text{V}$$

PROBLEM 3

Bioinorganic Chemistry

The square planar complex *cis*-diammine dichloroplatinum(II) is an important drug for the treatment of certain cancers.

3.1 Draw the structures of *cis*- and *trans*-diammine dichloroplatinum(II) and label each structure as *cis* or *trans*.

A number of ionic compounds also have the empirical formula $Pt(NH_3)_2Cl_2$.

3.2 Write molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has

1) empirical formula $Pt(NH_3)_2Cl_2$,
2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex,
3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound

3.3 How many *5d* electrons are there in the platinum(II) ion?

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3.4 Which of the five *5d* orbitals attain the highest energy (*i. e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 at biological conditions except that the temperature is 25 °C corresponding to the reactions:

$Fe^{III} + Tf \rightarrow (Fe^{III})Tf$ $\qquad K_1 = 4.7\times10^{20}$

$Fe^{III} + (Fe^{III})Tf \rightarrow (Fe^{III})_2Tf$ $\qquad K_2 = 2.4\times10^{19}$

In the diferric protein, $(Fe^{III})_2Tf$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(Fe^{III})Tf$, can be denoted $\{Fe^{III} . Tf\}$ and $\{Tf . Fe^{III}\}$. Their relative abundance at equilibrium is given by the constant

$K = [\{Tf . Fe^{III}\}] [\{Fe^{III} . Tf\}]^{-1} = 5.9$.

3.5 Calculate the values of the two constants $K_1' = [\{Fe^{III} . Tf\}] [Fe^{III}]^{-1} [Tf]^{-1}$ and $K_1'' = [\{Tf . Fe^{III}\}] [Fe^{III}]^{-1} [Tf]^{-1}$, respectively, corresponding to the formation of each monoferric form of transferrin.

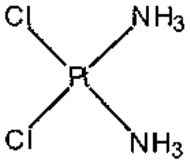
3.6 Calculate the values of the two constants $K_2' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Fe^{III} . Tf\}]^{-1}$ and $K_2'' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Tf . Fe^{III}\}]^{-1}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms.

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

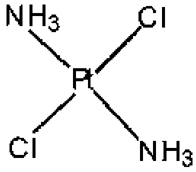
3.7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

SOLUTION

3.1 The structures of *cis*- and *trans*-diammine dichloroplatinum(II)



cis



trans

3.2 $[Pt(NH_3)_4] [PtCl_4]$

$[Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

$[Pt(NH_3)_3Cl]_2 [PtCl_4]$

$[Pt(NH_3)_4] [Pt(NH_3)Cl_3]_2$

3.3 Eight *d*-electrons.

3.4 Orbital $5\,d_{x^2-y^2}$. In a square planar complex the four ligand atoms fall on the *x* and *y* axes along which this orbital, if filled, would also have electron density concentrated.

3.5 The concentration of monoferric forms of transferrin is

$[(\text{Fe}^{m})\text{Tf} = [\{\text{Fe}^{m}\text{ -Tf}\}] + [\{\text{Tf-Fe}^{III}\}]$

$K_1^{'} + K_1^{''} = K_1 \qquad K_1^{'} K = K_1^{''}$

$$K_1^{'} = \frac{K_1}{1+K} = \frac{4.7\times10^{20}}{1+5.9} = 6.8\times10^{19}$$

$$K_1^{''} = K_1 - K_1^{'} = (4.7-0.68)\times10^{20} = 4.0\times10^{20}$$

3.6 $K_1^{'} K_2^{'} = K_1^{''} K_2^{''} = K_1 K_2$

$$K_1^{'} = \frac{K_1 K_2}{K_1^{'}} = \frac{4.7\times10^{20}\times2.19\times10^{19}}{6.8\times10^{19}} = 1.7\times10^{20}$$

$$K_1^{''} K_2^{''} = K_1 K_2$$

$$K_2^{''} = \frac{K_1 K_2}{K_1^{''}} = \frac{4.7\times10^{20}\times2.4\times10^{19}}{4.0\times10^{20}} = 2.8\times10^{19}$$

3.7 (= 2 $(\text{CO}_3^{2-}) + 1$ (Asp(O$^-$)) + 2 (2 × Tyr(O$^-$))

PROBLEM 4

A Naturally Occurring Compound

A naturally occurring compound **A** containing only C, H and O has the following elemental composition, percentage mass,

C: 63.2 %, H: 5.3%, O: 31.5%.

4.1 Derive the empirical formula of compound **A**.

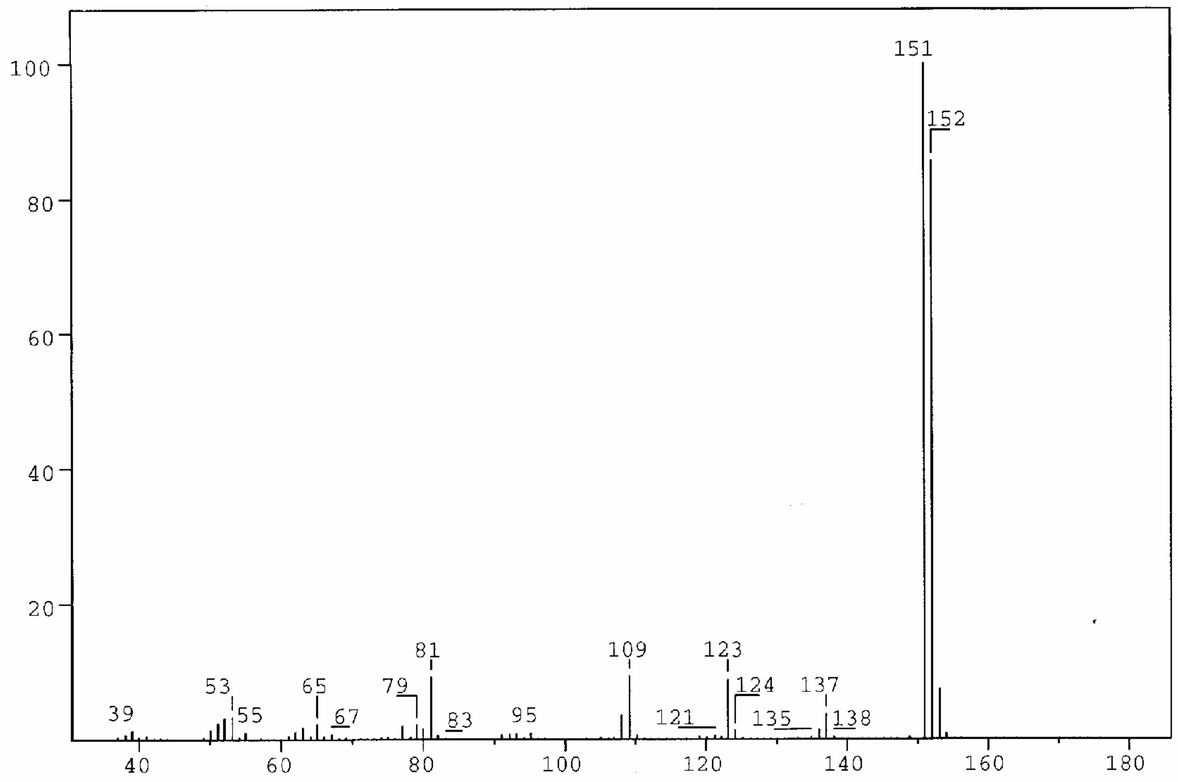


Figure 1

The mass spectrum of compound **A** is shown in Figure 1.

4.2 What is the molecular formula for compound **A**?

A solution of **A** in ether is shaken with an aqueous solution of NaOH. After this, no **A** remains in the ether phase. Another solution of **A** in ether is shaken with an aqueous solution of $NaHCO_3$. **A** remains in the ether phase.

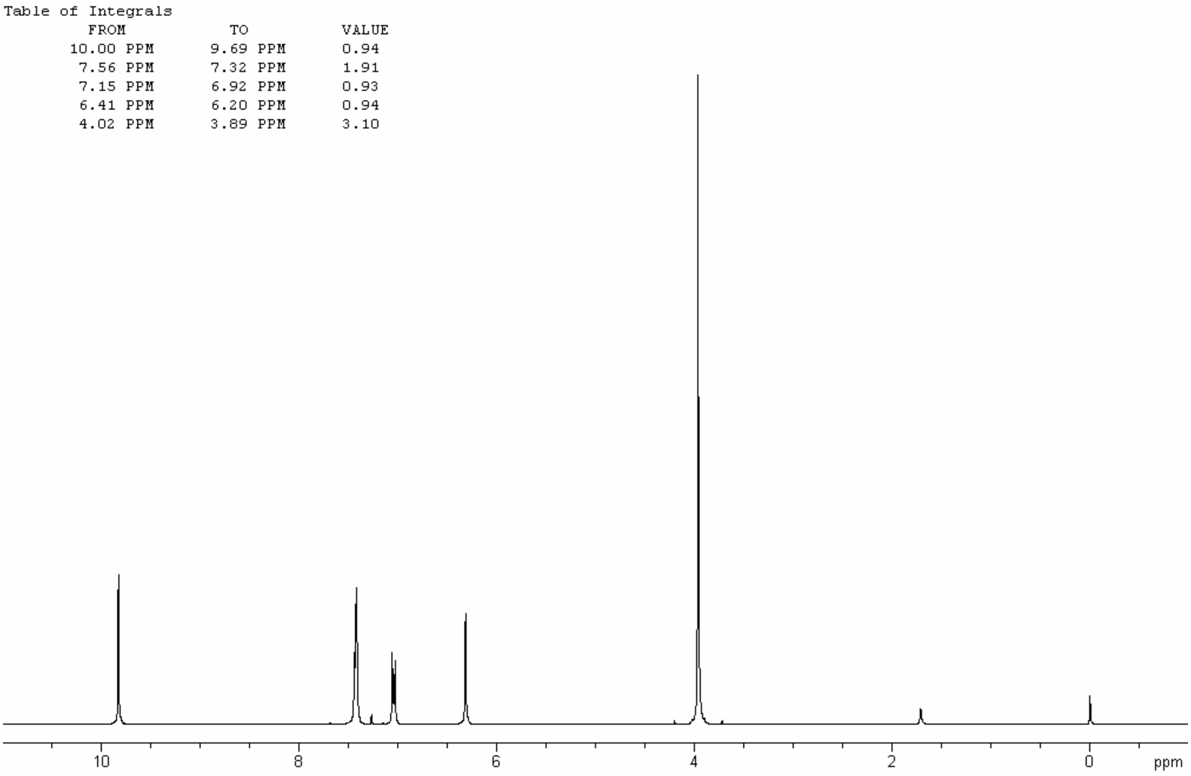
4.3 Which of the following classes of compounds does **A** belong to according to these experiments? Mark with an X.

alcohol ☐ phenol ☐ aldehyde ☐ ketone ☐
acid ☐ ester ☐ ether ☐

Compound **A** gave rise to formation of a silver mirror with Tollens' reagent ($Ag(NH_3)_2^+$).

4-1 Which of the following functional groups does this indicate the presence of in **A**? Mark with an X.

hydroxy group of an alcohol ☐ hydroxy group of a phenol ☐
carbonyl group of an aldehyde ☐ carbonyl group of a ketone ☐
carboxylic group ☐ ester group ☐
alkoxy group of an ether ☐



```
Table of Integrals
        FROM          TO          VALUE
       10.00 PPM     9.69 PPM     0.94
        7.56 PPM     7.32 PPM     1.91
        7.15 PPM     6.92 PPM     0.93
        6.41 PPM     6.20 PPM     0.94
        4.02 PPM     3.89 PPM     3.10
```

Figure 2a

The ^{1}H NMR spectrum of compound **A** recorded at 300 MHz is shown in Figure 2a (solvent $CDCl_3$ (7.27 ppm), reference tetramethylsilane). The signals at 3.9, 6.3 and 9.8 ppm are singlets. Figure 2b is an expansion of the region 6.9 – 7.6 ppm.

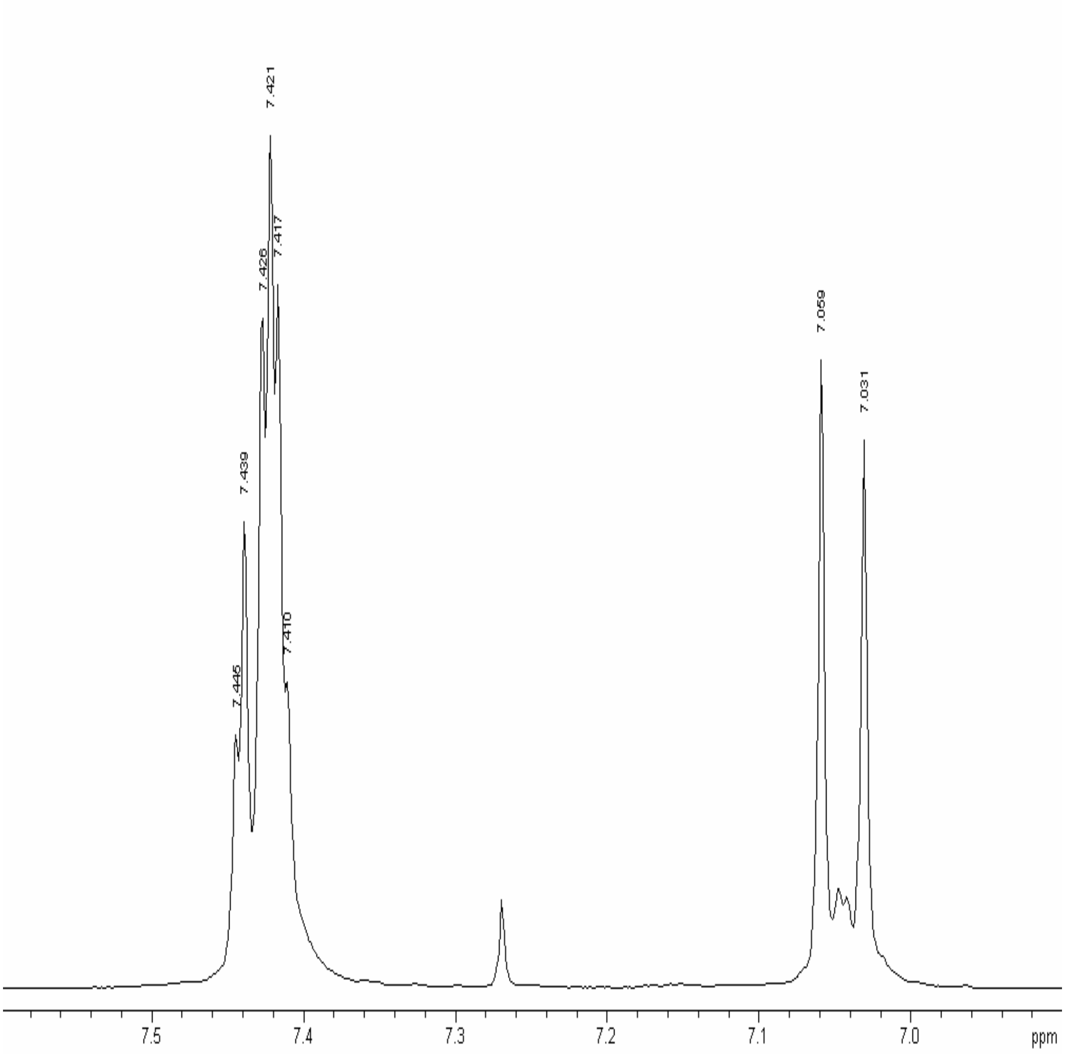


Figure 2b

Selected chemical shift and coupling constant values are given in Table 1.

The signal at 6.3 ppm disappears when a drop of D_2O is added.

4.5 Which of the following does this indicate? Mark with an X.

Exchange of carbon-bonded hydrogen ☐
Exchange of oxygen-bonded hydrogen ☐
Dilution effect ☐
Hydrolysis ☐

The same signal moves to a lower ppm value upon dilution with $CDCl_3$.

4.6 Which of the following does this indicate?

Indicate the true statements (more than one).

Increased hydrogen bonding ☐
Decrease in hydrogen bonding ☐
Intermolecular hydrogen bonding ☐
Intramolecular hydrogen bonding ☐
No hydrogen bonding ☐

4.7 Draw the four possible structural formulas for compound **A** based on the information given above

4.8 Give structural formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum.

4.9 Two of the isomers have a lower pK_a value than the others. Write the formulas for those.

Table 1. ^{1}H Chemical Shift δ

Hydrogens attached to carbon		
Methyl	CH_3–C– CH_3–C=O– CH_3–O–R CH_3–OCOR	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
Methylene	CH_2–C– CH_2–C=O– CH_2–OR CH_2–OCOR	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
Methine	CH–	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
Alkene		4.0 – 7.3 ppm depending on the substituent
Aldehyde	R–CHO	9.0 – 10.0 ppm

Table 1 (continued) ^{1}H Chemical Shift δ

Hydrogens attached to oxygen		
Alcohols	ROH	0.5 – 5.0 ppm
Phenols	ArOH	4.0 – 7.0 ppm
Carboxylic acids	RCOOH	10.0 – 13.0 ppm
Selected spin-spin coupling constants		
Alkanes (free notation)	H-C-C-H vicinal	6 – 8 Hz
Alkenes	trans cis geminal	11 – 18 Hz 6 – 12 Hz 0 – 3 Hz
Aromates	ortho meta para	6 – 10 Hz 1 – 4 Hz 0 – 2 Hz

SOLUTION

4.1 The empirical formula of **A** is $C_8H_8O_3$.

4.2 The molecular formula of compound **A**: $C_8H_8O_3$.

4.3 The compound **A** is a phenol.

4.4 Compound **A** forms a mirror with Tollen's reagent. This indicates the presence of carbonyl group of an aldehyde.

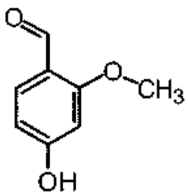
4.5 It indicates exchange of oxygen-bonded hydrogen.

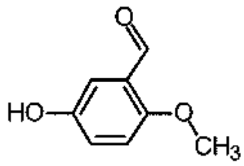
4.6 It indicates:

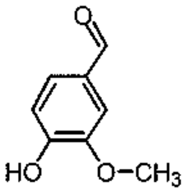
decrease in hydrogen bonding,

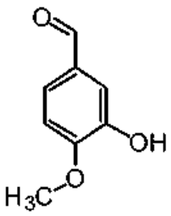
intermolecular hydrogen bonding.

4.7 Four possible structural formulas for compound **A**:



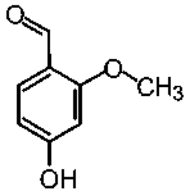


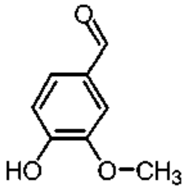




4.8 Formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum: CH_3, HC=O.

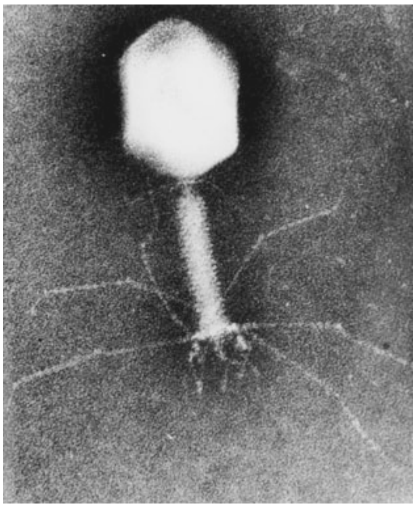
4.9 Two isomers having a lower *pK_a* value than the others:





PROBLEM 5

Protein and DNA



DNA is composed of 2’-deoxy-nucleotides carrying the bases adenine (A), guanine (G), cytosine (C) and thymine (T). The molar mass of the 2’-deoxy-nucleotide-5’-triphosphates is given in table 2:

Table 2

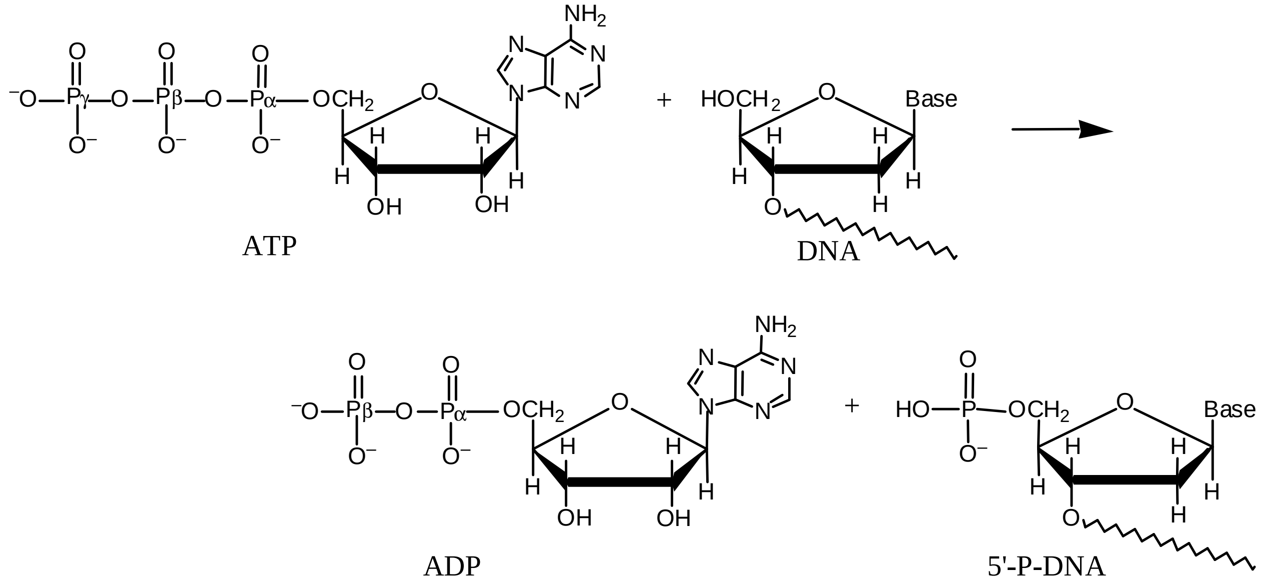
dNTP	**Molar mass /g mol^{-1}**
dATP	487
dGTP	503
dCTP	464
dTTP	478

5.1 Calculate the molar mass of a double stranded DNA fragment consisting of 1000 base pairs with a uniform distribution of the four bases.

This DNA fragment can be isolated and cloned by using the PCR method (polymerase chain reaction), in which a heat stable DNA polymerase enzyme multiplies the number of molecules of a specific piece of DNA in a cyclic process. Under optimal conditions the number of double-stranded DNA copies doubles in each cycle. Using the PCR method you perform 30 cycles starting from a single double stranded DNA molecule.

5.2 Calculate the approximate mass of the DNA you obtain from this experiment.

The bacteria-virus T4 enzyme - polynucleotide kinase (PNK) catalyzes the transfer of the terminal phosphate of ATP (γ-orthophosphate) to the 5'-hydroxyl termini of ribo- and deoxyribonucleotides:



PNK is commonly used to label DNA at the 5'-end with the radioactive phosphorus isotope ^{32}P using ATP in which the γ-P (the outermost of the phosphorus atoms) is replaced with ^{32}P. The amount of ^{32}P and thus the amount of labelled DNA can be measured.

A 10 µL solution containing double stranded DNA is labelled 100 % with [γ-^{32}P]ATP by PNK. 37 days ago, the specific activity of [γ-^{32}P]ATP was 10 Ci/mmol or 370 $\cdot 10^9$ Bq/mmol. ^{32}P has a half-life of 14.2 days, and during the decay a β-particle is emitted. Now the labelled DNA emits 40000 β-particles/s.

5-3 Calculate the concentration of the DNA solution.

In an experiment in which PNK is incubated with [γ-^{32}P]ATP and single stranded DNA, the reaction can be monitored by isolating labeled DNA and measuring the β-particle emission. Using this kind of measurements in a 1 cm^3 experimental mixture, a labeling of 9 nmol DNA/min was calculated. PNK has a catalytic rate constant (turnover number) of 0.05 s^{-1} and molar mass of 34620 g mol^{-1}.

5.4 Calculate the concentration (in mg/cm3) of PNK in the experimental mixture.

Aromatic amino acids, tryptophan, tyrosine and phenylalanine absorb UV light of a wavelength between 240 nm and 300 nm. In a protein containing several aromatic amino acids, the sum of the molar absorptivity per amino acid $\Sigma\varepsilon_{\text{amino acid}}$, is approximately equal to the molar absorptivity, $\varepsilon_{\text{protein}}$, for the protein. The molar absorptivity, $\varepsilon_{\text{amino acid}}$, at 280 nm for tyrosine, tryptophan and phenylalanine is 1400 M^{-1} cm^{-1}, 5600 M^{-1} cm^{-1} and 5 M^{-1} cm^{-1}, respectively. The absorbance of a 10 μM solution of PNK is 0.644 at 280 nm and with 1.00 cm light path. The amino acid sequence of PNK contains 14 tyrosines and 9 phenylalanines.

(M = mol dm^{-3})

5.5 Calculate the number of tryptophan residues in a PNK molecule.

SOLUTION

5.1 Calculation of the molar mass of a double stranded DNA fragment under given conditions:

dNTP average mass = 483 g mol^{-1}; $M(\text{HP}_2\text{O}_7^{2-})$ = 175 g mol^{-1};

1000 bp double stranded DNA M(DNA) = ((483 – 175) × 2 × 1000 + 2 × 17) g mol^{-1} = 616034 g mol^{-1}.

5.2 Calculation of the approximate mass of the DNA you obtaining from the described experiment.

2^{30} copies = 1073741824 copies

Total mass of DNA: m(DNA) = 1073741824 / N_A × 616350 g mol^{-1} = 1.1 ng

5.3 Calculation of the concentration of the DNA solution.

$$A = A_0\,\text{e}^{-kt} \text{ and } k = \frac{\ln 2}{t_{1/2}} \Rightarrow A_0 = \frac{40000}{\text{e}^{-0.0488\times 37}}\,\text{dps} = 243464\,\text{dps}$$

It corresponds to $\frac{243464}{370}\,\text{pmol } 5'\text{–}^{32}\text{P-DNA} = 658\,\text{pmol } 5'\text{–}^{32}\text{P-DNA}$.

Since volume of the labelled DNA is 10 μL, the concentration of the DNA is thus approx. 66 μM.

5.4 Since 9 nmol DNA is labelled per min and the turnover number is 0.05 s^{-1} the amount of PNK that catalyses the labelling is:

$$\frac{9\ \text{nmol}\ \text{min}^{-1}}{0.05 \times 60\ s} = 3\ \text{nmol}$$

which corresponds to 3 nmol × 34620 g mol^{-1} = 0.1 mg.

The concentration of the PNK in mg cm^{-3} is is thus 0.1 mg cm^{-3}-

5-5 $\varepsilon_{\text{Tryptophan}}$ = 5600 M^{-1} cm^{-1};

$\varepsilon_{\text{Tyrosine}}$ = 1400 M^{-1} cm^{-1};

$\varepsilon_{\text{Phenylalanine}}$ = 5 M^{-1} cm^{-1}

$$\varepsilon = \frac{A}{c\ l} \ \Rightarrow\ \varepsilon_{\text{PNK}} = \frac{0.644}{10\ \mu\text{M} \times 1.00\ \text{cm}} = 64400\ \text{M}^{-1}\ \text{cm}^{-1}$$

$\Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{Phenylalanine}}) = (14 \times 1400) + (9 \times 5)\ \text{M}^{-1}\ \text{cm}^{-1} = 19645\ \text{M}^{-1}\ \text{cm}^{-1}$

$\Sigma\varepsilon_{\text{Tryptophan}} = \varepsilon_{\text{PNK}} - \Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{Phenylalanine}}) \ \Rightarrow$

$\Sigma\varepsilon_{\text{Tryptophan}} = (64400 - 19645)\ \text{M}^{-1}\ \text{cm}^{-1} = 44755\ \text{M}^{-1}\ \text{cm}^{-1}$

The number of tryptophan residues in a PNK molecule is thus:

$$\frac{44755\ \text{M}^{-1}\ \text{cm}^{-1}}{5600\ \text{M}^{-1}\ \text{cm}^{-1}} = 8\ \text{residues}$$

PROBLEM 6

Hard Water

In Denmark the subsoil consists mainly of limestone. In contact with ground water containing carbon dioxide some of the calcium carbonate dissolves as calcium hydrogen carbonate. As a result, such ground water is hard, and when used as tap water the high content of calcium hydrogen carbonate causes problems due to precipitation of calcium carbonate in, for example, kitchen and bathroom environments.

Carbon dioxide, CO_2, is a diprotic acid in aqueous solution. The pK_a-values at 0 ℃ are:

$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ pK_{a1} = 6.630

$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$ pK_{a2} = 10.640

The liquid volume change associated with dissolution of CO_2 may be neglected for all of the following problems. The temperature is to be taken as being 0 ℃.

6.1 The total concentration of carbon dioxide in water which is saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar is 0.0752 mol dm^{-3}. Calculate the volume of carbon dioxide gas which can be dissolved in one litre of water under these conditions.

The gas constant R = 8.314 J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

6.2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO_2 in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.3 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium hydrogen carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.4 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effects.

6.5 The solubility of calcium carbonate in water at 0 °C is 0.0012 g per 100 cm3 of water. Calculate the concentration of calcium ions in a saturated solution of calcium carbonate in water.

The hard groundwater in Denmark is formed via contact of water with limestone in the subsoil which reacts with carbon dioxide dissolved in the groundwater according to the equilibrium equation:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\ HCO_3^-(aq)$$

The equilibrium constant, K, for this reaction is $10^{-4.25}$ at 0 °C.

6.6 Calculate the concentration of calcium ions in water in equilibrium with calcium carbonate in an atmosphere with a partial pressure of carbon dioxide of 1.00 bar.

6.7 A 0.0150 M solution of calcium hydroxide is saturated with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the solution by considering the equilibrium equation given above in connection with problem 6.6.

6.8 The calcium hydroxide solution referred to in problem 6.7 is diluted to twice the volume with water before saturation with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the resulting solution saturated with CO_2.

6.9 Calculate the solubility product constant for calcium carbonate from the data given above.

SOLUTION

6.1 $c(CO_2) = 0.0752$ M $\quad n(CO_2) = 0.0752$ mol

The ideal gas equation: $\quad p\,V = n\,R\,T$

$1.00 \text{ bar} \times V = 0.0752 \text{ mol} \times 0.08314 \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}$

$V = 1.71 \text{ dm}^3$

6.2 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$[H^+] = [HCO_3^-] = x$ and $[CO_2] + [HCO_3^-] = 0.0752$

$$K_a = 10^{-6.63} = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} = \frac{x^2}{0.0752 - x}$$

$[H^+] = 0.000133$ and $[CO_2] = 0.0751$

6.3 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$[CO_2] = 0.0751$ and $[HCO_3^-] = 0.0100$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x\ \ 0.0100}{0.0751}$$

$\underline{x = [H^+] = 1.76\times10^{-6}}$

6.4 $CO_2(aq) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2\ HCO_3^-(aq)$ $[HCO_3^-] = 0.0200$

$CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x\ \ 0.0200}{0.0751}$$

$x = [H^+] = 8.8\times10^{-7}$

6.5 0.0012 g $CaCO_3$ in 100 cm^3 of water

0.0012 g /100 × 0872 g mol^{-1} = 0.000012 mol $CaCO_3$ in 100 cm^3 of water

$[Ca^{2+}] = 1.2\times10^{-4}$ $c(Ca^{2+}) = 1.2\times10^{-4}$ mol dm^{-3}

6.6 $K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = 10^{-4.25}$ and $2\ [Ca^{2+}] = [HCO_3^-]$

$\frac{4\ [Ca^{2+}]}{0.0751} = 10^{-4.25}$ $[Ca^{2+}] = 1.02\times10^{-2}$ $c(Ca^{2+}) = 1.02\times10^{-2}$ mol dm^{-3}

6.7 $c(Ca(OH)_2) = 0.015$ mol dm^{-3}

$OH^-(aq) + CO_2(aq) \rightarrow HCO_3^-(aq)$

All hydroxide has been consumed ($K = 10^{7.37}$).

From problem 6.6 we found that the maximum possible calcium ion concentration is smaller, *i.e.* precipitation of $CaCO_3$

$[Ca^{2+}] = 1.02\times10^{-2}$ $c(Ca^{2+}) = 1.02\times10^{-2}$ mol dm^{-3}

6.8 $c(Ca(OH)_2) = 0.0075$ mol dm^{-3}

From problem 6.6 we found that the maximum possible calcium ion concentration we can have, is 1.02×10^{-2} mol dm^{-3}, *i.e.* no precipitation of $CaCO_3$ occurs.

$[Ca^{2+}] = 0.75\times10^{-2}$ $c(Ca^{2+}) = 0.75\times10^{-2}\ \text{mol dm}^{-3}$

6.9

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]}\times\frac{[CO_3^{2-}][H^+]}{[CO_3^{2-}][H^+]} = \frac{K_{sp}\,K_{a1}}{K_{a2}}$$

$K_{sp} = 10^{-8.26}$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

This experiment includes one preparation of a metal complex salt and two analyses of a provided sample of the same compound. The compound is a “classic” within inorganic photo chemistry.

Preparation of Potassium tris(oxalato)manganate(III) Hydrate, $K_3[Mn(C_2O_4)_3]\cdot xH_2O$

Note 1: The $[Mn(C_2O_4)_3]^{3-}$ ion is photosensitive and should therefore be protected from light as far as possible. Also, the thermal stability of the title compound is low.

Note 2: Before starting the synthesis, write down the thermometer reading in ice-water.

The synthesis comprises a reduction of manganese(VII) to manganese(II) with oxalic acid at 70 – 75 °C. After the addition of the sufficient amount of potassium ions in form of potassium carbonate, manganese(III) is formed by the addition of manganese(VII) at a temperature below 2 °C.

$$2\ MnO_4^-(aq) + 8\ C_2O_4H_2(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 3\ C_2O_4^{2-}(aq) + 8\ H_2O(l)$$

$$C_2O_4H_2(aq) + CO_3^{2-}(aq) \rightarrow C_2O_4^{2-}(aq) + CO_2(g) + H_2O(l)$$

$$4\ Mn^{2+}(aq) + MnO_4^-(aq) + 11\ C_2O_4^{2-}(aq) + 4\ C_2O_4H_2(aq) \rightarrow$$
$$\rightarrow 5\ [Mn(C_2O_4)_3]^{3-}(aq) + 4\ H_2O(l)$$

Dissolve 5.00 g of $C_2O_4H_2 \cdot 2\ H_2O$ in 35 cm^3 of water in a 150 cm^3 beaker by heating to 70 °C. Slowly add 1.00 g of $KMnO_4$ with magnetic stirring. The temperature must not exceed 70 - 75 °C. When the mixture is colourless, add 1.10 g of K_2CO_3 in small portions and cool the mixture in ice. When the temperature of the mixture has fallen to 25 - 30 °C, add 25 g of crushed ice. Meanwhile, cool the hotplate with a beaker containing ice.

Maintain the temperature of the reaction mixture not more than 2 °C above your reported temperature of ice-water while adding 0.24 g of $KMnO_4$ in small portions with vigorous stirring. Stir for another 10 min and filter off the white precipitate and unmelted ice, if any, using the 60 cm^3 filter syringe (see procedure A). Collect the filtrate in a 250 cm^3 beaker cooled in ice. Add 35 cm^3 of ice-cold ethanol to the cherry-red filtrate (just swirl the beaker; stirring will lead to the formation of tiny crystals), wrap the beaker in aluminium foil and cool it in ice for 2 h (swirl the beaker three or four times during this period).

Clean the filter - first with 4 M HCl, then with water. Collect the cherry-red crystals by filtration using a 60 cm^3 filter syringe, then wash them two times 5 cm3 of ethanol and then two times with 5 cm^3 of acetone, and dry the product in air and protect it from light for at least one hour. A brown vial with lid should be taken to be tared by the lab assistant. When dry, the product is placed in the vial. Write name and student code on the vial. Then close the vial and take it and your answer sheet to the lab. assistant who will weigh your sample. The theoretical yield is 7.6 mmol.

1.1 Record the yield in grams.

1.2 Suggest a molecular formula of the white precipitate which is removed in the first filtration.

Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x\ H_2O$ for Oxidizing Ability

Note 3: The burette contains a cleanser and should therefore be rinsed 3 - 4 times with water before use.

Manganese(III) is reduced to manganese(II) by iodide ions and the triiodide ions formed are then titrated with thiosulfate.

$$2\ Mn^{III}(aq) + 3\ I^-(aq) \rightarrow 2\ Mn^{II}(aq) + I_3^-(aq)$$

$$I_3^-(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 3\ I^-(aq) + S_4O_6^{2-}(aq)$$

In a 250 cm^3 conical flask dissolve 1.0 g of KI in 25 cm^3 of demineralized water and add 10 cm^3 of 4 **M** HCl. Immediately after an accurately preweighed sample (approx. 200 mg) of the provided complex is transferred (as much as possible is poured directly into the liquid in small portions before the residue is washed down) quantitatively with demineralized water to the flask. Titrate the I_3^- formed with the standardized, approx. 0.025 M $Na_2S_2O_3$ solution. When the brown colour has faded to light yellow, add 2 cm^3 of starch indicator solution and continue the titration until the colour changes from blue to colourless.

1.3 Calculate the molar mass of the analyzed compound from the titration data.

Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x\, H_2O$ for Reducing Ability

Note 4: The burette should be rinsed 2 - 3 times with water before this titration.

Manganese(III) is reduced to manganese(II) by the oxalate ligands, and excess oxalate is titrated with permanganate.

$$2\,[Mn(C_2O_4)_3]^{3-}(aq) + 10\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 2\,CO_2(g) + 5\,C_2O_4H_2(aq)$$

$$5\,C_2O_4H_2(aq) + 2\,MnO_4^-(aq) + 6\,H^+(aq) \rightarrow 10\,CO_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$

Transfer an accurately preweighed sample (approx. 200 mg) of the provided complex quantitatively with demineralized water to a 250 cm^3 conical flask. Add 25 cm^3 of 2 M sulphuric acid and heat the solution to 75 – 80 °C. Without further heating, titrate with the standardized, approx. 0.025 M $KMnO_4$ solution. Near the end of the titration add the titrant slowly, until one drop gives the solution a rose colour which does not fade on standing for 0.5 min.

1.4 Calculate the molar mass of the analyzed compound from the titration data.

The results of the two types of analysis may differ by up to 10 %. Use only the result from the titration with $KMnO_4$ for the following calculation.

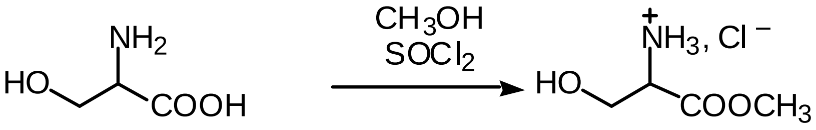
1.5 Calculate the value of x in the formula $K_3[Mn(C_2O_4)_3] \cdot x\, H_2O$ and the yield of your preparation in percent of the theoretical yield.

PROBLEM 2 (Practical)

Synthesis of Amino Acid Methyl Ester Hydrochloride

In the synthesis of peptides, one amino acid is reacted with another to form an amide bond between them. In order to ensure that the individual amino acids do not form amide bonds with themselves and that only one product is formed, the amino group in the first amino acid and the carboxyl group in the second amino acid are masked before the peptide synthesis.

The procedure described below can be used for masking the carboxylic acid groups in amino acids before peptide formation.



The experiment should be performed in a ventilated hood since thionyl chloride is an irritant and since irritating gases are evolved during the reaction.

Thionyl chloride is a corrosive acid chloride. Avoid contact with skin and eyes. Splashes in eyes or on skin should be flushed immediately with water. Thionyl chloride in larger amounts reacts violently with water.

Procedure

Absolute methanol (2.0 cm^3) is transferred quickly to a dry test tube which is then closed with a piece of aluminium foil. The foil is used as a lid throughout the subsequent manipulations with the tube. This protects the content from moisture from the air. The methanol is cooled in an ice-bath for 1 – 2 min. Thionyl chloride, handle with care, see above (0.52 cm^3) is drawn up into a 1 cm^3 graduated syringe with polyethylene tube tip, as described in separate procedure B, and is cautiously added to the methanol over a period of approximately 5 min.

The mixture is kept at 0 °C for approx. 2 min. (*S*)-Serine (0.210 g, weighed sample provided) is added and the mixture is kept at room temperature for approx. 2 min before gently heating to boiling (using a sand bath) for 10 min. All material should then have dissolved.

The mixture is cooled in an ice-bath for approx. 2 min. Dry *tert*.-butyl methyl ether (10 cm^3) is then added. The inside wall of the test tube is scratched at the surface region of the solution with a glass spatula for about 1 min. and the test tube is then left in the ice-bath for a further 5 –15 min for crystallization. The separated crystals are then isolated by filtration as described in separate procedure A. The filtrate is collected in a 100 cm^3 beaker.

The crystals are washed two times on the filter, each time with 1 cm^3 of *tert*.-butyl methyl ether. The filter cake is finally pressed with the piston, and the crystals are pre-dried by pumping air through the filter cake with the piston.

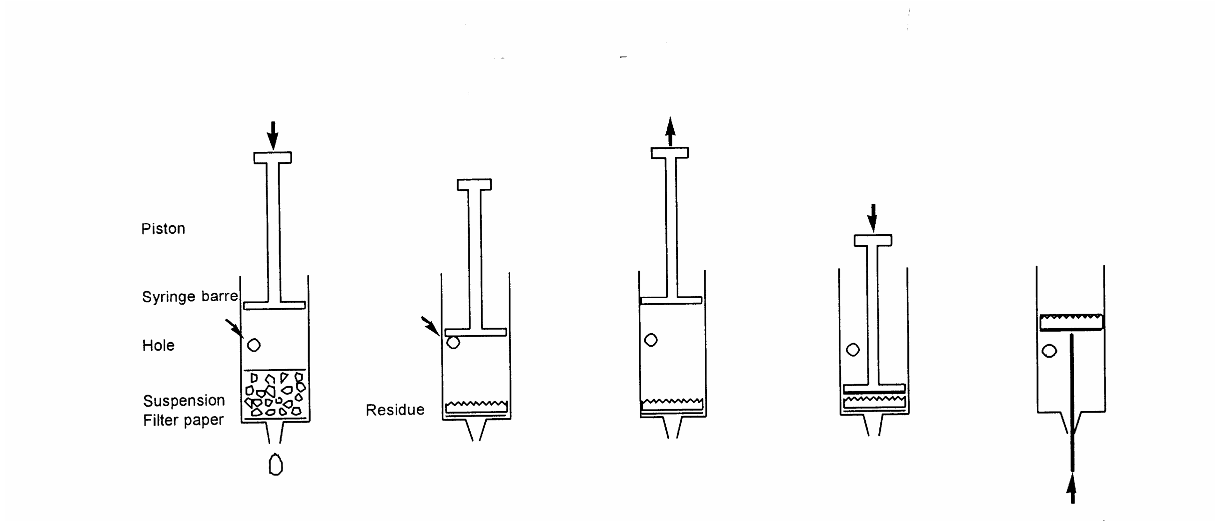
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

PROCEDURE A

Filtration procedures

Modified syringes are used for filtration in the laboratory tasks. A 60 cm^3 syringe with a disc of porous polypropylene is used in task 1, while a 10 cm^3 syringe with a disc of filtration paper is used in task 2. The procedure is sketched on Fig. 1.

Fig. 1: Micro-scale filtration in plastic syringe



Procedure:

1. Fill the syringe from above with suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Close hole and press piston for filtration.
3. Stop before passing the hole.
4. Open hole and draw piston back.
5. Repeat steps 2-4 a couple of times.
6. Remove piston and place filter paper on top of the filter cake.
7. Press piston against filter cake.
8. Push filter cake out with straightened- out paper clip.

Filtration procedure for practical problem 1

The provided filter syringe to be used in this experiment is made from a 60 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 35 cm^3 mark. With a plastic spatula a disc of porous polypropylene, which fits tightly inside the syringe, is pressed down to be positioned at the base of the syringe. The mixture to be filtered is applied without the piston inserted. Drops of solution may be moved downwards by tapping the syringe against a solid surface,

The piston is now placed in the syringe and gently pressed down while keeping the hole closed with a finger so to promote the passage of solvent through the filter. When the piston reaches just above the hole, the finger is removed from the hole, and the piston is drawn back again to the top position. This cycle can then be repeated a couple of times, until the filter cake looks dry. Remember to close the drilled hole, then the piston is moved downwards and to open the hole, when the piston is moved upwards. The filter cake can be washed and the washing solution pressed out using similar cycles.

Solvent remaining in the outlet can be sucked up with a small piece of tissue paper. The solid is then removed from the syringe and collected on a piece of weighing paper for drying.

Filtration procedure for practical problem 2

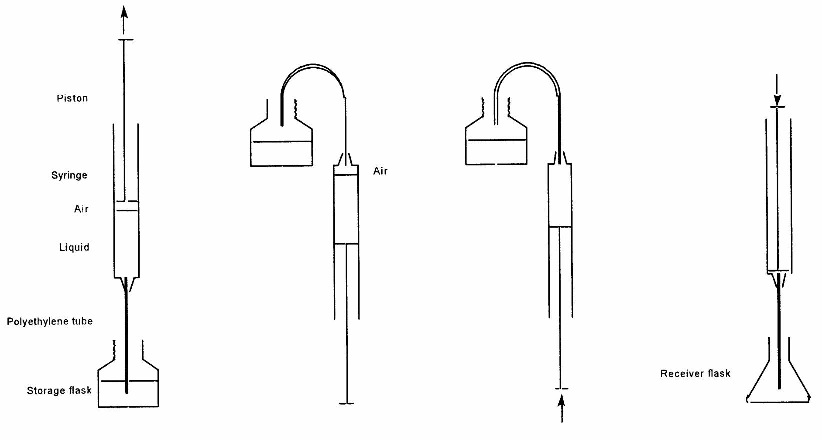
The provided filter syringe to be used in this experiment is made from a 10 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 5.5 cm^3 mark. A piece of filter paper which fits snugly in the syringe is pressed down to the bottom with the piston. Filtration and washing are then performed as described for task 1. Before removing the filter cake the piston is withdrawn. A piece of filter paper fitting the syringe is then pressed all the way down to the filter cake using the piston. The filter cake is pressed by means of the piston. Then the piston is then drawn back and out the syringe (slowly, until the hole is reached).

This leaves the filter cake between two pieces of filter paper. Solvent remaining in the outlet can be sucked up with a small piece of tissue paper.

The filter cake is cautiously pushed out of the syringe using an straightened-out metal paper clip introduced through the outlet of the syringe. The solid material is then removed from the syringe, if possible as a coherent plug. The residue is collected on a piece of filter paper for drying by using a small metal spatula. Filter paper from the filtration can be fixed with the paper clip tip while adhering solid is removed using the spatula.

PROCEDURE B

Fig. 2. Measuring volumes of liquids using a syringe



Procedure:

1. Suck up a slight excess of liquid in syringe.

2. Turn syringe upside down; the tip of the tube is kept in the storage nottle. Air in the syringe is accumulated at its top.
3. Air in the syringe is removed by pressing the piston. Press further until desired volume of liquid is left in the syringe. The tip of the tube is kept in the storage bottle.
4. Turn the syringe, place tip of the tube in the receiver flask and press piston until desired volume of liquid has left the syringe.

33rd

International Chemistry Olympiad

7 theoretical problems
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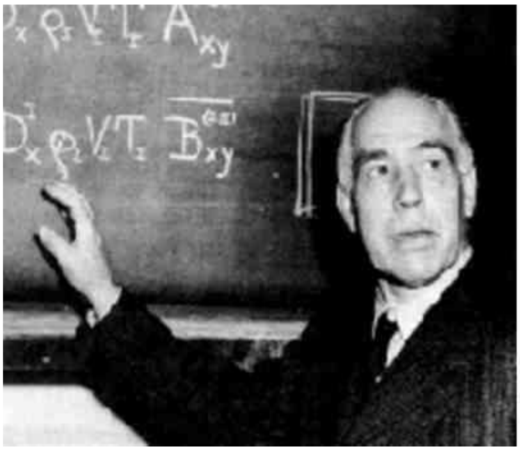
THEORETICAL PROBLEMS

PROBLEM 1

Hydrogen Atom and Hydrogen Molecule



Niels Bohr (1885-1962)

The observed wavelengths in the line spectrum of hydrogen atom were first expressed in terms of a series by Johann Jakob Balmer, a Swiss teacher. Balmer's empirical formula is

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right); \quad n = 3, 4, 5, ...$$

Here,
$$R_H = \frac{m_e e^4}{8 \varepsilon_0^2 h^3 c} = 109\,678 \text{ cm}^{-1}$$

is the Rydberg konstant, m_e is the mass of an electron. Niels Bohr derived this expression theoretically in 1913. The formula is easily generalized to any one electron atom/ion.

1.1 Calculate the longest wavelength in Å (1 Å = 10^{-10} m) in the 'Balmer series' of singly ionized helium (He^+). Ignore nuclear motion in your calculation.

1.2 A formula analogous to Balmer's formula applies to the series of spectral lines which arise from transitions from higher energy levels to the lowest energy level of hydrogen atom. Write this formula and use it to determine the ground state energy of a hydrogen atom in eV.

A 'muonic hydrogen atom' is like a hydrogen atom in which the electron is replaced by a heavier particle, the muon. The mass of a muon is about 207 times the mass of an electron, while its charge is the same as that of an electron. A muon has a very short lifetime, but we ignore its unstable nature here.

1.3 Determine the lowest energy and the radius of the first Bohr orbit of the muonic hydrogen atom. Ignore the motion of the nucleus in your calculation. The radius of the first Bohr orbit of a hydrogen atom

(called the Bohr radius, $a_0 = \frac{\varepsilon_0 h^2}{m_e e^2 \pi}$) is 0.53 Å.

The classical picture of an "orbit" in Bohr's theory has now been replaced by the quantum mechanical notion of an 'orbital'. The orbital $\psi_{1\sigma 1s}$ (r) for the ground state of a hydrogen atom is given by

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

where r is the distance of the electron from the nucleus and a_0 is the Bohr radius.

1.4 Consider a spherical shell of radius a_0 and thickness $0.001a_0$. Estimate the probability of finding the electron in this shell. Volume of a spherical shell of inner radius r and small thickness Δr equals $4\pi r^2 \Delta r$.

The H_2 molecule can dissociate through two different channels:

(i) $H_2 \rightarrow H + H$ (two separate hydrogen atoms)

(ii) $H_2 \rightarrow H^+ + H^-$ (a proton and a hydride ion)

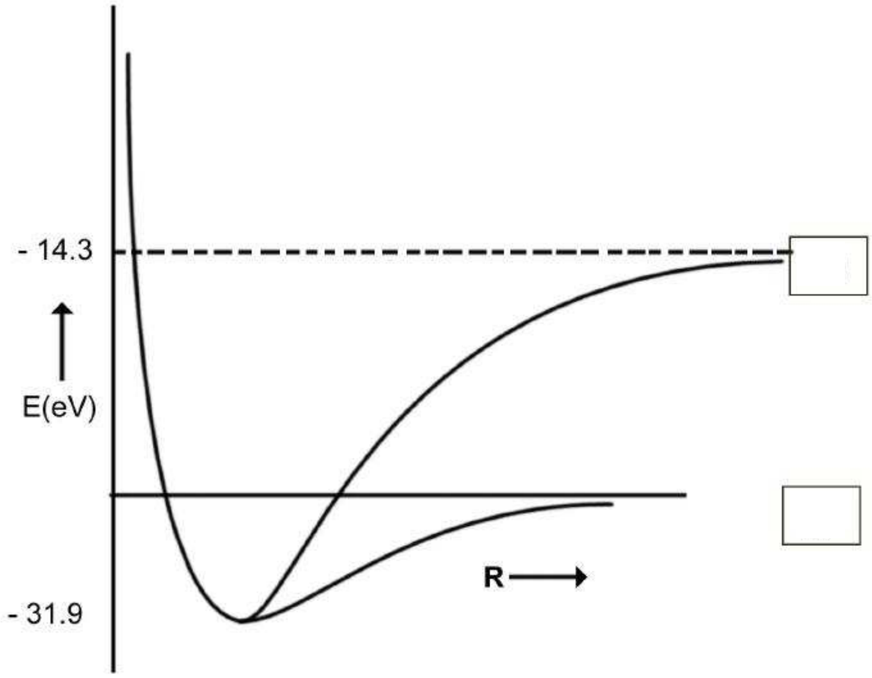
The graph of energy (E) vs internuclear distance (R) for H_2 is shown schematically in the figure. The atomic and molecular energies are given in the same scale.

1.5 Put appropriate channel labels (i) or (ii) in the boxes below.

1.6 Determine the values of the dissociation energies (D_e in eV) of the H_2 molecule corresponding to

channel (i) ☐

channel (ii) ☐



1.7 From the given data, calculate the energy change for the process

$H^- \rightarrow H + e^-$

1.8 H^- is a two-electron atomic system. Assuming that the Bohr energy formula is valid for each electron with nuclear charge Z replaced by Z_{eff}, calculate Z_{eff} for H^-.

SOLUTION

1.1 Longest wavelength A_L corresponds to n = 3

For He^+

$$\frac{1}{\lambda} = 4R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

λ_L = 1641.1 Å

1.2 $\frac{1}{\lambda} = 4R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4, ...$

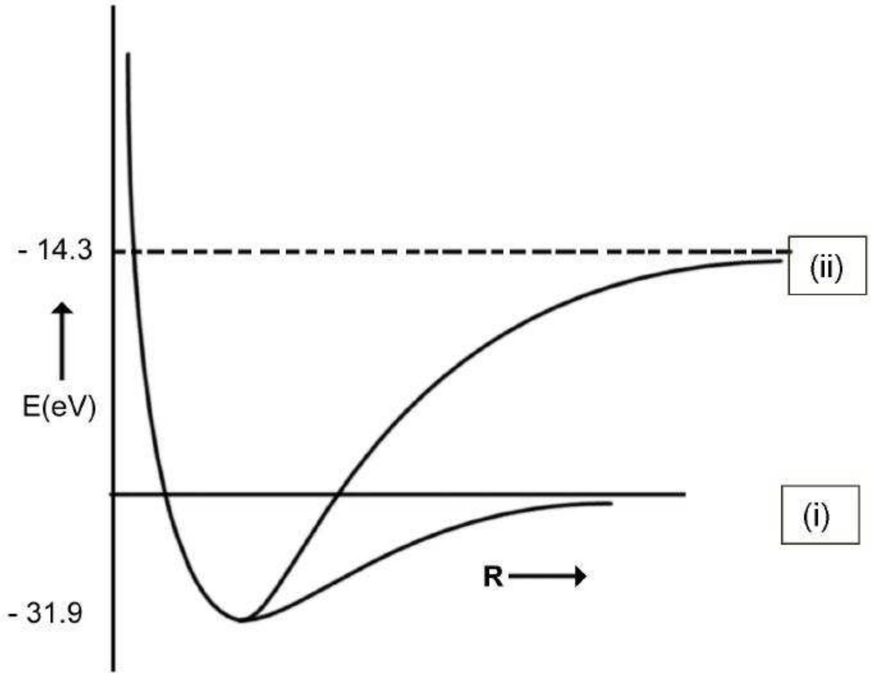
$E = -hcR_H = -13.6$ eV

1.3 Lowest energy = – 207 × 13.6 = –2.82 keV

Radius of the first Bohr orbit = 0.53 / 207 = 2.6×10^{-3} Å

1.4 Probability = $|\psi(a_0)|^2\, 4\pi a_0^2 \times 0.001 a_o = 0.004\, e^{-2} = 5.41\times10^{-4}$

1.5



1.6 Channel (i): 4.7 eV

Channel (ii): 17.6 eV

1.7 Electron affinity = – 13.6 – (– 14.3) = 0.7 eV

1.8 $Z_{\text{eff}} = -13.6 + 27.2\, Z^2_{\text{eff}} = 0.7$

PROBLEM 2

Phosphoric Acid

Phosphoric acid is of a great importance in fertilizer industry. Besides, phosphoric acid and its various salts have a n umber of applications in metal treatment, food, detergent and toothpaste industries.

2.1 The pK values of the three successive dissociations of phosphoric acid at 25 ℃ are:

pK_{1a} = 2.12

pK_{2a} = 7.21

pK_{3a} = 12.32

Write down the conjugate base of dihydrogen phosphate ion and determine its pK_b value.

Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and root beers. A cola having a density of 1.00 g cm^{-3} contains 0.05 % by weight of phosphoric acid.

2.2 Determine the *pH* of the cola (ignoring the second and the third dissociation steps for phosphoric acid). Assume that the acidity of the cola arises only from phosphoric acid.

2.3 Phosphoric acid is used as a fertiliser for agriculture. 1.00×10^{-3} M phosphoric acid is added to an aqueous soil suspension and the *pH* is found to be 7.00.

Determine the fractional concentrations of all the different phosphate species present in the solution. Assume that no component of the soil interacts with any phosphate species.

2.4 Zinc is an essential micronutrient for plant growth. Plant can absorb zinc in water soluble form only. In a given soil water with *pH* = 7.0, zinc phosphate was found to be the only source of zinc and phosphate. Calculate the concentration of [Zn^{2+}] and [PO_4^{3-}] ions in the solution. Ksp for zinc phosphate is 9.1×10^{-33}.

SOLUTION

2.1 The conjugate base of dihydrogen phosphate ($H_2PO_4^-$) is monohydrogen phosphate (HPO_4^{2-}) :

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_{2a}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad K_{2b}$$

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w$$

$pK_{2a} + pK_{2b} = pK_w = 14$

$pK_{2b} = 6.79$

2.2 Concentration of $H_3PO_4 = \dfrac{0.5}{98} = 0.0051$ M

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$

0.0051-x x + x

$pK_{1a} = 2.12$ gives $K_{1a} = 7.59\times10^{-3}$

$$7.59\times10^{-3} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = \frac{x^2}{0.0051 - x}$$

$x = [H_3O^+] = 3.49\times10^{-3}$

$pH = 2.46$

2.3 Let $f_0 = \dfrac{[H_3X]}{C}$, $f_1 = \dfrac{[H_2X^-]}{C}$,

$f_2 = \dfrac{[HX^{2-}]}{C}$ and $f_3 = \dfrac{[X^{3-}]}{C}$

denote the fractional concentrations of different phosphate species. C is the total initial concentration of H_3X. (X = PO_4)

$$f_0 + f_1 + f_2 + f_3 = 1$$

$$K_{1a} = \frac{[H_2X^-][H_3O^+]}{[H_3X]} = \frac{f_1}{f_0}[H_3O^+]$$

$$K_{2a} = \frac{[HX^{2-}][H_3O^+]}{[H_2X^-]} = \frac{f_2}{f_1}[H_3O^+]$$

$$K_{3a} = \frac{[X^{3-}][H_3O^+]}{[HX^{2-}]} = \frac{f_3}{f_2}[H_3O^+]$$

These equations lead to

$$f_0 = \frac{[H_3O^+]^3}{D}, \qquad f_1 = \frac{K_{1a}[H_3O^+]^2}{D}, \qquad f_2 = \frac{K_{1a}K_{2a}[H_3O^+]}{D}, \qquad f_3 = \frac{K_{1a}K_{2a}K_{3a}}{D}$$

where D = $K_{1a}\ K_{2a}\ K_{3a}$ + $K_{1a}\ K_{2a}\ [H_3O^+]$ + $K_{1a}\ [H_3O^+]^2$ + $[H_3O^+]^3$

From the values of pK_{1a}, pK_{2a}, pK_{3a} and pH one gets

K_{1a} = 7.59×10^{-3} ; K_{2a} = 6.17×10^{-8} ; K_{3a} = 4.79×10^{-13}; $[H_3O^+]$ = 1×10^{-7}

The fractional concentrations of different phosphate species are:

H_3PO_4 (f_0) = 8.10×10^{-6}

$H_2PO_4^-$ (f_1) = 0.618

HPO_4^{2-} (f_2) = 0.382

PO_4^{3-} (f_3) = 1.83×10^{-6}

2.4 Let S (mol dm^{-3}) be the solubility of $Zn_3(PO_4)_2$ in soil water.

$[Zn^{2+}]$ = 3 S

Total concentration of different phosphate species = 2 S

$[PO_4^{3-}]$ = $f_3 \times 2\ S$

f_3 can be determined from the relation derived in **2.3**

For pH = 7, f_3 = 1.83×10^{-6}

K_{sp} = $[Zn^{2+}]^3\ [PO_4^{3-}]^2$

9.1×10^{-33} = $(3\ S)^3\ (f_3 \times 2\ S)^2$

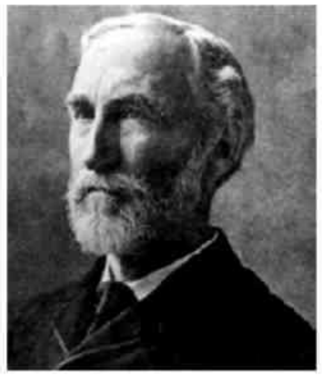
$[Zn^{2+}]$ = 9×10^{-5}

$[PO_4^{3-}]$ = 1.1×10^{-10}

Solubility of $Zn_3(PO_4)_2$ = 3.0×10^{-5} mol dm^{-3}

PROBLEM 3

Second Law of Thermodynamics



J.W.Gibbs (1839 –1903)

The second law of thermodynamics is a fundamental law of science. In this problem we consider the thermodynamics of an ideal gas, phase transitions and chemical equilibrium.

3.00 mol of CO_2 gas expands isothermically (in thermal contact with the surroundings; temperature = 15 °C) against a fixed external pressure of 1.00 bar. The initial and final volumes of the gas are 10.0 dm^3 and 30.0 dm^3, respectively.

3.1 Choose the correct option for change in the entropy of the system (ΔS_{sys}) and of the surroundings (ΔS_{sur}):

(a) $\Delta S_{sys} > 0$ $\Delta S_{sur} = 0$ ☐

(b) $\Delta S_{sys} < 0$ $\Delta S_{sur} > 0$ ☐

(c) $\Delta S_{sys} > 0$ $\Delta S_{sur} < 0$ ☐

d) $\Delta S_{sys} = 0$ $\Delta S_{sur} = 0$ ☐

(Mark X in the correct box.)

3.2 Calculate ΔS_{sys} assuming CO_2 to be an ideal gas.

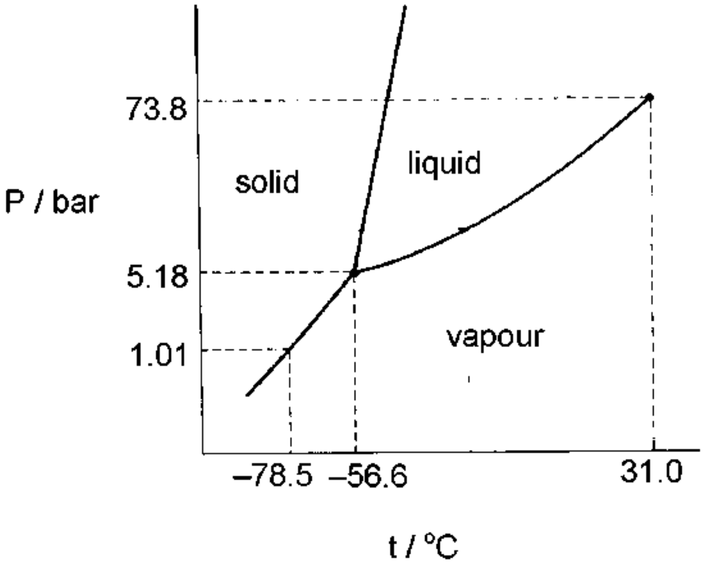
3.3 Calculate ΔS_{sur}.

3.4 Calculate the change in entropy of the universe.

Does your answer agree with the Second Law of Thermodynamics? ☐ Yes ☐ No

(Mark X in the correct box.)

The pressure – temperature phase diagram of CO_2 is given below schematically. The diagram is not to scale.



Phase diagram of CO_2

3.5 CO_2 gas, initially at a pressure of 4.0 bar and temperature of 10.0 °C is cooled at constant pressure. In this process,

(a) it goes first to the liquid phase and then to the solid phase. ☐

(b) it goes to the solid phase without going through the liquid phase. ☐

3.6 Starting with the same pressure and temperature as above (in 3.5), CO_2 is compressed isothermatically. In this process,

(a) it goes first to the liquid phase and then to the solid phase. ☐

(b) it goes to the solid phase without going through the liquid phase. ☐

3.7 From the data given in the phase diagram, calculate the molar enthalpy change of sublimation of CO_2. Write down the formula used.

3.8 CO gas, used extensively in organic synthesis, can be obtained by reacting CO_2 gas with graphite. Use the data given below to show that the equilibrium constant at 298.15 K is less than unity.

At 298.15 K

$CO_2(g)$:	ΔH_f^0 = –393.51 kJ mol^{-1};	S^0 = 213.79 J K^{-1} mol^{-1}
CO(g):	ΔH_f^0 = –110.53 kJ mol^{-1};	S^0 = 197.66 J K^{-1} mol^{-1}
C(graphite)	S^0 = 5.74 J K^{-1} mol^{-1}	

3.9 Estimate the temperature at which the reaction would have an equilibrium constant equal to 1. Ignore slight variations in the thermodynamic data with temperature.

3.10 The reaction above (in 3.8) is carried out between CO_2 and excess hot graphite in a reactor maintained at about 800 °C and a total pressure of 5.0 bar. The equilibrium constant K_p under these conditions is 10.0. Calculate the partial pressure of CO at equilibrium.

SOLUTION

3.1 Correct solution: (c) $\Delta S_{\text{sys}} > 0$ $\Delta S_{\text{sur}} < 0$

3.2 Since ΔS_{sys} is independent of path, it is the same as for isothermal reversible expansion of an ideal gas.

$$\Delta S_{\text{sys}} = nR \ln \frac{V_{\text{f}}}{V_{\text{i}}} = 27.4 \text{ J K}^{-1}$$

3.3 q = $p_{\text{ext}}\,\Delta V$

$$\Delta S_{\text{sur}} = -\frac{q}{T} = -\,6.94 \text{ J K}^{-1}$$

3.4 $\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 20.5 \text{ J K}^{-1}$

The answer agrees with the second law of thermidynamics (correct is YES)

3.5 Correct answer:

(b) it goes to the solid phase without going through the liquid phase.

3.6 Correct answer:

(a) it goes first to the liquid phase and then to the solid phase.

3.7 $$\ln \frac{p_2}{p_1} = -\frac{\Delta H_{\text{sub}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H_{\text{sub}} = 26.1 \text{ kJ mol}^{-1}$

3.8 $\Delta H^0 = 172.45\ \text{kJ mol}^{-1}$

$\Delta S^0 = 176\ \text{J K}^{-1}\text{mol}^{-1}$

$\Delta G^0 = \Delta \text{H}^0 - T\Delta \text{S}^0 = 120\ \text{kJ mol}^{-1}$

$\Delta G^0 > \text{O}$ implies $K < 1$

3.9 $\Delta G^0 = 0$ when $\Delta \text{H}^0 = T\Delta \text{S}^0$

$T = 980\ \text{K}$

3.10

$$\text{CO}_2\ (g) + \text{C(s)} \rightleftharpoons 2\ \text{CO (g)}$$

$$1 - \alpha \qquad\qquad 2\alpha$$

Partial pressure: $\dfrac{1-\alpha}{1-\alpha} \times 5$ $\qquad$ $\dfrac{2\alpha}{1-\alpha} \times 5$

$$K_p = \frac{p^2(\text{CO})}{\text{p}(\text{CO}_2)}$$

$p(\text{CO}) = 3.7\ \text{bar}$

PROBLEM 4

Beach Sand Mineral in Kerala

Beach sand mineral, monazite, is a rich source of thorium, available in large quantities in the state of Kerala in India. A typical monazite sample contains about 9 % ThO_2 and 0.35 % U_3O_8. ^{208}Pb a ^{206}Pb are the stable end-products in the radioactive decay series of ^{232}Th and ^{238}U, respectively. All the lead (Pb) found in monazite is of radiogenic origin.

The isotopic atom ratio $^{208}Pb/^{232}Th$, measured mass spectrometrically, in a monazite sample was found to be 0.104. The half-lives of ^{232}Th and ^{238}U 1.41×10^{10} years and 4.47×10^{9} years, respectively. Assume that ^{208}Pb, ^{206}Pb, ^{232}Th and ^{238}U remained entirely in the monazite sample since the formation of monazite mineral.

4.1 Calculate the age (time elapsed since its formation) of the monazite sample.

4.2 Estimate the isotopic atom ratio $^{206}Pb/^{238}U$ in the monazite sample.

4.3 Thorium-232 is a fertile material for nuclear energy. In thermal neutron irradiation, it absorbs a neutron and the resulting isotope forms ^{233}U by successive β^- decays. Write the nuclear reactions for the formation of ^{233}U from ^{232}Th.

In nuclear fission of ^{233}U a complex mixture of radioactive fission products is formed. The fission product ^{101}Mo initially undergoes radioactive decay as shown below:

$$^{101}_{42}Mo \xrightarrow[t_{1/2}\,=\,14.6\,min]{} {}^{101}_{43}Tc \xrightarrow[t_{1/2}\,=\,14.3\,min]{} {}^{101}_{44}Ru$$

4.4 A freshly prepared radiochemically pure sample of ^{101}Mo contains 5000 atoms of ^{101}Mo initially. How many atoms of

i) ^{101}Mo

ii) ^{101}Tc

iii) ^{101}Ru

will be present in the sample after 14.6 min?

SOLUTION

4.1 $N = N_0\ \mathrm{e}^{-\frac{0.6931\ t}{t_{1/2}}}$

$$\frac{N_0 - N}{N} = \mathrm{e}^{\frac{+0.6931\ t}{t_{1/2}}} - 1$$

(N_0 - N) = Total number of ^{232}Th atoms decayed. = Total number of ^{208}Pb atoms formed.

$$\frac{N_0 - N}{N} = 0.104$$

$$\mathrm{e}^{\frac{0.6931\ t}{1.41\times10^{10}}} = 1.104$$

t = 2.01×10^9 years.

4.2 Let x be the required ratio.

$$\mathrm{x} = \mathrm{e}^{\frac{+0.6931\ t}{t_{1/2}}} - 1$$

where t = 2.01×10^9 years, and $t_{1/2}$ = 4.47×10^9 years.

x = 0.366

4.3 $^{232}\mathrm{Th} \xrightarrow{(\mathrm{n},\gamma)} {}^{233}\mathrm{Th} \xrightarrow{\beta^-} {}^{233}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}\mathrm{U}$

4.4 (i) The number of atoms of ^{101}Mo (N_1) in the sample after one half-life is :

N_1 = 2500

(ii) The number of atoms of ^{101}Tc (N_2) is given by

$$N_2 = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1}(\mathrm{e}^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where N_0 (= 5000) is the initial number of atoms of ^{101}Mo.

$$\lambda_1 = \frac{0.693}{14.6}\ \mathrm{min}^{-1}$$

$$\lambda_2 = \frac{0.693}{14.3}\ \mathrm{min}^{-1}$$

At t = 14.6 min

N_2 = 1710

(iii) Number of atoms of ^{101}Ru (N_3) at t = 14.6 min is :

$N_3 = N_0 - N_1 - N_2$ = 790 atoms

PROBLEM 5

Halogen Chemistry

Halogens in their reactions among themselves and with a variety of other elements give rise to a large number of compounds with diverse structure, bonding and chemical behaviour. Metal halides, halogen derivatives and interhalogens represent major types of halogen compounds.

(A) Photography

A "black and white" photographic film contains a coating of silver bromide on a support such as cellulose acetate.

5.1 Write the photochemical reaction that occurs when light falls on AgBr(s) coated on a film.

5.2 During the developing process, unexposed AgBr is washed away by complexation of Ag(I) by sodium thiosulphate solution. Write down this chemical reaction.

5.3 These washings are often disposed of as waste. However, metallic silver can be recovered from them by adding cyanide, followed by zinc. Write down the reactions involved.

(B) Shapes, spectra and reactivity

The most reactive halogen, fluorine, reacts with other halogens Cl_2, Br_2 and I_2 under controlled conditions giving a tetra-atomic, hexa-atomic and an octa-atomic molecule, respectively.

5.4 Write the formulae and 3-dimensional structures of these interhalogen molecules on the basis of VSEPR theory. Show the disposition of the lone pairs on the central atom, where appropriate.

A mixture of iodine vapour and chlorine gas when fed into a mass spectrometer gave two sets (A and B) of mass spectral peaks corresponding to molecular ions of two chemical species at *m*/*z*:

A: 162, 164

B: 464, 466, 468, 470, 472, 474, 476

5.5 Identify the molecular species corresponding to *m*/*z* = 162, 164, 466 and 476. Draw the structure of the heaviest species (*m*/*z* = 476) indicating clearly the lone pairs on atom(s) of I (iodine). Show the isotopic composition of each species.

In aqueous medium chlorine gas oxidises sodium thiosulphate to an ion containing the highest oxidation state of sulphur.

5.6 Write down the chemical equation for this reaction.

5.7 Write down the Lewis dot structure of the thiosulphate ion. Circle the sulphur atom that has the lower oxidation state.

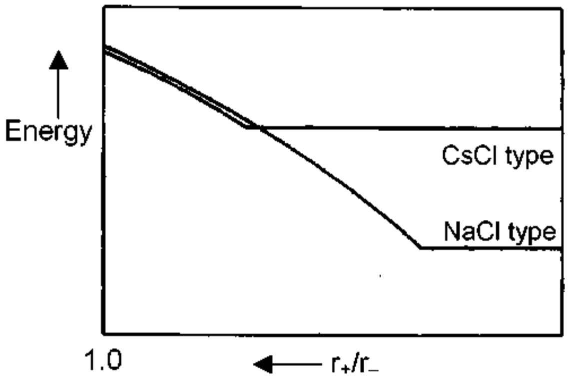
5.8 Chlorine dioxide reacts with sodium hydroxide as shown below. Identify the products X and Y (both containing chlorine) and balance the equation.

5.9 Reaction of chlorine an alkali is used by manufacturing bleach. Write the chemical reaction for its formation.

5.10 Write the oxidation state(s) of chlorine in bleach.

(C) Alkali metal halides and X-ray crystallography

X-ray crystallography reveals many aspects of the structure of metal halides. The radius ratio (r_+/r_-) is a useful parameter to rationalise their structure and stability. A table of radius ratio (r_+/r_-) for some alkali halides with radius ratio (r_- kept constant) is shown schematically for NaCl-type and CsCl-type crystal structures.



	Li^+	Na^+	K^+	Rb^+	Cs^+
Cl^-	0.33	0.52	0.74	0.82	0.93
Br^-	0.31	0.49	0.68	0.76	0.87
I^-	0.28	0.44	0.62	0.69	0.78

5.11 For a given anion, the graph for NaCl-type structure levels off at low r_+/r_- values because of

(a) cation-cation contact along the face diagonal. ☐

(b) anion-anion contact along the face diagonal. ☐

(c) cation-anion contact along the cell edge. ☐

(Mark X in the correct box.)

5.12 Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl-type to CsCl-type structure with change of temperature and / or pressure?

5.13 Show by calculation the radius ratio (r_+/r_-) at which the energy of CsCl-type structure levels off.

5.14 Using CuKα X-rays (λ = 154 nm), diffraction by a KCl crystal (fcc structure) is observed at an angle (θ) of 14.2 °. Given that (i) diffraction takes place from the planes with $h^2 + k^2 + l^2 = 4$, (ii) in a cubic crystal $d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$, where "d" is the distance between adjacent hkl planes and "a" is a lattice parameter, and (iii) reflections in an fcc structure can occur only from planes with "all odd" or "all even" hkl (Miller) indices, calculate the lattice parameter "a" for KCl.

5.15 Indicate in the table given below the required information for the 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

5.16 Determine the lowest value of diffraction angle θ possible for the KCl structure.

SOLUTION

5.1 $2\ AgBr\ (s) \xrightarrow{h\nu} 2\ Ag\ (s) + Br_2\ /2\ Br\bullet$

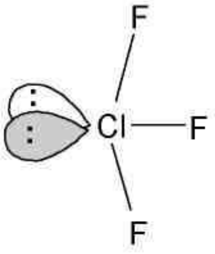
5.2 $AgBr(s) + 2\ Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

5.3 $[Ag(S_2O_3)_2]^{3-} + 2\ CN^- \rightarrow [Ag(CN)_2]^- + 2\ S_2O_3^{2-}$

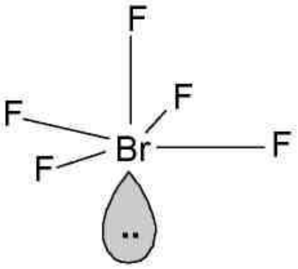
$2\ [Ag(CN)_2]^- + Zn \rightarrow [Zn\ (CN)_4]^{2-} + 2\ Ag\downarrow$

5.4

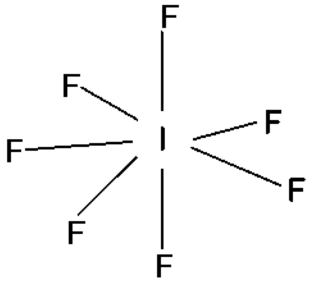
ClF_3



BrF_5



IF_7

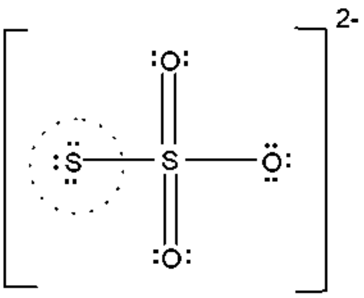


5.5.

Mass:	162	164	466	476
Species:	$I\,{}^{35}Cl$	$I\,{}^{37}Cl$	$I_2{}^{35}Cl_5{}^{37}Cl$	$I_2{}^{37}Cl_6$

5.6 $4\ Cl_2 + S_2O_3^{2-} + 5\ H_2O \rightarrow 8\ Cl^- + 2\ SO_4^{2-} + 10\ H^+$

5.7



5.8 $2\ ClO_2 + 2\ NaOH \rightarrow \underset{X}{NaClO_2} + \underset{Y}{NaClO_3} + H_2O$

5.9 $Cl_2 + Ca(OH)_2 \rightarrow Ca(Cl)(OCl) + H_2O$

or

$Cl_2 + CaO \rightarrow Ca(Cl)(OCl)$

or

$2\ OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O$

5.10 The oxidation state(s) of chlorine in bleach is (are): -I and I

5.11 Correct answer: (b) anion–anion contact along the face diagonal.

5.12 RbBr

5.13 In CsCI-type structure,

Cell edge, a = 2 r

Body diagonál: $\sqrt{3\,a} = 2(r_+ + r_–)$

$$\frac{r_+}{r_-} = \sqrt{3} - 1 = 0.732$$

5.14 $\lambda = 2d \sin \theta$

$$d_{200} = \frac{\lambda}{2 \sin\theta} = 314 \text{ pm}$$

$$d_{200} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} = \frac{a}{(2^2 + 0^2 + 0^2)^{1/2}} = \frac{a}{2}$$

a = 628 pm

5.15 The 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)
12	+	444	8	-	544

5.16 Lowest θ value is for the plane with hkl = (111)

$$d = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{628}{\sqrt{3}} = 363 \text{ pm}$$

$$\sin\theta_{111} = \frac{\lambda}{2\,d_{111}} = \frac{154 \text{ pm}}{2 \times 363 \text{ pm}} = 0.212$$

$$\theta_{111} = 12.2\,^\circ$$

PROBLEM 6

Organic Chemistry of Indian Spices

The rhizomes of ginger (*Zingiber officinale*) are well known for their medicinal and flavouring properties. In Ayurveda (the traditional system of medicine in India) different formulations of ginger are used for the treatment of gastrointestinal problems, common cold and other aliments. Several compounds are responsible for the pungency of ginger. Many are simple substituted aromatic compounds with different side chains. Three of them, Zingerone, (+)[6] Gingerol (to be referred hereafter as Gingerol only), and Shogaol are particularly important.

Zingerone: $C_{11}H_{14}O_3$
Gingerol: $C_{17}H_{14}O_4$
Shogaol: $C_{17}H_{24}O_3$

6.1 Zingerone gives positive FeCl3 and 2,4-DNP (2,4-dinitrophenylhydrazine) tests. It does not react with Tollen's reagent. Therefore, Zingerone contains the following functional groups: (Mark X in the correct boxes.)

(a) alcoholic hydroxyl ☐
(b) aldehydic carbonyl ☐
(c) ketonic carbonyl ☐
(d) phenolic hydroxyl ☐
(e) ester ☐
(f) alkoxyl ☐
(g) unsaturation ☐

The data obtained from the ^{1}H NMR spectrum of Zingerone are shown in Table 1. Some other relevant information is given in Table 2.

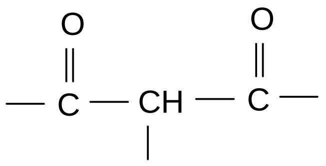
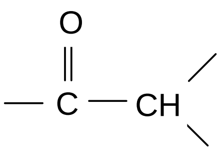
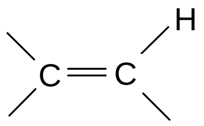
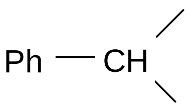
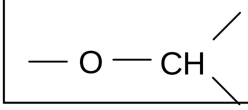
Table 1: ^{1}H NMR spectral data on Zingerone

Chemical shifts (δ)	Multiplicity	Relative intensity
2.04	singlet	3
2.69, 2.71	two (closely spaced) triplets of equal intensity	4
3.81	singlet	3
5.90	broad singlet (D_2O exchangeable)	1
6.4 – 6.8	two doublets with similar chemical shifts and one singlet	3

*) For clarity, some of the data have been altered slightly.)

Table 2: Approximate 1H chemical shifts (δ) and spin-spin coupling constants (J) of some protons

^{1}H Chemical shifts

alkyl - H	0.9 - 1.5		3.4 - 3.6
	2.0 - 2.7		4.0 - 7.0
	2.3 - 2.9	Ph — H	6.0 - 8.0
	3.3 - 3.9	Ar — OH	4.0 - 11.0

Spin–spin coupling constants (J)

Alkenes	*cis*	5 – 14 Hz (commonly around 6 – 8 Hz)
	trans	11 – 19 Hz (commonly around 14 – 16 Hz)

Zingerone on bromination with bromine water gives only one nuclear mono brominated product. The IR spectrum of Zingerone indicates the presence of a week *intramolecular* hydrogen bond. The same is present even after Clemmensen reduction (Zn – Hg/HCl) of Zingerone.

6.2 From the information above deduce the following:

i) side chain in Zingerone $\boxed{}$

ii) substituent on the aromatic ring $\boxed{}$

iii) relative positions of the substituents on the ring $\boxed{}$

6.3 Draw a possible structure of Zingerone based on the above inferences.

6.4 Complete the following reaction sequence for the synthesis of Zingerone.

$$\boxed{} + \boxed{} \xrightarrow{\text{aq. NaOH}} \textbf{C}$$

A + **B** (C_3H_6O)

$$\boxed{} \xrightarrow{H_2\text{/ Catalyst}} \text{Zingerone } (C_{11}H_{14}O_3)$$

C

6.5 Zingerone can be easily converted into Gingerol by the following reaction sequence:

$$\underset{(C_{11}H_{14}O_3)}{\text{Zingerone}} \xrightarrow[\text{(ii) LDA, 78 °C}]{\text{(i) } Me_3SiCl\text{ / }(Me_3Si)_2NH} \textbf{D} \xrightarrow[\text{(ii) } H_2O\text{/ H+}]{\text{(i) hexanal}} \underset{(C_{17}H_{28}O_4)}{\text{Cingerol}}$$

Notes: (1) Me_3SiCl / $(Me_3Si)_2NH$ is used to convert OH into $–OSiMe_3$; the group $–SiMe_3$ can be removed by acid hydrolysis.

(2) LDA is lithium disopropylamine, a strong, very hindered, non.nucleophilic base.

i) Draw the structure of **D.**

ii) Draw the structure of Gingerol.

iii) Complete the Fischer projection of the *R*-enantiomer of Gingerol.

iv) In the above reaction sequence (6.5), about 2 – 3 % another constitutional isomer (**E**) of Gingerol is obtained. Draw the likely structure of **E**.

v) Will the compound **E** be formed as

(a) a pair of enatiomers? ☐

(b) a mixture of diastereomers? ☐

(c) a mixture of an enantiomeric pair and a meso isomer? ☐

(Mark X in the correct box.)

vi) Gingerol ($C_{17}H_{26}O_4$) when heated with a mild acid (such as $KHSO_4$) gives Shogaol ($C_{17}H_{24}O_3$). Draw the structure of Shogaol.

6.6 Turmeric (*Curcuma longa*) is a commonly used spice in Indian food. It is also used in Ayurvedic medicinal formulations. Curmunin ($C_{21}H_{20}O_6$), an active ingredient of turmeric, is structurally related to Gingerol. It exhibits keto-enol tautomerism. Curcumin is responsible for the yellow colour of turmeric and probably also for the pungent taste.

The ^{1}H NMR spectrum of the keto form of Curcumin shows aromatic signal similar to that of Gingerol. It also shows a singlet around δ 3.5 (2H) and two doublets (2H each) in the region δ 6 – 7 with J = 16 Hz. It can be synthesized by condensing TWO moles of **A** (refer to **6.4**) with one mole of pentan-2,4-dione.

i) Draw the stereochemical structure of Curcumin.

ii) Draw the structure of the enol form of Curcumin.

iii) Curcumin is yellow in colour because it has

(a) a phenyl ring ☐

(b) a carbonyl group ☐

(c) an extended conjugation ☐

(d) a hydroxyl group ☐

(Mark X in the correct box.)

SOLUTION

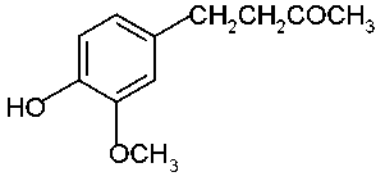
6.1 Zingerone contains the following functional groups:

(c) ketonic carbonyl

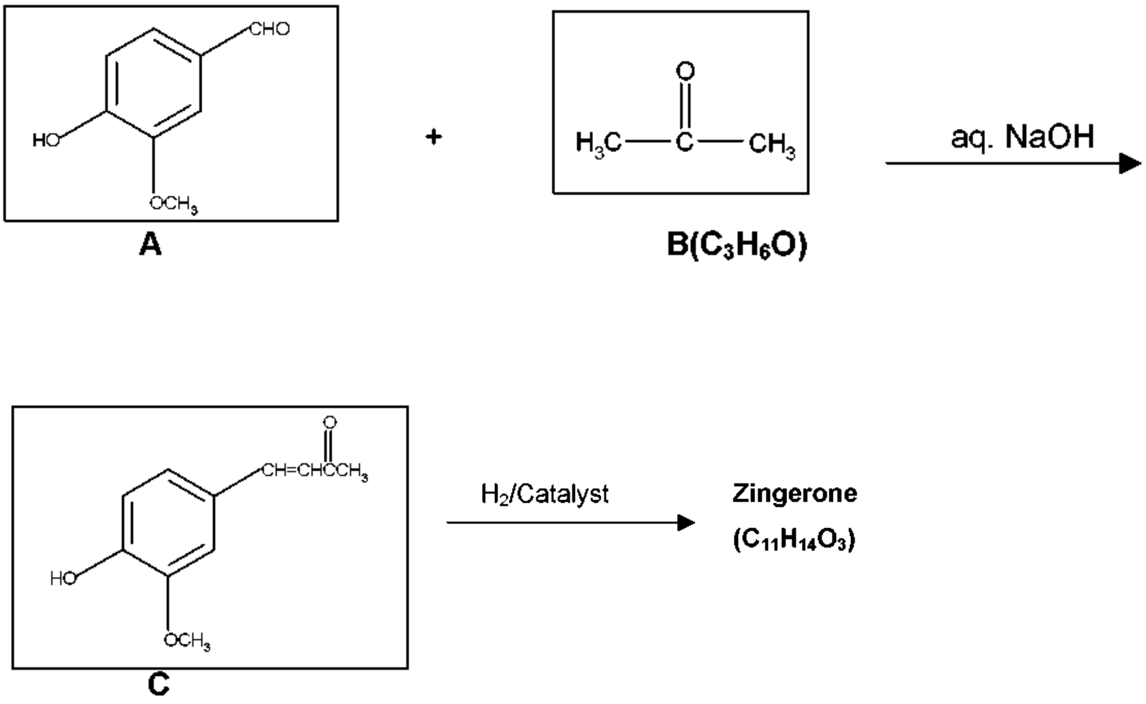
(d) phenolic hydroxyl

6.2	i)	side chain in Zingerone:	$CH_2CH_2COCH_3$
	ii)	substituents on the aromatic ring:	OH, OCH_3
	iii)	relative positions of the substituents on the ring:	1, 2, 4

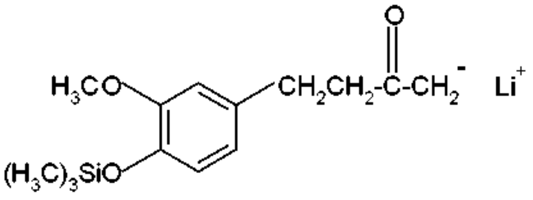
6.3



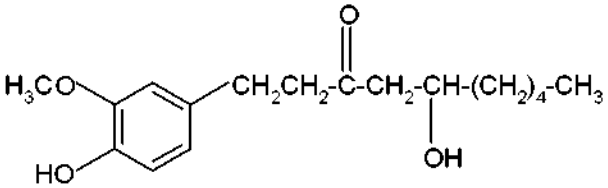
6.4



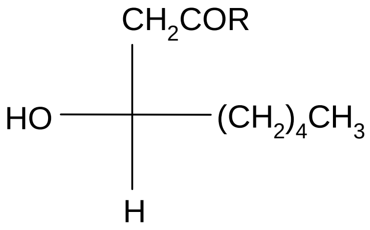
6.5 i)



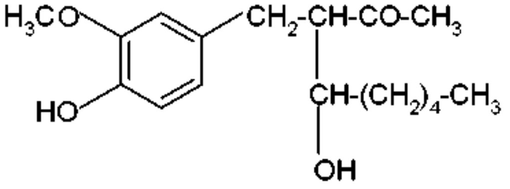
ii)



iii)

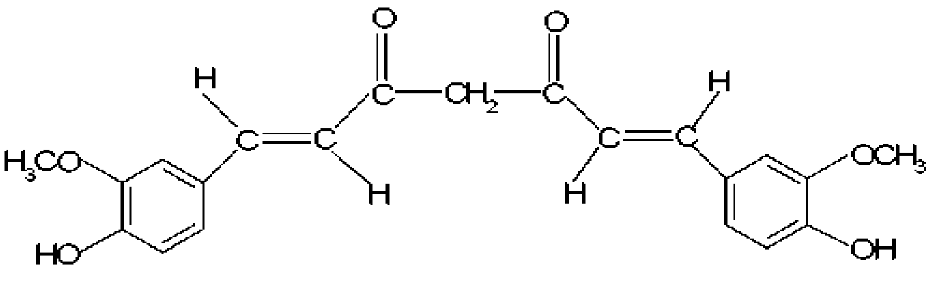


iv)

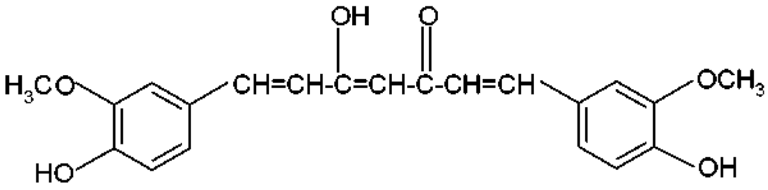


v) Compound **E** will be formed as: (b) a mixture of diastereomers

6.6 i)



ii)

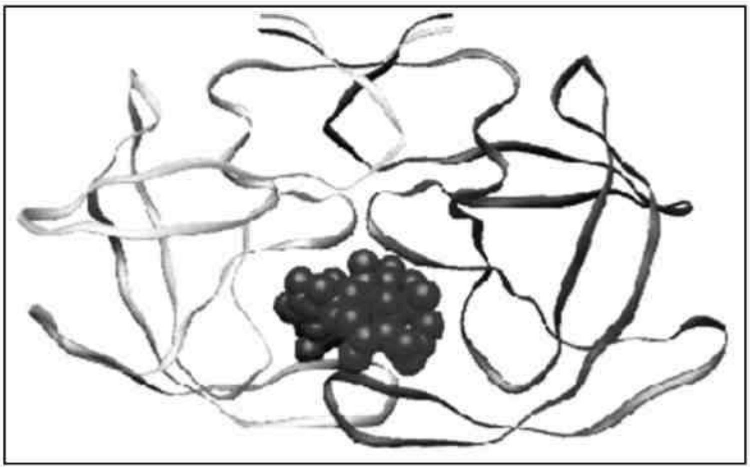


iii) Curcumin is yellow in coulour because it has:

(c) an extended conjugation.

PROBLEM 7

Peptides and Proteins



Protein folding

Proteins (polypeptides) are known to assume a variety of backbone conformations. In one conformation, the backbone is almost fully extended arrangement (as in a parallel or anti-parallel β-sheet), and in another conformation it is in a fully folded arrangement (as in an α-helix).

7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately:

(a) 10 Å ☐

(b) 15 Å ☐

(c) 20 Å ☐

(d) 25 Å ☐

(Mark X in the correct box.)

7.2 Assuming that the following hexapeptide is a α-helix conformation, draw a connecting arrow between an oxygen atom and an amide NH with which it is hydrogen bonded.

7.3 The following hexapeptides (**A** and **B**) display contrasting conformations in water at *pH* 7.0, especially when their serine hydroxyls are phosphorylated. **A** is moderately helical and it becomes a stronger helix on serine phosphorylation. **B** is weakly helical and it is completely disorded on serine phosphorylation. Draw connecting arrows to indicate the interactions between the residues that are responsible for this differing behaviour.

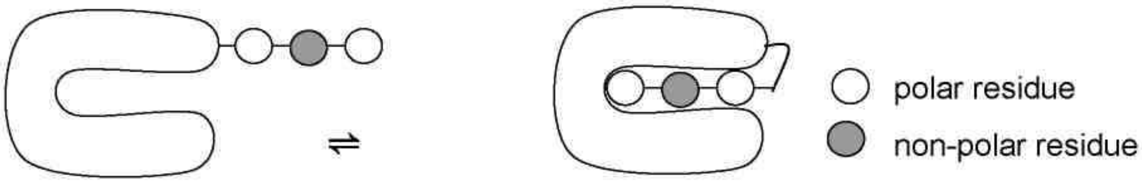
Consider the following process of folding/unfolding of a tripeptide segment in a large protein. The free energy change (AG) will depend on the interaction of the unfolded tripeptide with the solvent (water) and with the rest of the protein in the folded state (see below). Assume that the tripeptide is made up of one non-polar (hydrophobic; shaded) and two polar (hydrophilic; unshaded) residues. Assume the following approximate changes in the interaction free energies :

(a) a non-polar residue and the solvent (water): ΔG = +8 kJ mol^{-1}

(b) a non-polar residue and the rest of the protein: ΔG = – 4 kJ mol^{-1}

(c) a polar residue and the solvent (water): ΔG = – 16 kJ mol^{-1}

(d) a polar residue and the rest of the protein: ΔG = – 14 kJ mol^{-1}



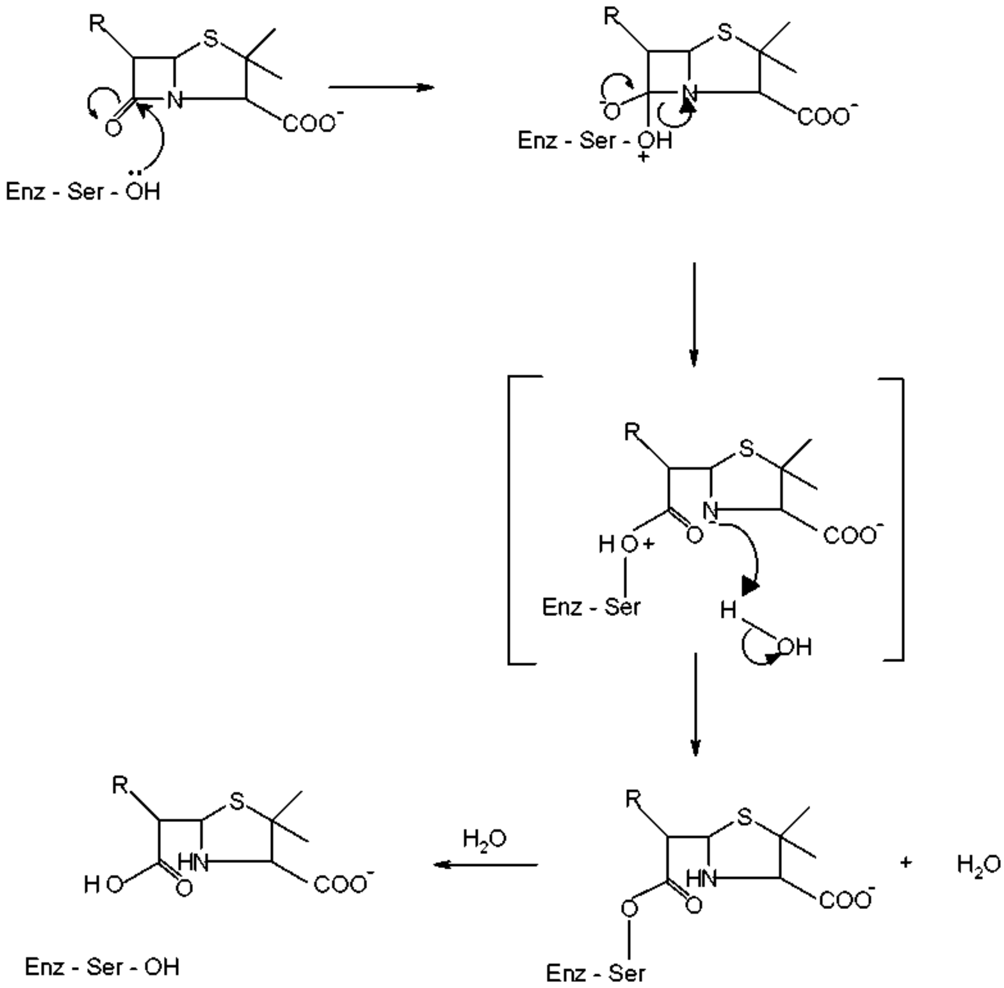
Tripeptide segment in unfolded form   Tripeptide segment in folded form

7.4 Calculate ΔG for the foldinq of the tripeptide segment.

7.5 Calculate ΔG for the folding of the tripeptide segment if all the three residues are polar.

β - lactamase and drug resistance

Penicillins are effective drugs in combating bacterial infections. An alarming development over the years has, however, been the emergence of drug resistant bacteria. Penicillin resistance arises due to the secretion of an enzýme called (3-lactamase (also known as penicillinase), which inactivates penicillin by opening its (3-lactam ring. The mechanism for this (3-lactam ring opening involves the nucleophilic attack by serine-OH at the active site of the enzýme as shown below.



An attempt was made to characterize the b–lactamase from *Staphylococcus aureus*. When the pure enzyme was treated with a radiolabelled [^{32}P] phosphorylating agent, only the active site serine got labelled. On analysis, this serine {molecular mass = 105 mass units (Da)} constituted 0.35% by weight of the b–lactamase.

7.6 Estimate the minimal molecular mass of this b–lactamase.

7.7 The approximate number of amino acid residues present in a protein of this size is :

(a) 100 ☐
(b) 150 ☐
(c) 275 ☐
(d) 375 ☐

[Mark X in the correct box.]

To map its active site, the b–lactamase was hydrolysed using trypsin, a specific enzyme. This resulted in a hexapeptide P1 containing the active site serine. Amino acid analysis revealed the following in equimolar proportion : Glu, Leu, Lys, Met, Phe and Ser. Treatment of P1 with Edman's reagent (phenyl isothiocyanate) yielded phenyl thiohydantoin (PTH) derivative of phenyalanine and a peptide P2.

Treatment of P1 with cyanogen bromide (CNBr) gave an acidic tetrapeptide P3 and a dipeptide P4.

Treatment of P2 with 1–fluoro–2,4–dinitrobenzene, followed by complete hydrolysis, yielded N–2,4–dinitrophenyl–Glu. P1, P2, and P3 contain the active site serine.

7.8 From the above information, deduce the amino acid sequence of P1, P2, P3 and P4.

7.9 Calculate the molecular mass of P3 in mass units (Da) from the information given in the attached Table.

The β–lactamase active site provides a unique microenvironment that makes the catalytic serine**–**OH an unusually reactive nucleophile. The first order rate constant for β–lactamase catalysed reaction is 350 s^{-1}. For penicillin hydrolysis by free serine**–**OH (at 1 M) in solution, the pseudo first order rate constant is 0.5 s^{-1}.

7.10 From the information above, calculate the effective concentration of this nucleophile at the enzyme active site?

A molecule competing with penicillin for binding to the b–lactamase active site can inhibit the enzyme. Dissociation constants (K_D) for the inhibitor–lactamase complex for three different inhibitors are given below :

Inhibitor	Dissociation constant (K_D)
A	2.0×10^{-3}
B	1.0×10^{-6}
C	5.0×10^{-9}

7.11 Indicate which of these inhibitors is most effective in protecting penicillin against β–lactamase. [Mark X in the correct box]

A ☐

B ☐

C ☐

A β–lactamase inhibitor was designed rationally. On binding to the enzyme active site, a nucleophilic attack by the OH group of serine resulted in the opening of the β–lactam moiety of the inhibitor and elimination of Br^-. A reactive electrophile is generated as a result and it captures an active site residue X, inactivating the enzyme.

7.12 Based on the above information, identify the electrophile (A) generated and the final product (B) formed in the enzyme inactivation by the inhibitor shown.

Table

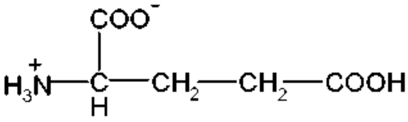
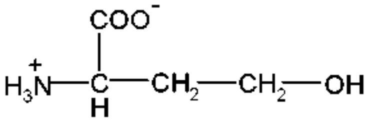
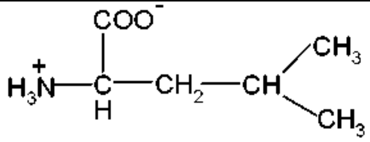
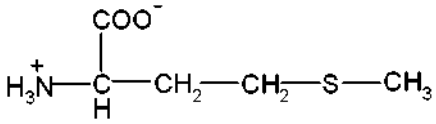
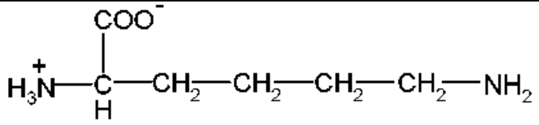
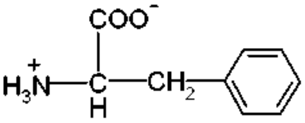
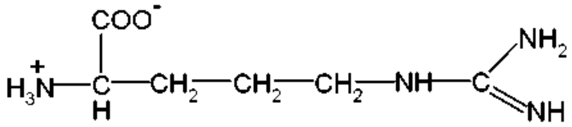
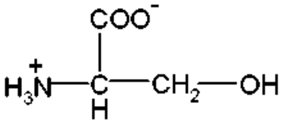
Amino Acid	Structure	Molecular mass (Da)
Glu – Glutamic acid	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-COOH$	147
Hms – Homoserine	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-OH$	119
Leu – Leucine		131
Met – Methionine	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-S-CH_3$	149
Lys – Lysine	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-CH_2-CH_2-NH_2$	146
Phe – Phenylalanine		165

Table (continued)

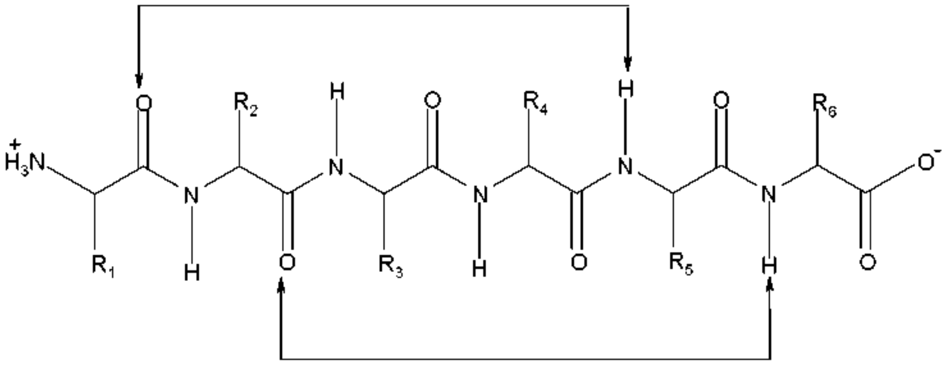
Arg – Arginine		174
Ser – Serine		105

SOLUTION

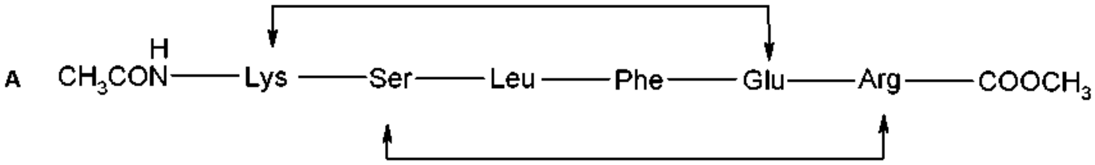
7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately :

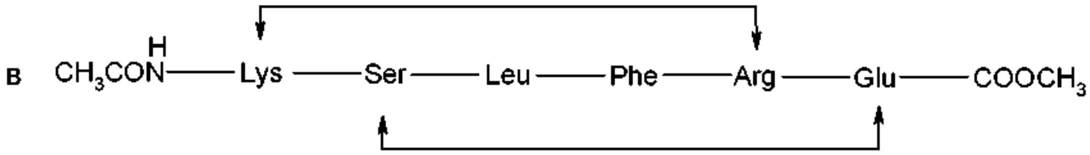
(c) 20 Å

7.2



7.3





7.4 $\Delta G = -8 - (-16 \times 2) + (-4 \times 1) + (-14 \times 2) = -8$ kJ mol^{-1}

7.5 $\Delta G = -(14 \times 3) - (-16 \times 3) = +6$ kJ mol^{-1}

7.6 $\frac{105 \times 100}{0.35} = 30000\ \text{Da}$

7.7 The approximate number of amino acid residues present in a protein of this size is:

(c) 275

7.8
P1: Phe – Glu – Ser – Met – Leu – Lys
P2: Glu – Ser – Met – Leu – Lys
P3: Phe – Glu – Ser – Hms/Met
P4: Leu – Lys

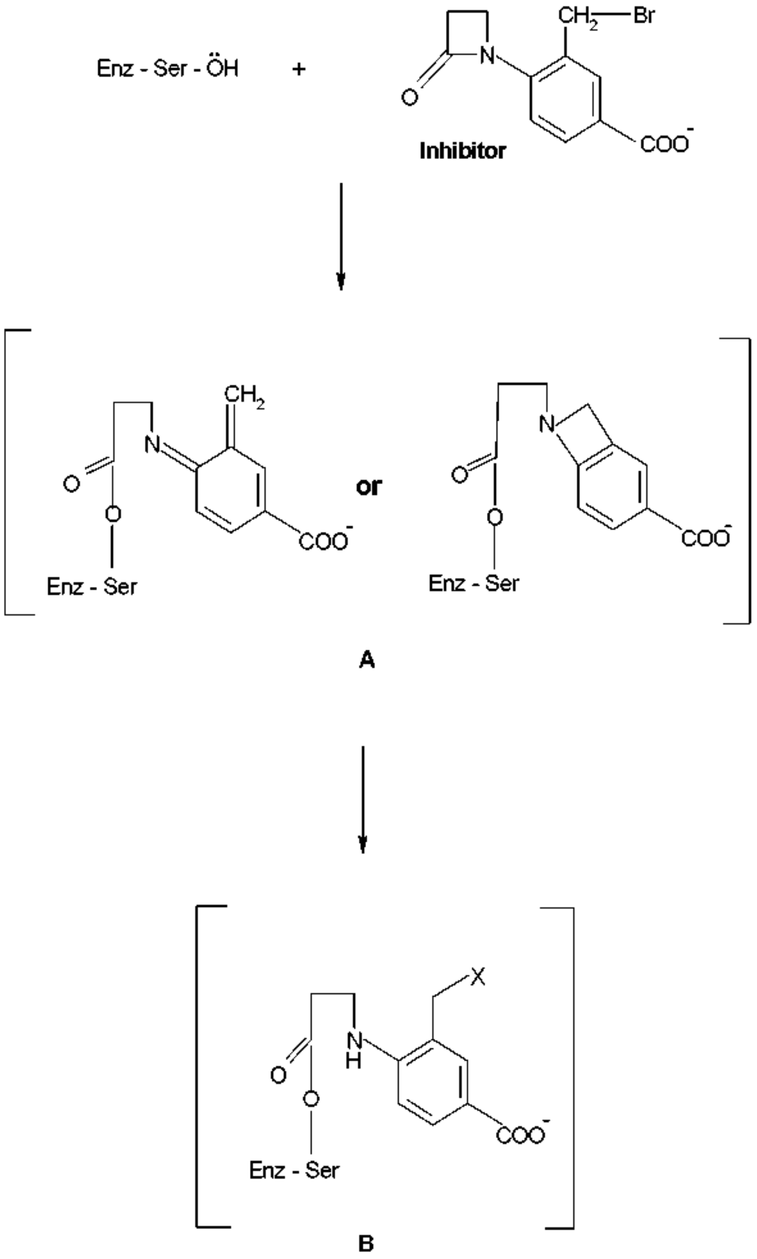
7.9 Phe - Glu - Ser - Hms

(165 + 147 + 105 + 119) – 3 H_2O = 536 – 54 = 482 Da

7.10 700 M

7.11 The most effective inhibitor is C.

7.12


Enz - Ser - ÖH
+
CH2—Br
N
O
Inhibitor
COO-
CH2
N
O
O
COO-
Enz - Ser
or
N
O
O
COO-
Enz - Ser
A
X
N
H
O
O
COO-
Enz - Ser
B

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Preparation of 2-Iodobenzoic Acid

This laboratory task involves preparation of 2-iodobenzoic acid from 2-aminobenzoic acid. The procedure consists of diazotization of 2-aminobenzoic acid followed by reaction with KI (in H_2SO_4).

Procedure

1) Quantitatively transfer the given sample of solid 2-aminobenzoic acid into a 100 cm^3 beaker placed in the ice-bath. Add 7.2 cm^3 of H_2SO_4 (2.6 M) (labelled H_2SO_4) and mix the contents thoroughly for 1 minute with the help of a glass rod. Cool the solution for 5 minutes.
2) Using a measuring cylinder, measure out 4.4 cm^3 of supplied cooled $NaNO_2$ solution from the vial placed in the ice-bath.
3) With the help of a dropper, slowly add the cooled $NaNO_2$ solution to the acid solution with constant gentle stirring using a glass rod to obtain an almost clear solution (3 – 5 minutes).
4) Remove the beaker from the ice bath and then slowly add 9.4 cm^3 of KI solution from the stoppered tube, with stirring.
5) Get hot water from the laboratory expert. Keep the beaker in hot water for 5 minutes.
6) Filter the crude product and wash it thoroughly with distilled water (10 cm^3). Collect the washings along with the main filtrate.
7) Neutralize the combined filtrate by gradually adding the given solid Na_2CO_3 until effervescence ceases. Dispose of the filtrate in the appropriate plastic bucket.

Purification of the crude product

Place the funnel containing the precipitate on a 100 cm^3 conical flask. Pour about 15 to 20 cm^3 of the supplied $NaHCO_3$ solution (using test tube) over the filter paper so as to dissolve the precipitate completely.

8) Add the supplied charcoal powder to the filtrate and mix it thoroughly. Filter the solution to remove charcoal.

9) Add dilute H_2SO_4 gradually to the filtrate till effervescence ceases. Filter the purified product. Use 10 -15 cm^3 distilled water to wash the precipitate. Keep the filter paper with the product on a watch glass.

10) Cover the product with the same funnel and hand over the product to the laboratory expert for drying (for a minimum of one hour).

Towards the end of the practical session have the product weighed by the laboratory expert and record the same.

SOLUTION

The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield (based on 2 aminobenzoic acid) in g.
- The yield obtained as a percentage of the theoretical yield.
- Colour of the product obtained.

Tasks:

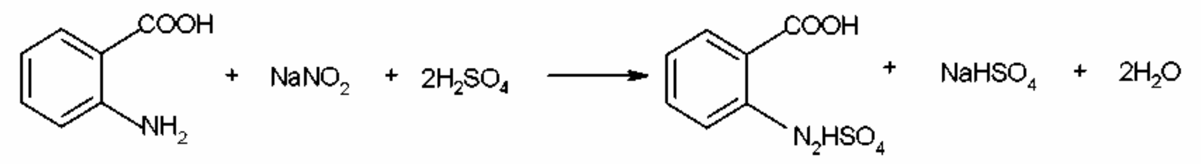
Write down the balanced chemical equations for:

(a) diazotization of 2-aminobenzoic acid using $NaNO_2$ and H_2SO_4.

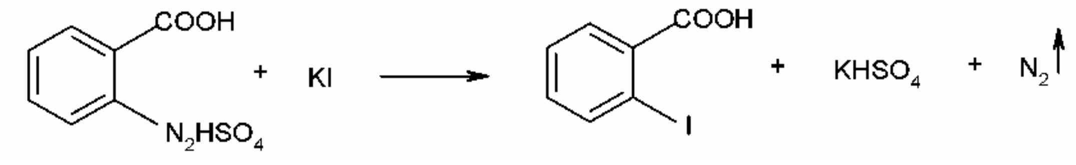
(b) the reaction of KI with the diazotized product.

Solutions of the tasks:

a)



b)



PROBLEM 2 (Practical)

Estimation of Mn(II) and Mg(II) Present in the Given Sample

In this experiment, estimation of the amounts of Mn (II) and Mg (II) present in the given sample is carried out by complexometric titration using standard Na_2EDTA solution. Total metal ion content is obtained from the first titration. At this stage, by using adequate solid NaF, selective and quantitative release of EDTA present in Mg-EDTA complex is achieved. The EDTA thus released is bound again by the addition of a known excess of standard Mn (II) solution. The unused Mn (II) is estimated by a back titration using the same standard Na_2EDTA solution. From these two different titre values, individual amounts of metal ions present can be obtained. Both the titrations are performed using a buffer (*pH* = 10) and Erichrome black T indicator.

The sample in duplicate is given in two 250 cm^3 conical flasks (labelled as Trial I and Trial II). Perform the titrations for both and record your readings on the answer sheet.

Procedure

Two burettes (25 cm^3) are supplied to you. Fill one with the given standard Na_2EDTA solution and the other with the given standard Mn (II) solution.

Titration 1

To the sample solution (supplied in the 250 cm^3 conical flask), add all of the solid hydroxylamine hydrochloride given in one vial followed by 50 cm^3 of distilled water. With the help of a measuring cylinder, add 10 cm^3 buffer solution (*pH* = 10) and one metal spatula full of the solid indicator. Shake the contents of the flask thoroughly and titrate the solution against the standard Na_2EDTA solution until the colour changes from wine red to blue. Record your burette reading (**A** cm^3). Ensure that you shake the contents of the flask thoroughly throughout the titration.

Titration 2

To the same flask, add all of the solid NaF given in one vial and shake the contents well for a minute. To this add 20 cm^3 of the given standard Mn (II) solution from the other burette. The addition of the Mn (II) solution should be done in small increments (2 – 3 cm^3) with thorough shaking. After addition of the total Mn (II) solution, shake the contents for two to three minutes. The colour of the solution will change from blue to wine red. Titrate the excess of Mn (II) in the solution against the standard Na_2EDTA solution till the colour changes from wine red to blue. Record your burette reading (**B** cm^3).

Repeat the same procedure for Trial II.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

2.2 Give the balanced chemical equation for the reactions of Mg(II) and Mn(II) with Na_2EDTA . (Use the symbol Na_2HY for Na_2EDTA.)

Answer: $Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2\,H^+$

$Mn^{2+} + H_2Y^{2-} \rightarrow MnY^{2-} + 2\,H^+$

2.3 Give the equation for the release of EDTA by the addition of NaF to the MgEDTA complex.

Answer: $MgY^{2-} + 2\,F^- \rightarrow MgF_2 + Y^{4-}$

2.4 Calculate the amount of Mg (II) and Mn (II) in gram for any one of the two trials. (Show the main steps in your calculation.)

2.5 The colour change at the end point (wine red to blue) in Titration 1 is due to

a) the formation of metal-indicator complex, ☐

b) the release of free indicator from metal-indicator complex, ☐

c) the formation of metal-EDTA complex. ☐

[Mark X in the correct box.]

Correct answer is (b).

PROBLEM 3 (Practical)

Determination of the Rate Constant for the Redox Reaction between Ethanol and Chromium (VI)

The oxidation of alcohols by chromium (VI) forms the basis for analysis of breath samples for measuring alcohol content. A dilute solution of $K_2Cr_2O_7$ in the presence of a strong acid (3.6 M HCl here) is a source of $HCrO_4^-$ which is the oxidant involved in the reaction.

In this experiment, the rate of the reaction between $HCrO_4^-$ and CH_3CH_2OH is determined titrimetrically. Under the given experimental conditions, the rate law reduces to

$$\text{rate} = k[HCrO_4^-]^x$$

where **x** is the order of the reaction.

At any given time, $[HCrO_4^-]$ is obtained by iodometric titration.

Procedure

You are given 100 cm^3 of standard $K_2Cr_2O_7$ solution in HCl in a bottle. Transfer all the absolute ethanol given in a vial into this bottle and stopper it. Mix the contents thoroughly, start the stopwatch immediately and regard this as time $t = 0$. Fill the burette with this solution.

After every 10 minutes, start to draw 10 cm^3 of this solution to a clean conical flask containing 4 cm^3 of the given KI solution. The solution will turn brown. Titrate this solution with the given standard $Na_2S_2O_3$ solution until the colour changes to pale greenish yellow. Add 2 cm^3 of starch indicator and continue the titration until the colour changes from blue to pale green. Record the burette reading in the answer sheet. Repeat this procedure at 10 minutes intervals to obtain four readings.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

3.1 Write down the possible oxidation products in the reaction of $HCrO_4^-$ and CH_3CH_2OH.

Solution: Acetic acid, CH_3COOH

Acetaldehyde, CH_3CHO

3.2 Write the chemical equation for the reaction between $HCrO_4^-$ and KI:

Solution: $2\ HCrO_4^- + 6\ I^- + 14\ H^+ \rightarrow 3\ \mathbf{I}_2 + 2\ Cr^{3+} + 8\ H_2O$

3.3 Write down the balanced chemical equation involved in the titration.

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

3.4 Give the main steps for the calculation of $HCrO_4^-$ concentration (mol dm^{-3}) for any one titration reading.

3.5 Give **c**oncentrations of $HCrO_4^-$ at different times (in a table attached).

3.6 Plot the graph of log $[HCrO_4^-]$ *vs.* time.

3.7 From the nature of the graph determine the order (**x**) of the reaction with respect to $HCrO_4^-$

3.8 Determine the rate constant for the reaction.

34th

International Chemistry Olympiad

10 theoretical problems
3 practical problems

THE THIRTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
5–14 JULY 2002, GRONINGEN, THE NETHERLANDS

THEORETICAL PROBLEMS

Theme 1 - Chemistry of Life

Life runs on chemistry. Understanding and monitoring life processes receive much attention in chemistry.

PROBLEM 1

OXYGEN IN YOUR LIFE

Oxygen is of vital importance for all of us. Oxygen enters the body via the lungs and is transported to the tissues in our body by blood. There it can deliver energy by the oxidation of sugars:

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

This reaction releases 400 kJ of energy per mol of oxygen. O_2 uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe^{2+} ion attached to four N atoms of a porphyrin^{2-} ligand. Oxygen can bind at the coordination site of Fe^{2+} giving a $Hm{\cdot}O_2$ complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O_2 does. The equilibrium constant K_1 for the reaction:

$$Hm + CO \rightleftharpoons Hm{\cdot}CO \qquad (1)$$

is 10 000 times larger than the equilibrium constant K_2 for the reaction:

$$Hm + O_2 \rightleftharpoons Hm{\cdot}O_2 \qquad (2)$$

Each Hb molecule can take up four molecules of O_2. Blood in contact with O_2 absorbs a fraction of this amount, depending on the oxygen pressure, as shown in Figure 1 (curve 1). Also shown are the curves (2) and (3) for blood with two kinds of deficient Hb. These occur in patients with certain hereditary diseases.

Relevant data: O_2 pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum flow of blood through heart and lungs is 4×10^{-4} m^3 s^{-1}. The red cells in blood occupy 40 % of the blood volume; inside the cells the concentration of Hb is 340 kg m^{-3}; Hb has a molar mass of 64 kg mol^{-1}. R = 8.314 J mol^{-1} K^{-1}. T = 298 K.

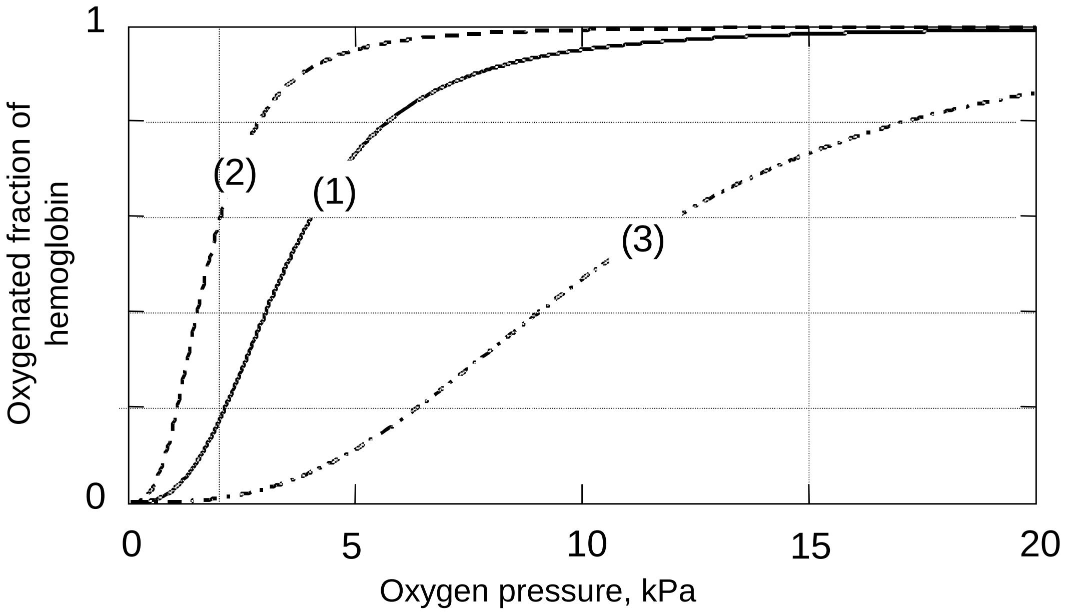


Figure 1

1.1 Using the relation between K and the standard Gibbs energy ΔG^0 for a reaction, calculate the difference between the ΔG^0 values for the heme reactions (1) and (2).

1.2 Estimate from Figure 1 (to 2 significant figures) how many moles of O_2 are deposited in muscle tissue when one mole of Hb travels from the lungs to the muscles and back again for the three different types of Hb.

1.3 The special S-shaped uptake curve 1 is the result of subtle structural features of Hb. The deficient Hb shown in curve 2 is not optimal because:

☐ The binding with O_2 is too weak.

☐ The binding with O_2 is too strong.

☐ The maximum oxygen capacity is too low.

☐ The deficiency is caused by carbon monoxide poisoning.

1.4 Calculate how much oxygen (in mol s^{-1}) can be deposited in tissue by blood with normal Hb (1).

1.5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

SOLUTION

1.1 $\Delta G_1^0 = -RT \ln K_1 \qquad \Delta G_2^0 = -RT \ln K_2$

$$\Delta G_2^0 - \Delta G_1^0 = RT \ln \frac{K_1}{K_2}$$

$$\Delta G_2^0 - \Delta G_1^0 = (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 10\,000) \text{ J} = 23 \text{ kJ mol}^{-1}$$

1.2 Hb-Typ 1: (0.98 – 0.17) mol × 4 = 3.2 mol

Hb-Typ 2: (1.00 – 0.60) mol × 4 = 1.6 mol

Hb-Typ 3: (0.73 – 0.01) mol × 4 = 2.9 mol

1.3 Correct answer: The binding with O_2 is too strong.

1.4 $(4\times10^{-4} \text{ m}^3 \text{ s}^{-1}) \times 0.4 \times (340 \text{ kg m}^{-3}) \times (3.2 \text{ mol } O_2 \text{ / mol Hb}) / (64 \text{ kg mol}^{-1}) =$

$= 2.72\times10^{-3} \text{ mol s}^{-1}$

1.5 $(2.72\times10^{-3} \text{ mol s}^{-1}) \times (400 \text{ kJ mol}^{-1}) = 1088 \text{ W}$

PROBLEM 2

Nitrogen Cycle in Nature

Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH_3 first to nitrite and then to nitrate, the storage form of nitrogen in the soil.

$$NH_3 + 2\,O_2 + NADH \xrightarrow[\textit{bacteria}]{\textit{Nitrosomonas}} NO_2^- + 2\,H_2O + NAD^+$$

NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD), NAD^+ is the oxidized form of the coenzyme NAD.

$$2\,NO_2^- + O_2 \xrightarrow[\textit{bacteria}]{\textit{Nitrobacter}} 2\,NO_3^-$$

2.1 Give the oxidation states of N in the following series: (Use the boxes below the compounds)

$$NH_3 \longrightarrow NO_2^- \longrightarrow NO_3^-$$

☐ ☐ ☐

The spectrophotometric analysis of nitrite is based on a reaction with an indicator. The coloured product then obtained has an absorbance maximum at λ = 543 nm. For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength λ = 543 nm is plotted against nitrite concentration in a series of standards.

2.2 The measurements are performed at the wavelength with the maximum absorbance because:

☐ There is no interference of impurities.

☐ There is no contribution of stray light.

☐ There is optimal accuracy of the measurement.

☐ None of these statements.

Mark the correct answer.

The absorption is measured with a single beam spectrophotometer. However 5 % of the light, the so-called stray light I_s, strikes the detector directly (see Figure 2).

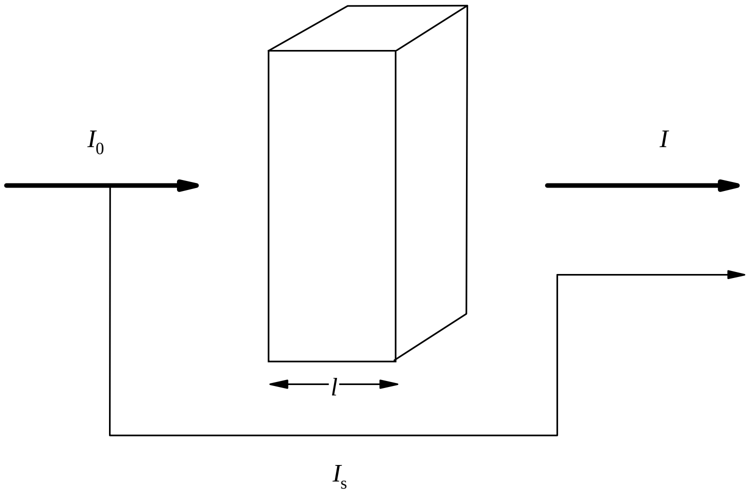


Figure 2

2.3 Calculate the value of the absorbance *A* shown by the spectrophotometer if ε = 6 000 M^{-1} cm^{-1}, l = 1 cm and c = 1×10^{-4} M

For a nitrite determination in water the following data have been measured.

Table 1

concentration of nitrite nitrogen (ppm)	absorbance at 543 nm (1.000 cm cell)
blank	0.003 (due to impurities in the solvent)
0.915	0.167
1.830	0.328

2.4 Determine (show calculation) from the data given above, using the values corrected for the solvent impurities, the slope m and the intercept b of the calibration curve *A* = *m c* + b.

The duplicate analyses of a water sample are given below. The measurements have been performed at a wavelength of 543 nm and in a 2.000 cm cell.

Table 2

water sample	absorbance
analysis 1	0.562
analysis 2	0.554

For the calculation of the concentration of the nitrite nitrogen (c in ppm) the equation obtained by the method of least squares

$$\text{corrected absorbance} = 0.1769\, c + 0.0015 \qquad \text{(a)}$$

may be applied, using the measurements in a 1.000 cm cell.

2.5 Calculate the average nitrite nitrogen concentration in ppm and μg cm^{-3}.

Hint: Take the blank from problem 2.4.

SOLUTION

2.1 NH_3: –III (–3) NO_2^-: III (3) NO_3^-: V (5)

2.2 Correct answer: There is optimal accuracy of the measurement.

2.3 $I_S = 0.05 \times I_0 \qquad A = \log \dfrac{I_0}{I + I_S}$ (see Figure 2)

The absorption of the solution A_{sol} is given by the relation:

$$A_{sol} = \log\ 0.95 \times \frac{I_0}{I} = \varepsilon\, c\, d$$

$$I = 0.95 \times I_0 \times 10^{-6000 \cdot 0.0001 \cdot 1} = 0.95\, I_0 \times 10^{-0.6}$$

$$A = \log \frac{I_0}{0.95 \times I_0 \times 10^{-0.6} + 0.05 \times I_0} = 0.54$$

2.4 The absorbance of the blank solution (see Table): $A = 0.003$.

Slope m of the calibration curve:

$$m = \frac{\Delta A}{\Delta c} = \frac{A_2 - A_1}{c_2 - c_1} = \frac{0.325 - 0.164}{1.830 - 0.915} = \frac{0.161}{0.915\ \text{M}} = 0.176\ \text{M}^{-1}$$

Note: Corrected absorbance values were used in the calculation.

$A = 0.176\, c + \text{b}$

For $c = 0$, $A = 0.003$.

Thus: b = 0.003

2.5 The average absorption in a 2 cm cell is 0.558; thus, in a 1 cm cell is 0.279.

Regarding the blank value (0.003) the corrected absorption has the value 0.276.

Substituting this value into the equation (a) gives:

$$c = \frac{0.276 - 0.0015}{0.1769}\ \text{ppm}$$

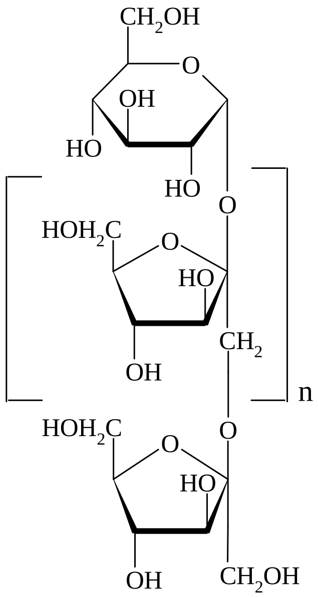
$$c = 1.55\ \text{ppm} = 1.55\ \mu\text{g cm}^{-3}$$

Theme II - Chemistry of Industrial Relevance

In our daily life we use many products that are produced on an industrial scale. Mastering the underlying chemistry is at the heart of this business.

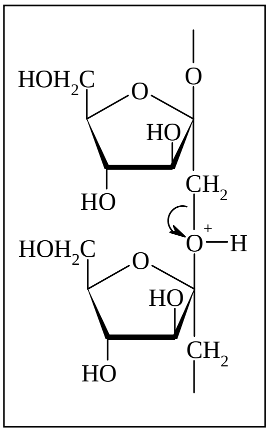
PROBLEM 3

Inulin, a New Renewable Raw Material



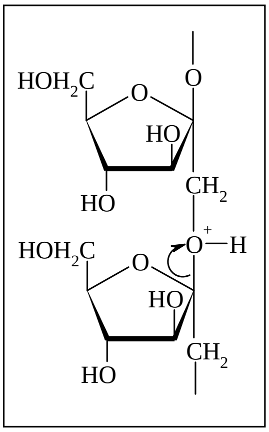
Inulin, which is produced from chicory roots in Belgium and The Netherlands, is used as a food additive as it has a beneficial effect on the intestinal flora. It is also used as source of fructose which is 1.9 times sweeter than sucrose, and for the production of mannitol which is used in chewing gum. Inulin is a linear polymer of fructose units with a glucose unit at one end; its Haworth projection formula is shown at the left. In this problem inulin has 10 fructose units (n = 9).

3.1 Inulin may be hydrolyzed under H$^+$-catalysis conditions. Of the four options below (**A**, **B**, **C** and **D**) indicate which C-O bond cleavage is most likely to occur.



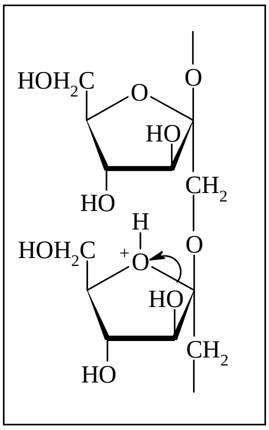
A

☐



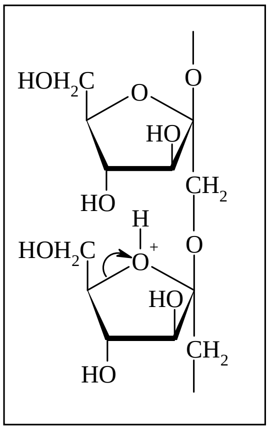
B

☐



C

☐



D

☐

Mark the correct cleavage mechanism for the most efficient hydrolysis.

Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can "see" deuterium (^2H) and the oxygen isotope ^{17}O.

3.2 Indicate which labelled water can <u>best</u> be used for this purpose. Mark the correct answer.

☐ ^2H_2O

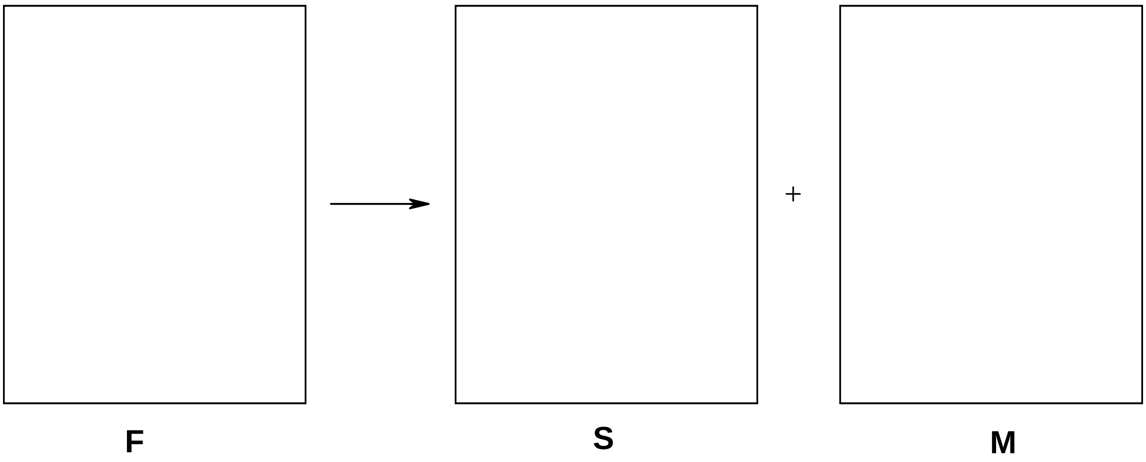
☐ $H_2{}^{17}O$

☐ $^2H_2{}^{17}O$

☐ None of them.

Upon catalytic hydrogenation glucose gives sorbitol (**S**), whilst fructose (**F**) gives mannitol (**M**) and sorbitol (**S**).

3.3 Draw the Fischer projections of fructose (**F**), sorbitol (**S**) and mannitol (**M**).



1.00 mol of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95 °C in a one step process. The selectivity of the hydrogenation of fructose to mannitol / sorbitol is 7 / 3.

3.4 How many moles of mannitol and sorbitol are obtained?

M:

S:

After completion of the reactions the catalysts are removed and the reaction mixture is cooled to 25 °C. The solubility of **M** is 0.40 mol kg^{-1} in water at 25 °C and the solubility of **S** is so high that it will not precipitate.

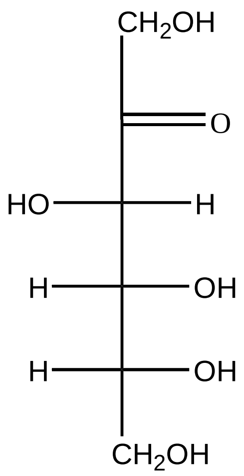
3.5 Calculate how many moles of **M** will precipitate.

SOLUTION

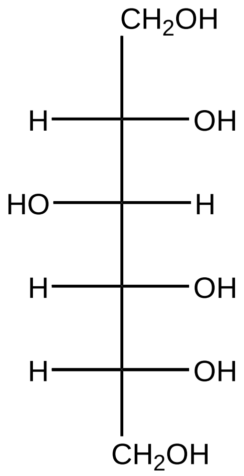
3.1 B is correct.

3.2 $H_2{}^{17}O$

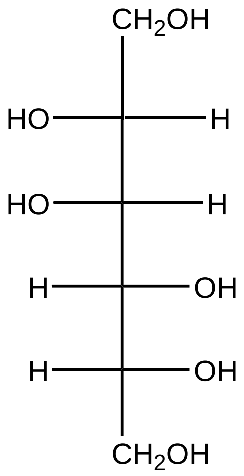
3.3



F



S



M

3.4 n(M): 7 mol n(S): 4 mol

3.5 Remaining amount of water:

$m(H_2O)$ = 2 kg – (10 × 0.018 kg) = 1.82 kg

$n(M)_{total}$ = 7 mol

$n(M)_{dissolved}$ = 1.82 × 0.4 mol = 0.73 mol

$n(M)_{precipitated}$ = 7.00 – 0.73 = 6.27 mol

PROBLEM 4

Production of Methanol

Methanol (CH_3OH) is a chemical that is used for the production of additives in gasoline and many common plastics. A factory, producing methanol, is based on the reaction:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Hydrogen and CO are obtained by the reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$$

The three units of the factory, namely, the "reformer" for the hydrogen / carbon monoxide production, the "methanol reactor" and a "separator" to separate methanol from CO and H_2, are schematically shown in Figure 1. Four positions are indicated by α, β, γ and δ.

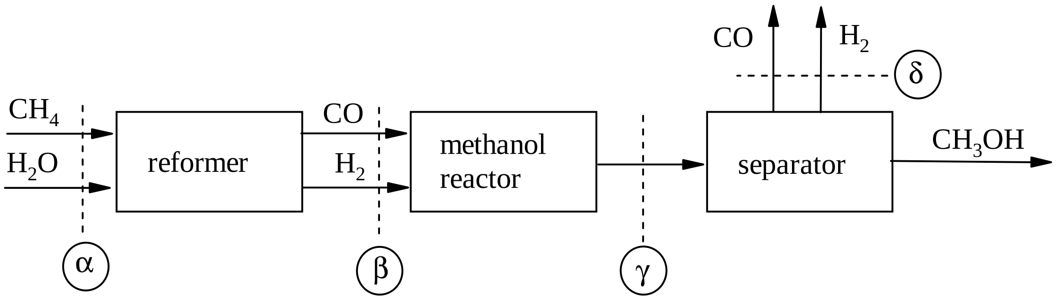


Figure 1

The flow of methanol at position **γ** is n[CH_3OH, **γ**] = 1000 mol s^{-1}. The factory is so designed that 2/3 of the CO is converted to methanol. Excess CO and H_2 at position **δ** are used to heat the first reactor. Assume that the reformer reaction goes to completion.

4.1 Calculate the flow of CO and H_2 at position **β**.

4.2 Calculate the flow of CO and H_2 at position **γ**.

4.3 Calculate the flows of CH_4 and H_2O needed at position **α**.

4.4 At point **γ** all species are gases. Calculate the partial pressures in MPa for CO, H_2 and CH_3OH at position γ using the equation:

$$p_i = p\,\frac{n_i}{n_{tot}}$$

wherein n_i is the flow and p_i the partial pressure of the compound i, n_{tot} is the total flow at the position considered, and p the total pressure in the system. (p = 10 MPa)

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures at point γ obey the equation:

$$K_p = \frac{p_{CH_3OH}\; p_0^2}{p_{CO}\; p_{H_2}^2}$$

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in Figure 2 (the vertical scale is logarithmic).

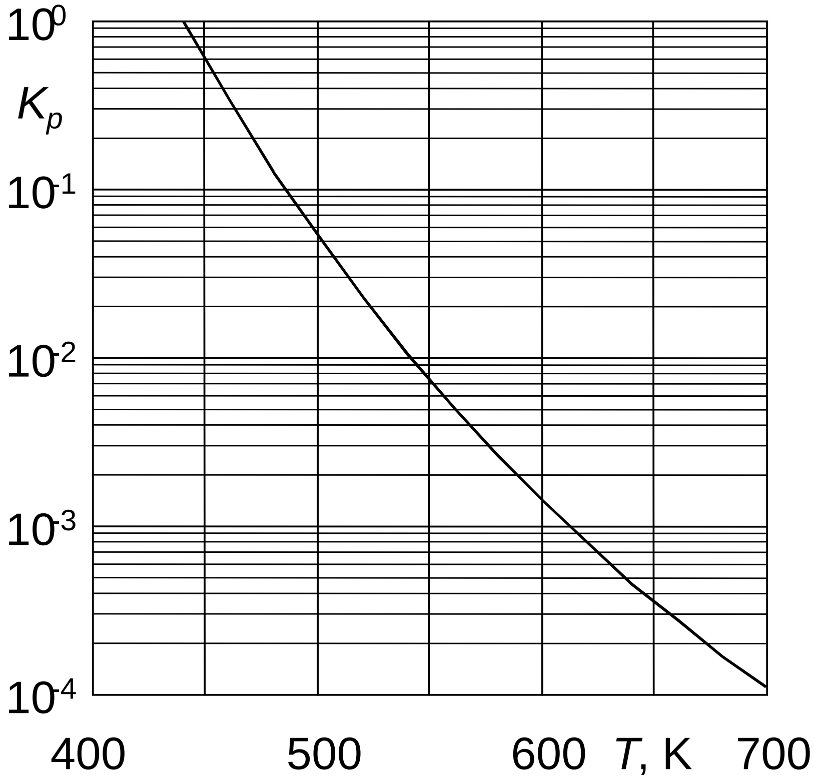


Figure 2

4.5 Calculate K_p and indicate at which temperature T the reaction must be operated to achieve this equilibrium.

SOLUTION

4.1 $n(CO, \beta) = 3/2 \times n(CH_3OH, \gamma) = 1500$ mol s^{-1}

$n(H_2, \beta) = 3 \times n(CO, \beta) = 4500$ mol s^{-1}

4.2 $n(CO, \gamma) = n(CO, \beta) - n(CH_3OH, \gamma) = (1500 - 1000)\ mol\ s^{-1} = 500\ mol\ s^{-1}$

$n(H_2, \gamma) = n(H_2, \beta) - 2 \times n(CH_3OH, \gamma) = (4500 - 2 \times 1000)\ mol\ s^{-1} = 2500\ mol\ s^{-1}$

4.3 $n(CH_4, \alpha) = n(CO, \beta) = 1500\ mol\ s^{-1}$

$n(H_2O, \alpha) = n(CO, \beta) = 1500\ mol\ s^{-1}$

4.4 $n_{tot} = (1000 + 500 + 2500)\ mol\ s^{-1} = 4000\ mol\ s^{-1}$

$p_i = p_{tot} \cdot (n_i/n_{tot})$

$p(CO, \gamma) = 10\ MPa \times (500/4000) = 1{,}25\ MPa$

$p(H_2, \gamma) = 10\ MPa \times (2500/4000) = 6{,}25\ MPa$

$p(CH_3OH, \gamma) = 10\ MPa \times (1000/4000) = 2{,}50\ MPa$

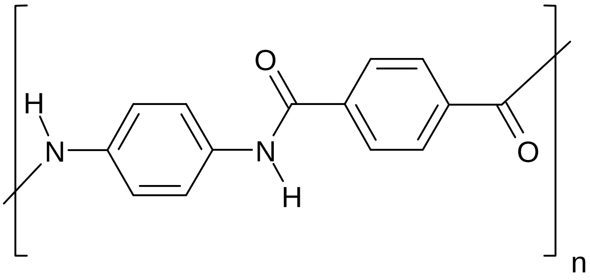
4.5 Calculation of K_p: $K_p = (2.5 \times 0.1^2) / (1.25 \times 6.25^2) = 5.12\times10^{-4}$.

The temperature corresponding to this value (see Fig. 2) is $\approx$ 630 K.

PROBLEM 5

Aramids, High-performance Polymeric Materials

Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north of The Netherlands. The PPTA chains are neatly packed into fibers with a sheet type structure.



PPTA

5.1 Draw the structure of these sheets (three chains suffice).

For a polymerisation of equimolar amounts of two monomers the average chain length is $\overline{P}_n$, the degree of conversion is p, which equals the fraction of functional groups that have reacted, the total number of chains is N_t and the total initial number of monomers is U_0.

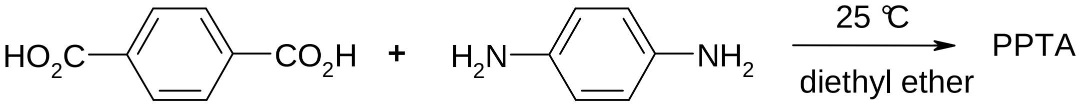
Assuming that the polymerization equilibrium can fully be described by:

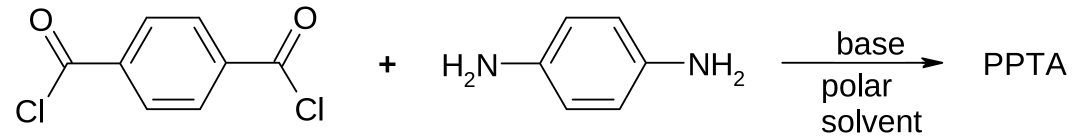
$$C + A \rightleftharpoons Am + H_2O$$

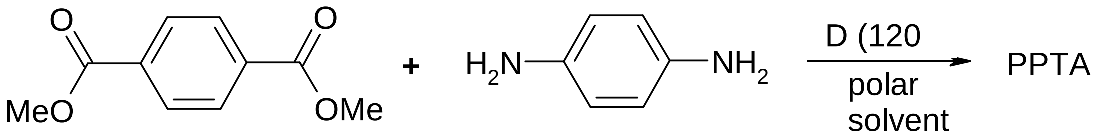
where C stands for any $–CO_2$ group, A stands for any $–NH_2$ group and Am stands for any amide group.

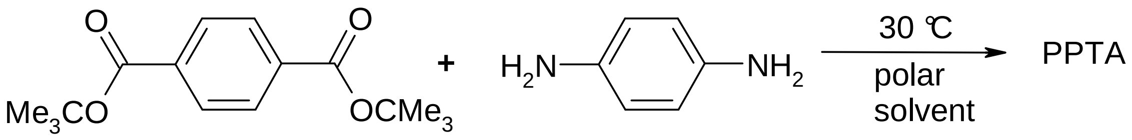
5.2 Calculate the degree of conversion needed to obtain an average chain length of 500.

5.3 For the synthesis of PPTA the following possibilities are considered. Which of the following reactions will work? Mark the correct answer(s).

☐ 

☐ 

☐ 

☐ 

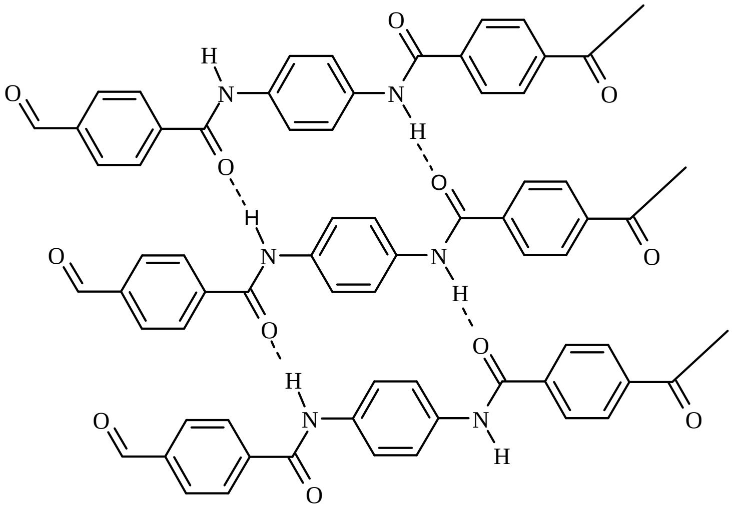
5.4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

(a) Give the structure of this aramid (n = 4)

(b) Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant *K* = 576.

SOLUTION

5.1



5.2 $\bar{P}_n = \frac{U_0}{N_t}$, $p = \frac{U_0 - N_t}{U_0}$ ➜

$p = 1 - \frac{N_t}{U_0}$, $\frac{N_t}{U_0} = 1 - p$ ➜ $\bar{P}_n = \frac{1}{1-p}$

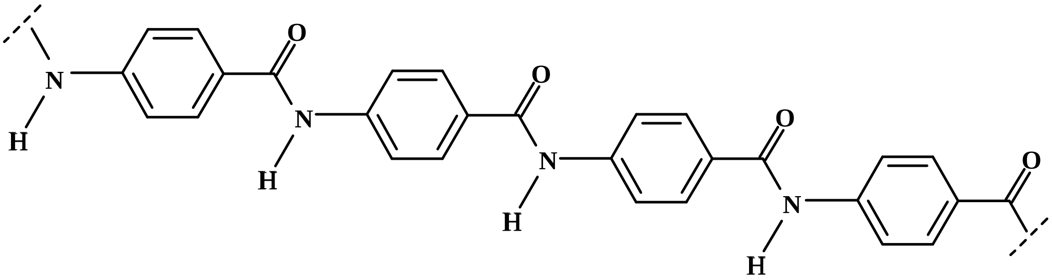
$500 = \frac{1}{1-p}$ $p = \frac{499}{500} = 0.998$

5.3

$\boxed{2}$ and $\boxed{3}$

5.4

a)



b) $K = \frac{[\text{Am}] \times [\text{H}_2\text{O}]}{[\text{C}] \times [\text{A}]} = \frac{p\,U_0 \times p\,U_0}{(1-p)^2 \times U_0^2} = \frac{p^2}{(1-p)^2} = 576 \quad \Rightarrow \; p = 0.96$

$\overline{P_n} = \frac{1}{1-p} = \frac{1}{1-0.96} = 25$

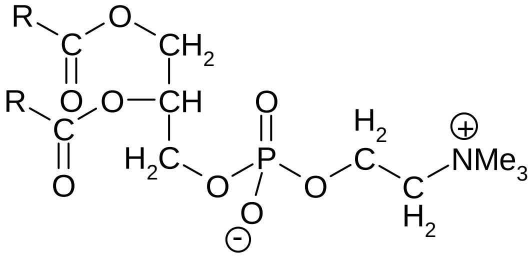
Theme III - Chemistry of Functional Molecules in Nature

A challenge in chemistry is to discover what nature does and how the structures of biologically active molecules are related to what they do.

PROBLEM 6

Phospholipids in Membranes

Biological cell membranes are complex, functional, non-covalent molecular assemblies, largely consisting of lipids and proteins. Their function is of vital importance for life processes. They separate the cell from its environment and also determine the specific flow of information between the cell contents and the environment. Phospholipids are among the most important components of cell membranes. An example is compound **A**.

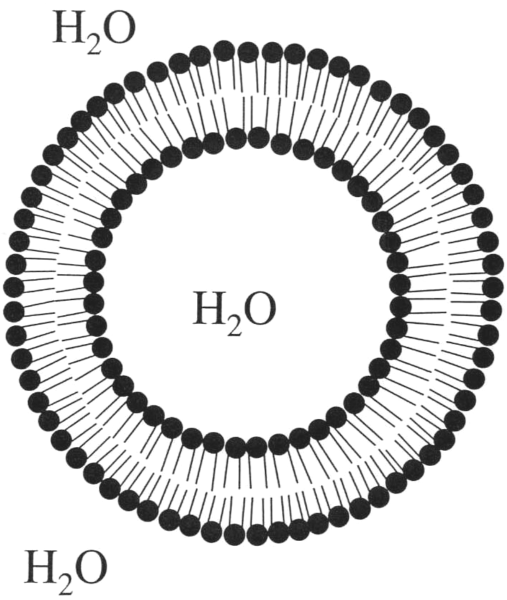


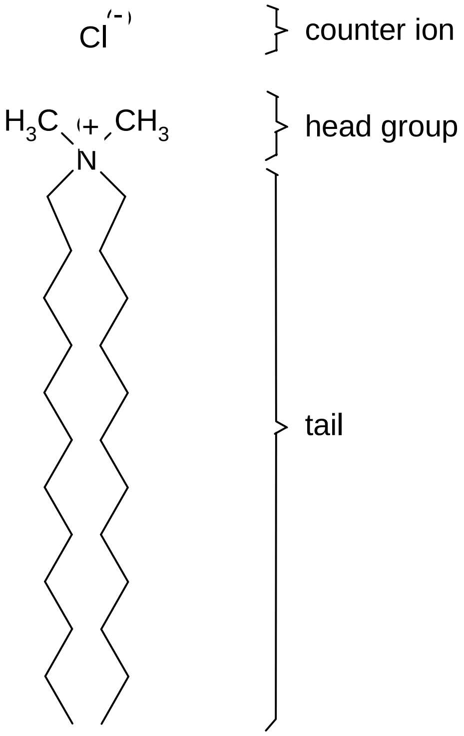
A

R = n-$C_{17}H_{35}$

Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or ionic head groups in contact with water and with the alkyl tails sequestered in a hydrophobic core. The bilayer structure encloses an aqueous inner compartment.

Double-tailed *synthetic* surfactants also form closed bilayer assemblies similar to liposomes but now called vesicles. An example is di-*n*-dodecyldimethylammonium chloride (**DDAC**).

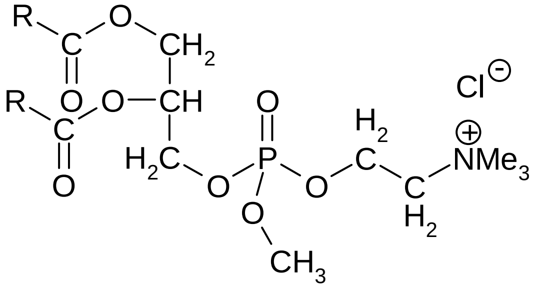




DDAC

6.1 **(a)** How many stereoisomers are possible for compound **A**?

(b) How many stereoisomers are possible for the trialkylphosphate **B**?

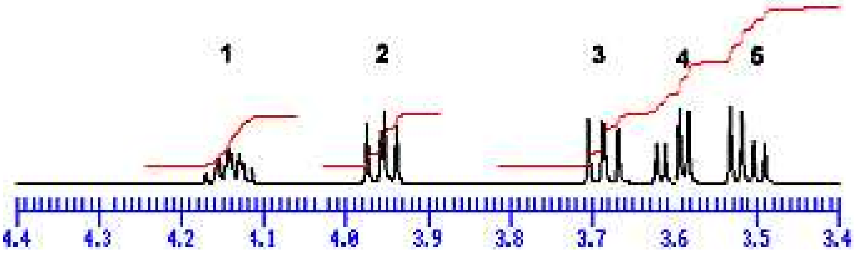


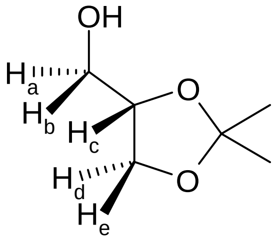
R = *n*-$C_{17}H_{35}$

B

A precursor for the synthesis of compound **A** is the acetonide **C** derived from glycerol. Part of the ^{1}H-NMR spectrum of compound **C** is shown below.

6.2 Which signal number in the ^{1}H-NMR spectrum corresponds to proton **H$_c$**?





C

The bilayer of a liposome can be characterized by V (the volume of the hydrocarbon chains), a_0 (optimal cross-sectional surface area of the head groups of the phospholipid in the aggregate) and l_c (the maximum chain length that the alkyl group can assume). A good approximation for unbranched alkyl tails containing n carbon atoms yields:

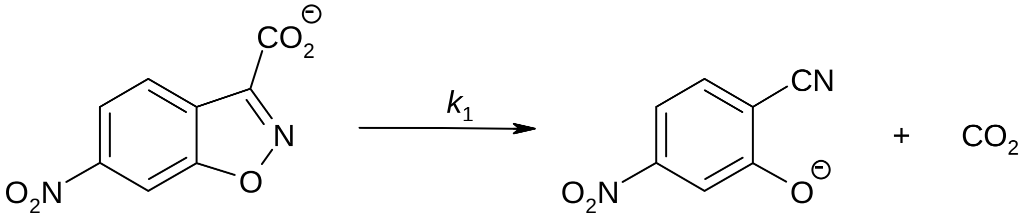
$V = (27.4 + 26.99\ n) \times 10^{-3}\ \text{nm}^3$

$l_c = (0.154 + 0.1265\ n)\ \text{nm}$

For very large n values, the intertail interactions dominate over the head group repulsions.

6.3 Calculate the minimum cross-sectional surface area of the head groups for such very large n values.

Vesicles formed from **DDAC** (above its critical vesicle concentration, cvc) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).



6-NBIC

In water at 25 °C $k_1 = 3.1 \times 10^{-6}\ s^{-1}$. At the concentration c_1 of **DDAC** at which **6-NBIC** becomes fully bound to the vesicles, $k_1 = 2.1 \times 10^{-3}\ s^{-1}$.

6.4 Sketch a plot of k_1 vs. [**DDAC**] for [**DDAC**] = 0 → 3 c_1.

6.5 The main reason for the efficient catalysis of the decarboxylation of **6-NBIC** by **DDAC** vesicles is:

☐ The decarboxylation is catalysed by the Cl^- ions bound to the surface of the vesicles.

☐ Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.

☐ Strong binding of CO_2 in the interior of the vesicle.

☐ Strong binding of the organic reaction product to the vesicles relative to that of 6-NBIC.

Mark the correct answer.

SOLUTION

6.1 (a) 2; (b) 4

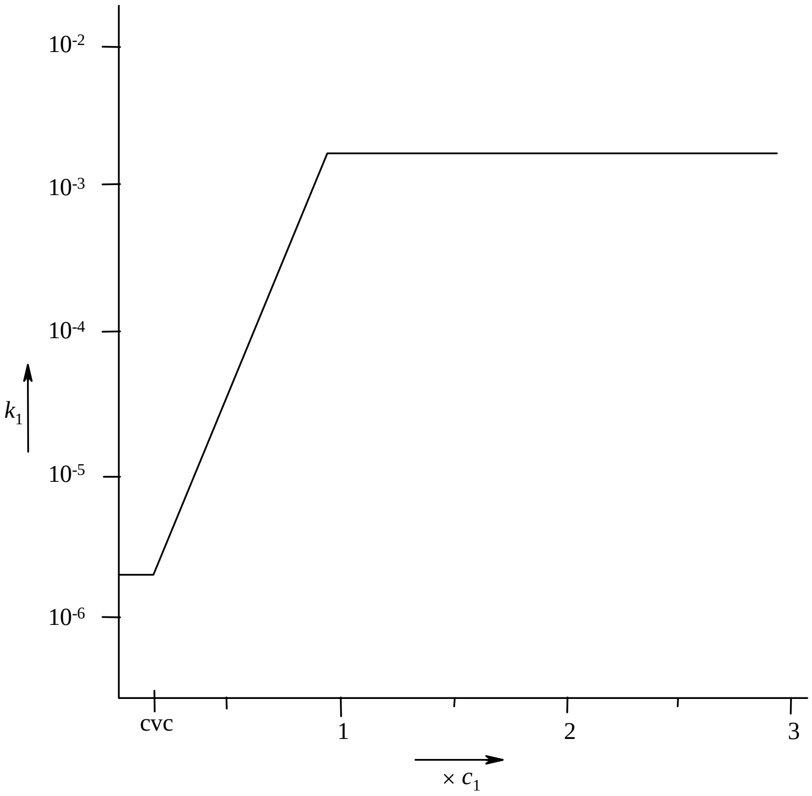
6.2 Signal No 1.

6.3 $a_0(\text{min}) = \dfrac{V}{l_c} = \dfrac{(27.4 + 26.99\,n) \times 10^{-3}}{(0.154 + 0.1265\,n)}\ \text{nm}^2$

For a large value of *n*: $a_0(\text{min}) = \dfrac{26.99 \times 10^{-3}}{0.1265}\ \text{nm}^2$

$a_0(\text{min}) = 0.213\ \text{nm}^2$

6.4



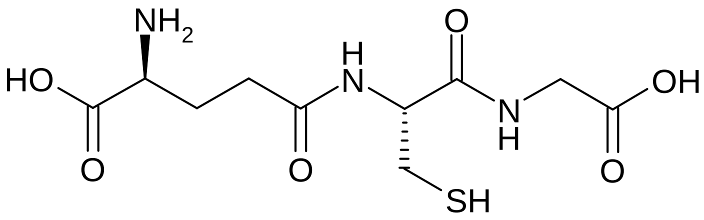
We expect curved bends in the graph, however, sharp corners (see the Figure) are also accepted.

6.5 The second answer is correct: Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.

PROBLEM 7

Glutathione, an Essential Mini-Peptide

Glutathione, abbreviated as GSH, is a small peptide that is present in almost all tissues of animals. GSH fulfils important biological functions, such as detoxification of electrophilic chemicals and reduction of (organic) peroxides in blood. An electrophilic compound reacts irreversibly with GSH, especially in the liver, to give a primary product that is converted by a series of biotransformations into a so-called *mercapturic acid*, which is excreted via the urine. Oxidants react with GSH to give the disulfide GSSG, which can be enzymatically reverted to GSH with reductases. The ratio GSH/GSSG in most cells is ≥ 500.

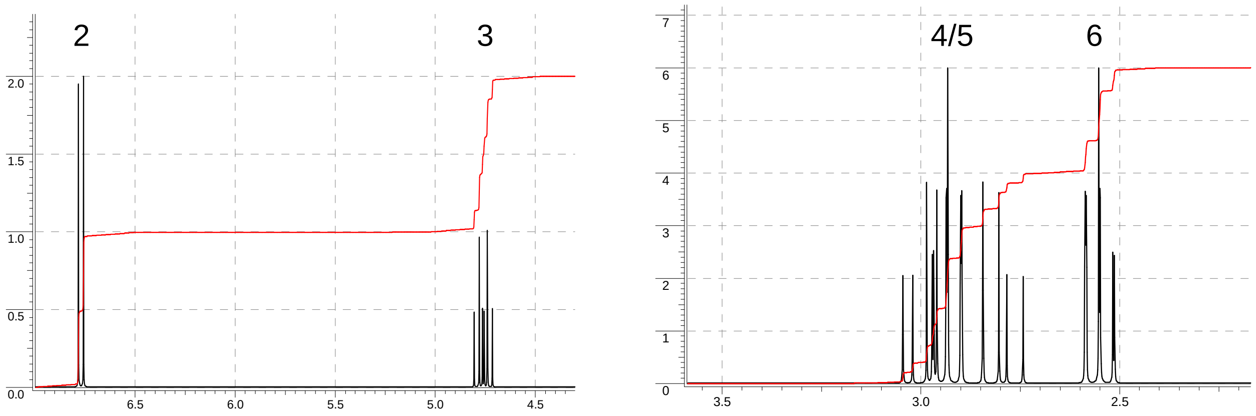


GSH

7.1 **(a)** How many amino acid residues are present in GSH?

(b) Draw the structures of the corresponding amino acids and mark the chiral centers with an asterisk.

A mercapturic acid **A** isolated from urine of a person who has been exposed to acrylonitrile ($H_2C=CH-CN$) has the molecular formula $C_8H_{12}N_2O_3S$. The ^1H-NMR spectrum of **A** in $(CD_3)_2SO$ is shown in Figure 1. When the product is pretreated with D_2O, the signals at δ 12.8 and δ 6.8 are no longer present and the signal 3 is simplified.



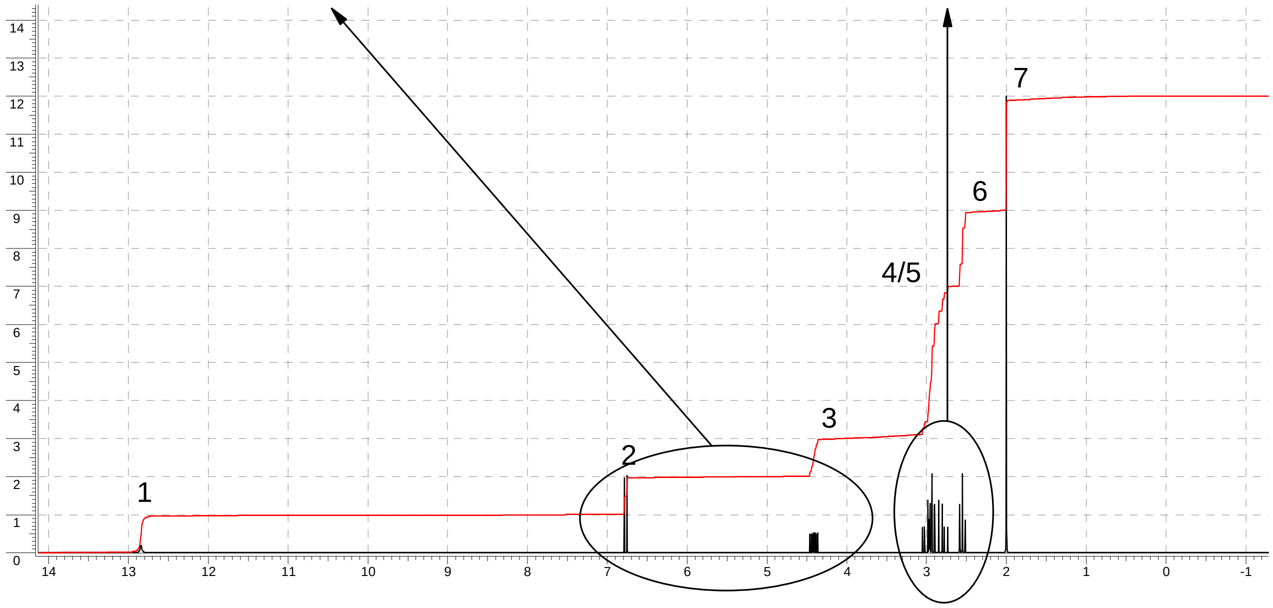


Figure 1

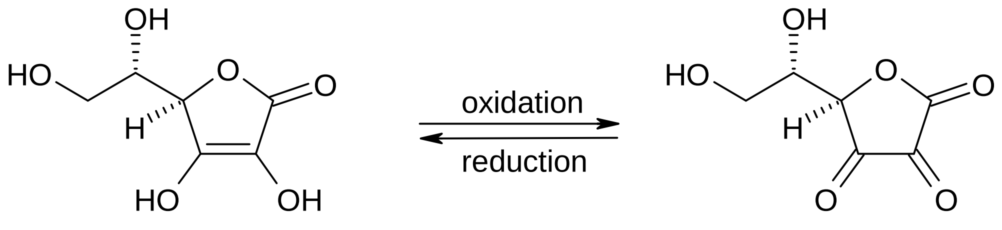
7.2 **(a)** The NMR-signals correspond with protons in the following groups: CH, CH_2, CH_3, OH and NH. Indicate the appropriate proton group in the boxes for the signals 1 – 7.

Signals	1	2	3	4/5	6	7
Protons						

(b) How many carbon atoms are present in compound **A** that do not carry any protons?

(c) Draw the structure of compound **A**.

Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**



vitamin C **D**

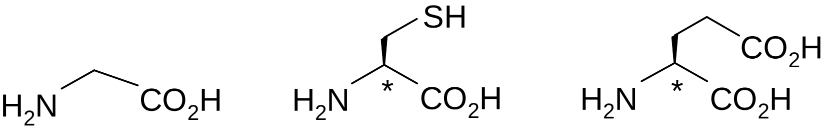
7.3 Eating fresh fruit and vegetables is healthy

- ☐ because vitamin C forms a complex with GSH.
- ☐ because vitamin C reacts with electrophilic compounds.
- ☐ because vitamin C removes oxidants and prevents undesired depletion of GSH.
- ☐ for many reasons, but none of them has anything to do with GSH.

SOLUTION

7.1 a) Three amino acid residues.

b)

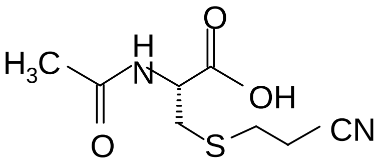


7.2 a)

Signal	1	2	3	4/5	6	7
Group of protons	OH	NH	CH	CH_2	CH_2	CH_3

b) 3

c)



7.3 The third answer is correct: Vitamin C removes oxidants and prevents undesired depletion of GSH.

Theme IV - Chemistry Related to Light and Energy

Chemistry plays a major role in meeting our needs of light and energy. Our life is unthinkable without artificial light and energy for mobility.

PROBLEM 8

LIGHTING LAMPS

Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal compounds like $CeBr_3$ are now included to reach a colour temperature of 6000 K in the lamp. These compounds are ionic solids at room temperature, and upon heating they sublime partially to give a vapour of neutral metal halide molecules. To achieve a high vapour pressure, the sublimation enthalpy should be as low as possible.

8.1 Give a thermochemical cycle (Law of Hess) for sublimation of $CeBr_3$, via a vapour of mononuclear ions. ($H_\mathrm{l} = H_\mathrm{lattice}$; $H_\mathrm{e} = H_\mathrm{electrostatic}$; $H_\mathrm{s} = H_\mathrm{sublimation}$; H is not absolute, H means ΔH)

$$\xrightarrow{-H_\mathrm{l}} \qquad +$$

$$+ \qquad \xrightarrow{+H_\mathrm{e}}$$

+

$$\xrightarrow{+H_\mathrm{s}} \qquad ;\ H_\mathrm{s} = -H_\mathrm{l} + H_e$$

The lattice energy of the solid can be calculated using the Born–Landé formula:

$$H_\mathrm{l} = f\,\frac{Z_+ Z_- A e^2}{r_+ + r_-}\left(1 - \frac{1}{n}\right)$$

The factor fe^2 (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is

2.985. The Born exponent *n* is 11. The charges of the ions Z_+ and Z_- are integer numbers (Z_- is negative). For the calculation of the energy of gaseous $CeBr_3$ (when formed from ions) the same Born-Landé formula can be used without A. The structure of $CeBr_3$ in the gas phase is planar triangular. The radius of Ce^{3+} is 0.115 nm and of Br^- is 0.182 nm.

8. 2 Calculate the enthalpy of sublimation of $CeBr_3$ (in integers; be aware of the signs!)

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of CsBr to the $CeBr_3$ in the lamp leading at room temperature to solid $CsCeBr_4$. When the sublimation temperature decreases the life time of the lamp will increase likewise. The $CsCeBr_4$ lattice has a NaCl structure with Cs^+ as cations and tetrahedral $CeBr_4^-$ as complex anions. Sublimation of $CsCeBr_4$ leads to a vapour of CsBr and $CeBr_3$ molecules.

8.3 Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve $CeBr_4^-$ ions, mononuclear ions and/or neutral molecules in the gas phase.

Step 1: $\xrightarrow{+\,H_1}$ +

Step 2: + $\xrightarrow{+\,H_2}$

Step 3: + $\xrightarrow{+\,H_3}$

Step 4: + $\xrightarrow{+\,H_4}$

Total: $(CsCeBr_4)_{lattice} \xrightarrow{+\,H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

8.4 Calculate the enthalpy of sublimation of $CsCeBr_4$ (in integers).

Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The

Cs–Ce distance in the lattice is 0.617 nm. The $CeBr_4^-$ anion is a tetrahedron in which the ratio between the edge and the distance between a corner of the tetrahedron and the centre of gravity (body-radius) amounts to $(2\sqrt{6})/3 = 1.633$. The Born exponent of CsBr is 11. The radius of Cs^+ is 0.181 nm.

8.5 Conclusion in relation to the previous answers: Was adding CsBr a good idea? Mark the correct answer.

☐ Adding CsBr is counterproductive.
☐ Adding CsBr has no influence.
☐ Adding CsBr is advantageous.
☐ From these data no clear answer can be given.

SOLUTION

8.1 $(CeBr_3)_{latitce} \xrightarrow{-H_l} Ce^{3+} + 3\ Br^-$

$Ce^{3+} + 3\ Br^- \xrightarrow{-H_e} (CeBr_3)_{molecule}$

$(CeBr_3)_{lattice} \xrightarrow{+H_s} (CeBr_3)_{molecule}$ $\qquad H_s = -H_l + H_e$

8.2 $$H_l = -\frac{139 \times 3 \times 1 \times 2.985}{0.297} \times \frac{10}{11}\ \text{kJ mol}^{-1} = -3810\ \text{kJ mol}^{-1}$$

$$H_e = \left(-3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11}\right) + \left(3 \times \frac{139 \times 1 \times 1}{0.297\sqrt{3}} \times \frac{10}{11}\right)\ \text{kJ mol}^{-1} = -3092\ \text{kJ mol}^{-1}$$

$H_s = 718\ \text{kJ mol}^{-1}$

8.3

Step 1: $(CsCeBr_4)_{lattice} \xrightarrow{+H_1} Cs^+ + CeBr_4^-$

Step 2: $CeBr_4^- \xrightarrow{+H_2} Ce^{3+} + 4\ Br^-$

Step 3: $Ce^{3+} + 3\ Br^- \xrightarrow{+H_3} (CeBr_3)_{molecule}$

Step 4: $Cs^+ + Br^- \xrightarrow{+H_4} (CsBr)_{molecule}$

Total $(CsCeBr_4)_{lattice} \xrightarrow{+H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

8.4 Step 1: The lattice energy of $CsCeBr_4$ with opposite sign is:

$$H_1 = \frac{139\times1\times1\times1.75}{0.617}\times\frac{10}{11}\ \text{kJ mol}^{-1} = 358\ \text{kJ mol}^{-1}$$

Step 2:

$$H_2 = 4\times\frac{139\cdot3\cdot1}{0,297}\cdot\frac{10}{11} - 6\times\frac{139\times1\times1}{0.297\times\frac{2}{3}\times\sqrt{6}}\times\frac{10}{11}\ \text{kJ mol}^{-1} = 3543\ \text{kJ mol}^{-1}$$

Step 3: The electronic energy in the gas phase of $CeBr_3$ is (see answer 8.2):

$$H_3 = -3\times\frac{139\times3\times1}{0.297}\times\frac{10}{11} + 3\times\frac{139\times1\times1}{0.297\times\sqrt{3}}\times\frac{10}{11}\ \text{kJ mol}^{-1} = -3092\ \text{kJ mol}^{-1}$$

Step 4: The electrostatic energy in the gas phase of CsBr is

$$H_4 = -\frac{139\times1\times1}{0.363}\times\frac{10}{11}\ \text{kJ mol}^{-1} = -348\ \text{kJ mol}^{-1}$$

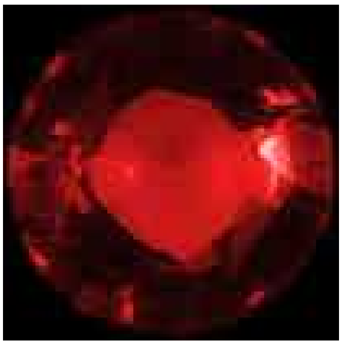
Total sum:

$$H_{\text{total}} = H_1 + H_2 + H_3 + H_4 = 461\ \text{kJ mol}^{-1}$$

8.5 The third answer is correct: Adding CsBr is advantageous.

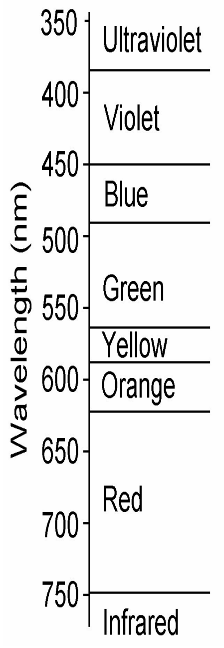
PROBLEM 9

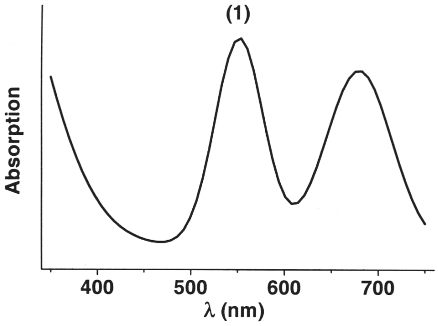
RED RUBY



Ruby crystals have a deep red colour and are well known for their use in jewellery. Not many people know that the heart of the first laser, built in 1960 by Maiman, was a big ruby crystal. The red colour of ruby originates from the absorption of light by Cr^{3+} ions that are incorporated in colourless aluminium oxide (Al_2O_3) crystals. The Cr^{3+} ion has 3 electrons in the 3*d* shell and the absorption of light is due to electronic transitions between 3*d* orbitals of lower and higher energy.

9.1 Indicate which of the four absorption spectra belongs to ruby.





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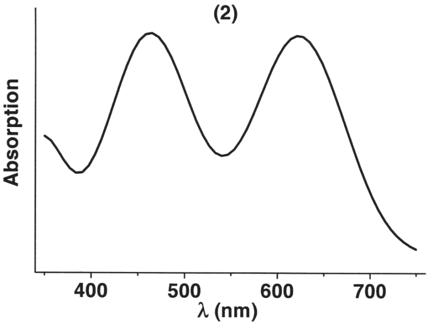

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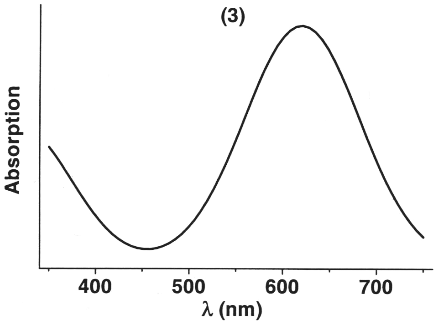

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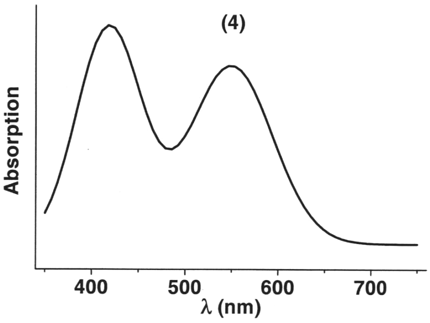


☐

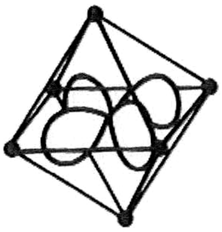
Figure 1

The rod used in ruby lasers is a cylinder with a length of 15.2 cm and a diameter of 1.15 cm. The amount of Cr^{3+} ions is 0.050 mass %. The density of Al_2O_3 is 4.05 g cm^{-3}. The atomic mass of Cr = 52u. (1u = 1.67×10^{-27} kg).

9.2 Calculate how many Cr^{3+} ions are in this laser rod.

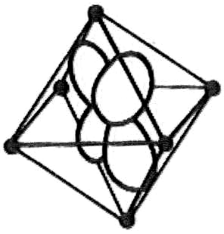
In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five 3*d* orbitals is shown below. The box below shows the splitting of the five 3*d* orbitals into a group of three orbitals at lower energy (t_{2g}) and a group of two at higher energy (e_g)..

9.3 Indicate in the boxes below which of the 3*d* orbitals (d_{z^2}, d_{xy}, d_{yz}, $d_{x^2-y^2}$, d_{xz}) belong to the t_{2g} group and which belong to the e_g group.



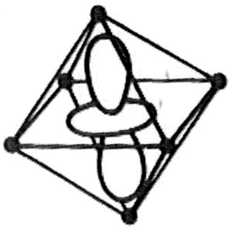
$d_{x^2-y^2}$

☐



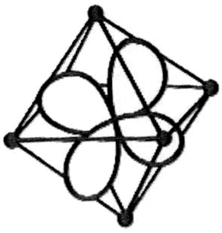
d_{yz}

☐



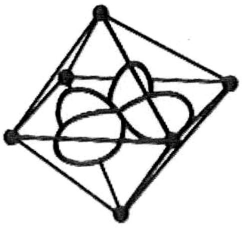
d_{z^2}

☐



d_{xz}

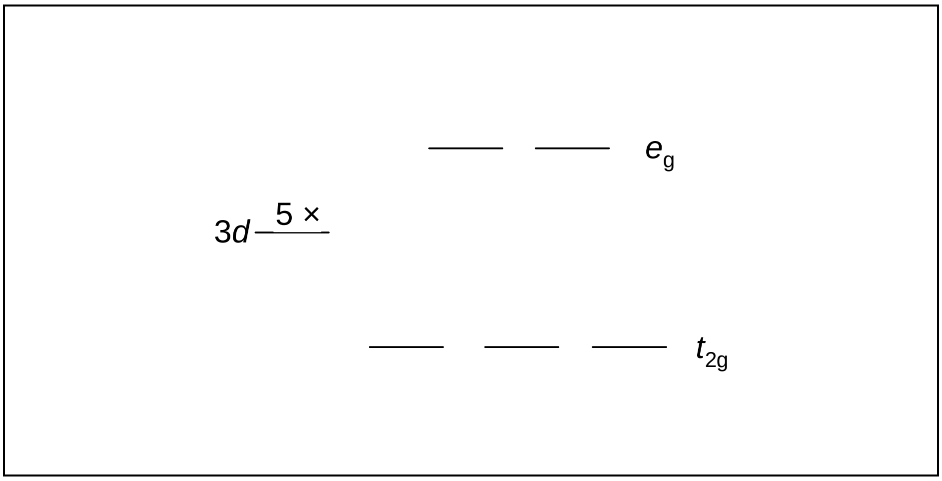
☐



d_{xy}

☐

9.4 Indicate with arrows the distribution and the direction of the magnetic spin moment of the three 3*d* electrons of Cr^{3+} over the five *d* orbitals in the lowest energy state of Cr^{3+}.



The ruby is placed on a (non-magnetic) scale. When the scale is in balance (Figure 2) a magnet is placed directly under the side with the ruby.

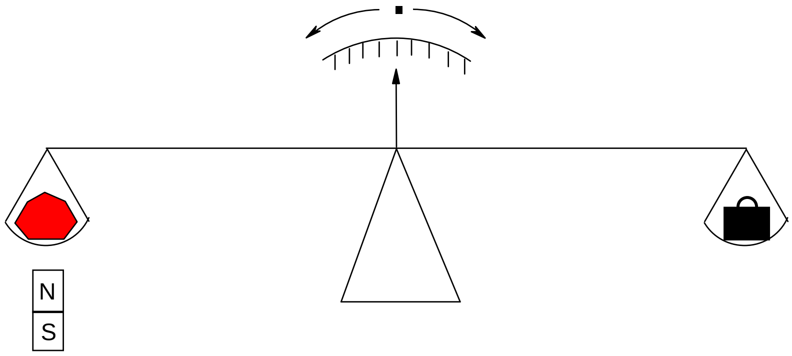


Figure 2

9.5 Indicate what will happen with the ruby (mark the correct answer)

- ☐ The magnet attracts the ruby (the ruby moves down)
- ☐ The magnet has no influence on the ruby (the ruby does not move)
- ☐ The magnet repels the ruby (the ruby moves up)
- ☐ The magnet has an oscillating effect on the ruby (the ruby moves up and down)

SOLUTION

9.1 The fourth spectrum is correct.

9.2 Volume of the rod = $\pi \times r^2 \times l$

$V = \pi \times 0.575^2 \times 15.2\ \text{cm}^3 = 15.79\ \text{cm}^3$

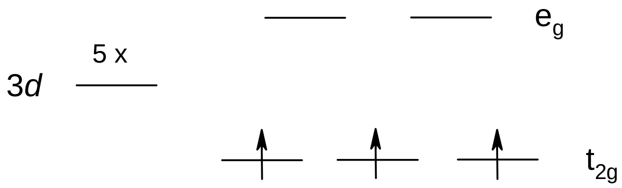
Mass of the rod: $m = 15.79 \times 4.05\ \text{g} = 63.94\ \text{g}$

Mass of chromium in the rod: $m_{\text{Cr}} = 63.94\ \text{g} \times 0.05 / 100 = 0.0319\ \text{g}$

Number od chromium ions: $N = 0{,}0319 \times 10^{-3}\ \text{kg} / (52 \times 1{,}67 \times 10^{-27}) = 3{,}68 \times 10^{20}$.

9.3 $d_{x^2-y^2}$: e_g d_{yz}: t_{2g} d_{z^2}: e_g d_{xz}: t_{2g} d_{xy}: t_{2g}

9.4



9.5 The correct answer: The magnet attracts the ruby (the ruby moves down).

PROBLEM 10

Vehicle Traction Batteries

Battery-powered electric vehicles (EV's) are likely to become increasingly common in the next 50 years because of growing concern over pollution caused by vehicles using combustion engines. The reason for the current meagre commercial success of EV's is that the battery specifications must have a performance and cost profile comparable to conventionally powered vehicles.

Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

In the current evolution of EV batteries, the most promising long-term solution is the rechargeable light weight lithium-ion battery. Such batteries are under intensive investigation worldwide and hold also promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery. Lithium is used as a negative electrode. It has a high specific capacity and electrode potential. A common positive electrode material is the environmentally benign spinel-type $LiMn_2O_4$. The spinel structure comprises a matrix of cubic close-packed oxide ions, stabilised by lithium ions in tetrahedral sites and manganese ions in octahedral sites. In $LiMn_2O_4$ half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:

$$Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \mid PbSO_4(s) \mid PbO_2(s) \mid (Pb(s))$$

A lithium battery is represented by:

$$Li(s) \mid Li^+\text{-conducting (solid) electrolyte(s)} \mid LiMn_2O_4(s)$$

Upon discharge the insertion product $Li_2Mn_2O_4$ is formed. Charging the battery leads to the products Li(s) and $LiMn_2O_4$.

10.1 Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.

10.2 Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.

10.3 Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of $LiMn_2O_4$.

A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1}.

10.4 Calculate the extra weight of the car if the petrol tank is replaced by an equivalent battery in an EV based on (**a**) lead-acid battery and (**b**) lithium battery. Assume that in all cases the engine efficiency is the same. Calculate:

(**a**) Extra weight of a lead-acid battery car.

(**b**) Extra weight of a lithium battery car.

SOLUTION

10.1 Reaction at the negative electrode:

$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$$

Reaction at the positive electrode:

$$PbO_2(s) + 3\,H^+(aq) + HSO_4^-(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$$

10.2 Reaction at the negative electrode:

$$Li(s) \longrightarrow Li^+ + e^-$$

Reaction at the positive electrode:

$$Li^+ + e^- + LiMn_2O_4(s) \longrightarrow Li_2Mn_2O_4(s)$$

10.3 Li – ions: coordination number = 4 Mn – ions: cordination number = 6

10.4 Distance of the petrol car = 500 km $\Rightarrow$ 50 kWh

Mass of petrol tank = 10 kg + 50 × (3.78 / 5) = 47.8 kg

(a) Mass of a lead-acid battery = 50000 Wh / 45 Wh kg^{-1} = 1111.1 kg

Extra weight of a lead-acid battery car = 1111.1 kg – 47.8 kg = 1063.3 kg

(b) Mass of the lithium battery = 1/3 of the mass of a lead-acid battery

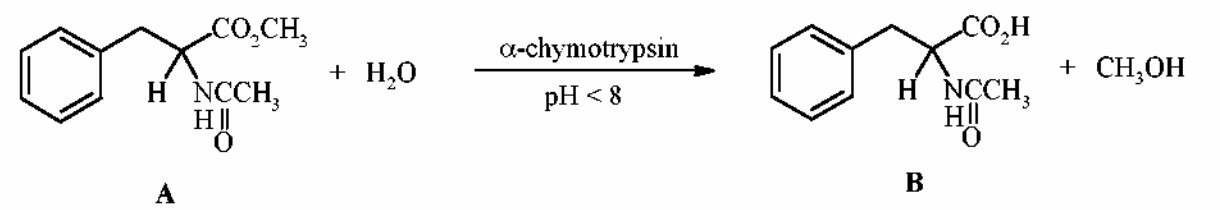
Extra weight of a lithium battery car = 1111.1 kg / 3 – 47.8 kg = 322.6 kg.

PRACTICAL PROBLEMS

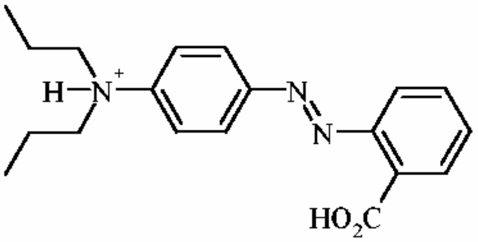
PROBLEM 1 (Practical)

Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

α-Chymotrypsin, a protease enzyme recognizing derivatives of natural α-amino acids, catalyses the hydrolysis of esters. In this experiment the enzymatic hydrolysis of racemic methyl N-acetyl-phenylalaninate **A** is investigated (Scheme).



The rate of formation of *N*-acetyl-phenylalanine **B** can be monitored by titration with 0.100 M NaOH in the presence of propyl red as a pH indicator.



Propyl red (protonated form)
At pH < 5: pink; at pH > 6: yellow

Procedure

Note: the required amount of α-chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.

Racemic methyl *N*-acetyl-phenylalaninate **A** [500 mg, the exact mass (± 1 mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 cm^3 Erlenmeyer flask and dissolved in methanol (~ 2.5 cm^3). Subsequently, propyl red (0.02 % solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α-chymotrypsin (10.0 cm^3 of a 0.05 % solution in distilled water) in one portion (*start the stopwatch*).

When the reaction mixture turns pink, it is immediately titrated with 0.100 M NaOH until the colour changes to yellow. When the pink colour reappears, add just enough titrant to restore the pale yellow colour, swirling the flask continually during the addition. You only need to record the reading on the burette every 5 minutes. (*Note: at the beginning colour changes occur very frequently.*)

Monitor the reaction for 75 minutes. A graph showing the amounts of NaOH consumed in cm^3 versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.

SOLUTION

The competitors were expected to show on the answer sheet the following data, tables, graphs or calculations:

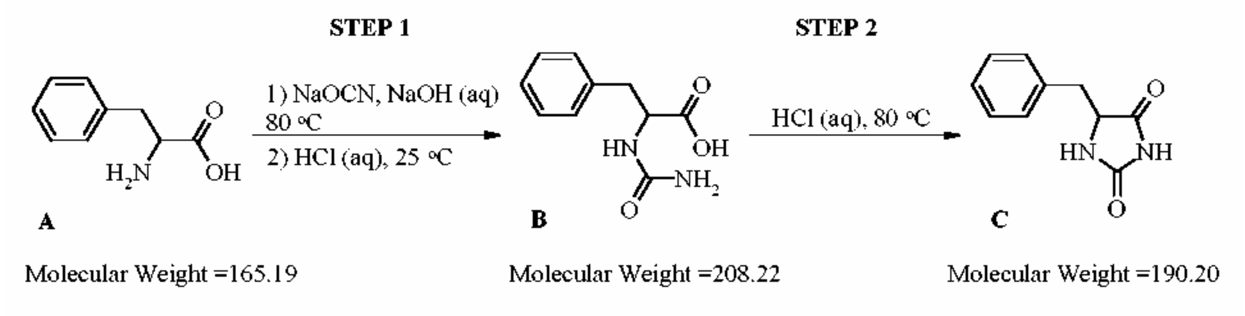
1. Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A** (in mg and mmol).
2. Table with time measured and the total consumption of NaOH in cm^3.
3. A graph of the total consumption of NaOH vs time.
4. Calculation of the amount of 0.100 M NaOH consumed in this experiment in mmol.
5. Calculation of the degree of hydrolysis of methyl *N*-acetyl-(*R,S*)-phenylalaninate **A** in mol %.

PROBLEM 2 (Practical)

Synthesis of Benzylhydantoin

Introduction

α-Amino acids are the building blocks for peptides and proteins. They are also frequently used as starting material for the synthesis of pharmaceuticals. In this experiment natural *S*-phenylalanine **A** is converted in two steps into benzylhydantoin **C**, which is a useful intermediate for the preparation of various physiologically active derivatives.



Procedure

STEP 1

Retain a tiny amount of starting material ***A*** *for the TLC analysis (see below).* A long-necked round-bottomed flask is charged with (*S*)-phenylalanine **A** (500 mg, 3 mmol, the exact amount is indicated on the label of the vial), sodium cyanate (300 mg, 4.6 mmol), water (3 cm^3) and a stirring bar. Two drops of aqueous sodium hydroxide (1 M) are added to the stirred suspension. The flask is equipped with a condenser (distillation column) and the reaction mixture is heated to 80 ^oC on a sand bath while stirring magnetically.

Important

In order to reach the appropriate temperature in time and not lose too much time, start the electric heating of the sand bath immediately at the beginning of this experiment. Check the temperature of the sand bath regularly and carefully with a thermometer.

After heating the reaction mixture at 80 ^oC for at least 30 minutes, the resulting clear solution is cooled to room temperature and poured into a small Erlenmeyer flask. Rinse the round-bottomed flask with a little water. The solution is acidified by dropwise addition of hydrochloric acid (4 M) to pH < 3 with magnetic stirring. Some water is added to the resulting white suspension in order to facilitate stirring.

The white precipitate is then filtered off by suction, washed with ample water (on the filter) and then washed twice with a small amount of di-isopropyl ether to remove most of the adhering water. The urea derivative **B** is left on the filter under suction for at least 3 minutes to remove as much solvent as possible.

A small amount of the obtained urea derivative **B** is retained for TLC-analysis later.

STEP 2

The urea derivative **B** is now transferred into a long-necked round-bottomed flask and hydrochloric acid (4 M, 3 cm^3) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 ^{o}C on a sand bath. A clear solution is obtained. After a reaction time of 30 minutes, the reaction mixture, which may already contain some precipitate, is cooled to room temperature. The obtained suspension is filtered by suction, washed thoroughly with water and finally washed twice with a small amount of di-isopropyl ether. The product is left on the filter under suction for at least 3 minutes. It is then collected on a filter paper and dried in the air for at least 30 minutes.

The final product **C**, its precursor **B** and starting material **A** (see above) are subjected to TLC-analysis. For this purpose small amounts of either compound are dissolved in a tiny amount of pure acetone. Small samples of these solutions are applied to a TLC plate, using the supplied capillary tubes. The analysis is carried out with two TLC plates in one run. The TLC-plates are developed with a solution of 2% formic acid in ethyl acetate as the eluent. After the elution the TLC-plates are analysed using a UV-lamp. The starting line, solvent front and the UV-active spots are clearly marked with a pencil. Copy the diagram in the box on the answer sheet. The R_f values are determined. Finally, the TLC-plate with the best analysis is wrapped in parafilm and placed in a plastic bag with a sealing strip.

The final product **C** is transferred into a sample vial of which the empty weight has been pre-determined (weight is indicated on the label). Weigh the vial with product and calculate the yield of the product **C**.

The examination committee will check the quality of the benzylhydantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations on the answer sheet:

1. Mass of your starting material **A** (see label on the vial) in mg.
2. Amount of benzylhydantoin **C** obtained.
3. Calculation of the yield of benzylhydantoin **C** in %.
4. R_f value of urea derivative **B.**
5. R_f value of benzylhydantoin **C.**
6. A copy of the TLC diagram with indication of the front base line of the solvent.
7. Conclusions from the TLC analysis:

   Compound **B**: is pure; contains some **A**; contains several contaminants.

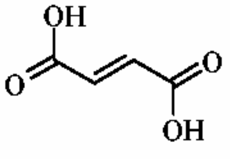
   Compound **C**: is pure; contains some **B**; contains some **A** and **B**; contains several contaminants.
8. Appearance of benzylhydantoin **C**: white colour, yellowish colour, sticky, crystalline, powder.
9. Melting point of benzylhydantoin **C** was determined by the examination committee.
10. The TLC plate was necessary to pack in an envelope and leave it to a laboratory superviser.

PROBLEM 3 (Practical)

Determination of Iron in Iron Pills

Introduction

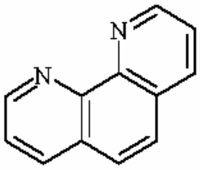
Iron is an essential component of hemoglobin, transporting oxygen in the blood to all parts of the body. It also plays a vital role in many metabolic reactions. Iron deficiency can cause anaemia resulting from low levels of hemoglobin in the blood. Iron deficiency is the most widespread mineral nutritional deficiency worldwide. One way to reduce iron shortage is by treatment with iron pills. The active ingredient in the iron pill to be examined, is iron(II) present as iron(II) fumarate. Besides this organic iron(II) compound the pill contains other compounds such as binding agents. The structure of fumaric acid is:



Fumaric acid

Iron(II) and 1,10-phenanthroline form an orange/red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The absorbance of this complex, determined at 510 nm in a buffer solution (pH=8) is a measure for the iron content of the iron pill. Since 1,10-phenanthroline only binds to iron(II) and iron(II) is readily oxidized to iron(III), hydroxylammonium chloride is added to reduce all iron(III) to iron(II). A simplified reaction scheme is:

$$2\,NH_2OH + 4\,Fe^{3+} \rightarrow N_2O + 4\,H^+ + H_2O + 4\,Fe^{2+}$$



1,10-Phenanthroline

Procedure

The weight of the iron pill is determined with an accuracy of 1 mg using a balance. The pill is carefully pulverized in a mortar and transferred quantitatively into a 100 cm^3 beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 cm^3, 4 M) is added. The content of the beaker is heated up to approximately 60 °C on a hotplate. The solution turns a yellow colour.

The beaker is then placed in an ultrasonic bath for at least 5 minutes. The beaker is kept in place by styrofoam. The suspension is filtered by suction using a Hirsch funnel containing a small layer of moistened hi-flow filter aid pressed onto the filter. The hi-flow filter aid is washed with ample distilled water. The filtrate is carefully transferred into a volumetric flask (250 cm^3) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 cm^3 is pipetted from this solution and transferred into a volumetric flask of 100 cm^3. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 cm^3 is pipetted and transferred into a volumetric flask of 100 cm^3. Subsequently, 1,10-phenanthroline solution (10 cm^3) and hydroxylammonium chloride solution (1 cm^3) are added. Then the volume is adjusted with buffer solution (pH 8).

The absorbance of this solution is measured with a spectrophotometer at 510 nm against water as a blank in a 1.000 cm cell.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient, ε) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 M^{-1}cm^{-1}.

Important

In order to eliminate deviations in absorbance typically connected to the spectrophotometer used, a correction factor is denoted on the spectrophotometer you will be using for your experiment. The absorbance observed must be multiplied by this factor in order to obtain the correct absorbance of the solution of the iron complex.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations:

1. Weight of the iron pill in mg.
2. Reading of the spectrophotometer and corrected absorbance.
3. Calculation of the concentration of iron(II)phenanthroline complex in the cell in mmol dm^{-3}.
4. Calculation of the total amount of iron(II) in the pill in mg.
5. Calculation of the iron content of the pill in weight %.

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THEORETICAL PROBLEMS

SECTION A: General Chemistry

QUESTION 1

The molar solubility s (mol dm^{-3}) of $Th(IO_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp} / 128)^{1/4}$ ( )
(b) $s = (K_{sp} / 256)^{1/5}$ ( )
(c) $s = 256\, K_{sp}^{1/4}$ ( )
(d) $s = (128\, K_{sp})^{1/4}$ ( )
(e) $s = (256\, K_{sp})^{1/5}$ ( )
(f) $s = (K_{sp} / 128)^{1/5} / 2$ ( )

QUESTION 2

Which one of the following equations must be used for the exact calculation of $[H^+]$ of an aqueous HCl solution at any concentration c_{HCl}? ($K_w = 1\times10^{-14}$).

(a) $[H^+] = c_{\text{HCl}}$ ( )
(b) $[H^+] = c_{\text{HCl}} + K_w / [H^+]$ ( )
(c) $[H^+] = c_{\text{HCl}} + K_w$ ( )
(d) $[H^+] = c_{\text{HCl}} - K_w / [H^+]$ ( )

QUESTION 3

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g mol^{-1} and N_A is the Avogadro constant. Which one of the following statements is not correct?

(a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 cm^3 of solution. ( )

(b) 1.00 mmol amount of glucose has a mass of 180 mg. ( )

(c) 0.0100 mol of glucose comprises of $0.0100 \times 24 \times N_A$ atoms. ( )

(d) 90.0 g glucose contain $3 \times N_A$ atoms of carbon. ( )

(e) 100 cm^3 of a 0.10 M solution contain 18 g of glucose. ( )

QUESTION 4

If the density of a liquid compound B is ρ (in g cm^{-3}), M is the molar mass of B and N_A is the Avogadro constant, then the number of molecules of B in 1 dm^3 of this compound is:

(a) $(1000 \times \rho) / (M \times N_A)$ ( )

(b) $(1000 \times \rho \times N_A) / M$ ( )

(c) $(N_A \times \rho) / (M \times 1000)$ ( )

(d) $(N_A \times \rho \times M) / 1000$ ( )

QUESTION 5

The equilibrium constant of the reaction:

$$Ag_2CrO_4(s) + 2\ Cl(aq)^- \rightleftharpoons 2\ AgCl(s) + CrO_4^{2-}(aq)$$

is given by the equation:

(a) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)^2$ ( )

(b) $K = K_{sp}(Ag_2CrO_4) \times K_{sp}(AgCl)^2$ ( )

(c) $K = K_{sp}(AgCl) / K_{sp}(Ag_2CrO_4)$ ( )

(d) $K = K_{sp}(AgCl)^2 / K_{sp}(Ag_2CrO_4)$ ( )

(e) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)$ ( )

QUESTION 6

How many cm^3 of 1.00 M NaOH solution must be added to 100.0 cm^3 of 0.100 M H_3PO_4 solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H_3PO_4 are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

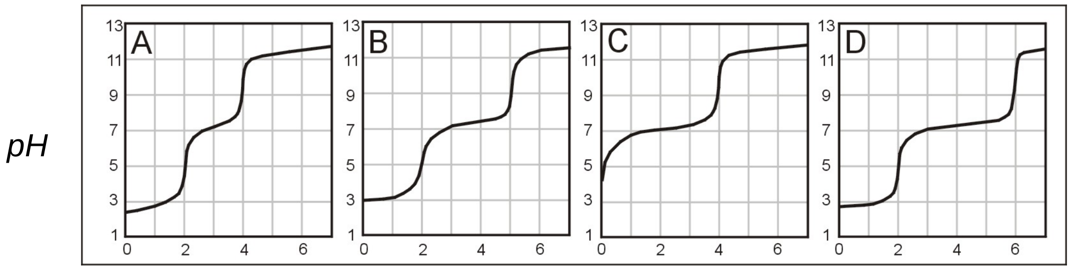
(a) 5.0 cm^3 ( )

(b) 10.0 cm^3 ( )
(c) 15.0 mL ( )
(d) 20.0 mL ( )

QUESTION 7

Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (*pH vs*. volume of titrant) shown in the figure:

(For H_3PO_4: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)



Volume of titrant (cm^3)

a) The sample contains H_3PO_4 only.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) The sample contains both in a mole ratio $H_3PO_4 : NaH_2PO_4 = 2 : 1$.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) The sample contains both in a mole ratio $H_3PO_4 : NaH_2PO_4 = 1 : 1$.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine $(CH_3)_2NNH_2$ and N_2O_4 (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N_2, CO_2 and H_2O are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of $(CH_3)_2NNH_2$?

(a) 8 ( )
(b) 9 ( )
(c) 10 ( )
(d) 11 ( )
(e) 12 ( )

QUESTION 9

The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

(a) F ( )

(b) (4/3) F ( )

(c) (3/2) F ( )

(d) 2 F ( )

(e) 3 F ( )

QUESTION 10

Identify particle X in each of the following nuclear reactions:

a) ${}^{68}_{30}\mathrm{Zn} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{65}_{28}\mathrm{Ni} + \mathrm{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

b) ${}^{130}_{..52}\mathrm{Te} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{131}_{..53}\mathrm{I} + \mathrm{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

c) ${}^{214}_{..82}\mathrm{Pb} \rightarrow {}^{214}{}_{83}\mathrm{Bi} + \mathrm{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

d) ${}^{23}_{11}\mathrm{Na} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{24}_{11}\mathrm{Na} + \mathrm{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

e) ${}^{19}_{..9}\mathrm{F} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{20}_{..9}\mathrm{F} + \mathrm{X}$ alpha ( ), beta ( ), gamma ( ), neutron ( )

QUESTION 11

10.0 cm^3 of 0.50 M HCl and 10.0 cm^3 of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 cm^3 of 0.50 M NaOH were used instead of 10.0 cm^3. Thermal losses are negligible and the specific heats of both solutions are taken as equal.

(a) (1/2) ΔT ( )

(b) (2/3) ΔT ( )

(c) (3/4) ΔT ( )

(d) ΔT ( )

QUESTION 12

Natural antimony consists of the following 2 stable isotopes: ^{121}Sb, ^{123}Sb. Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. Natural hydrogen consists of the following 2 stable isotopes: ^{1}H, ^{2}H. How many peaks are expected in a low resolution mass spectrum for the ionic fragment $SbHCl^+$?

(a) 4 ( )
(b) 5 ( )
(c) 6 ( )
(d) 7 ( )
(e) 8 ( )
(f) 9 ( )

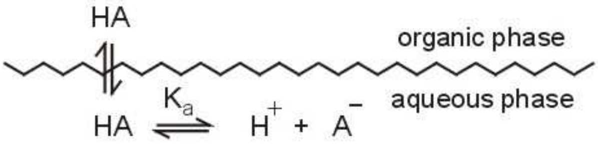
QUESTION 13

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5°. Based on this we must expect a beam of X-rays diffracted at:

(a) 22.0 degrees ( )
(b) 22.5 degrees ( )
(c) 23.0 degrees ( )
(d) 23.5 degrees ( )
(e) 24.0 degrees ( )
(f) 24.5 degrees ( )

QUESTION 14

The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

(a) The distribution constant (K_D) of the acid HA depends on the *pH* of the aqueous phase. (Y) (N)

(b) HA can be efficiently extracted only from acidic aqueous solutions. (Y) (N)

(c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. (Y) (N)

(d) The distribution ratio (D) of the acid HA depends mainly on its concentration. (Y) (N)

QUESTION 15

Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. (Y) (N)

(b) The absorbance is linearly related to the wavelength of the incident light. (Y) (N)

(c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. (Y) (N)

(d) The transmittance is inversely proportional to the logarithm of absorbance. (Y) (N)

(e) The transmittance is inversely proportional to the concentration of the absorbing compound. (Y) (N)

QUESTION 16

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics:

a) 3000 Å 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

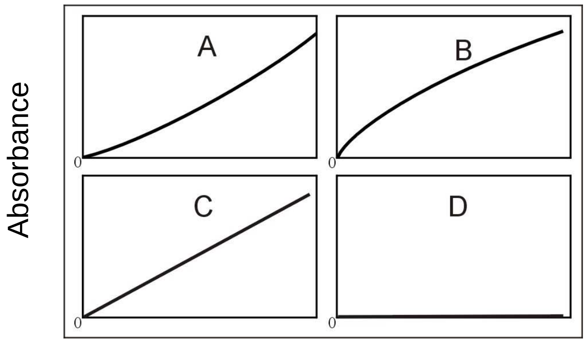
b) 5×10^{14} Hz 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

c) 2000 cm^{-1} 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

d) 2×10^{6} GHz 150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

QUESTION 17

The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:



Total concentration of HX

a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 18

Which of the following acids is the strongest?

a) perchloric acid, $HClO_4$ ( )

b) chloric acid, $HClO_3$ ( )

c) chlorous acid, $HClO_2$ ( )

d) hypochlorous, HClO ( )

(e) All of them are equally strong because they all contain chlorine ( )

QUESTION 19

Which structure describes best the crystal system of iron in which the coordination number is 8?

a) simple cubic ( )
b) body-centered cubic ( )
c) cubic closest packed ( )
d) hexagonal closest packed ( )
e) none of the above ( )

QUESTION 20

Which of the following elements has the largest third ionization energy?

a) B ( )
b) C ( )
c) N ( )
d) Mg ( )
e) Al ( )

QUESTION 21

Which second period (row) element has the first six ionization energies (*IE* in electron volts, eV) listed below?

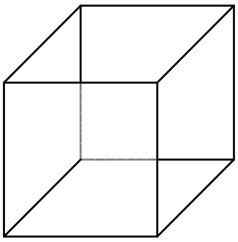
IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

a) B ( )
b) C ( )
c) N ( )
d) O ( )
e) F ( )

QUESTION 22

Silver metal exists as a face-centered cubic (fcc) packed solid.

a) Draw an fcc unit cell.



b) How many atoms are present in the fcc unit cell?

c) The density of silver has been determined to be 10.5 g cm^{-3} . What is the length of each edge of the unit cell?

d) What is the atomic radius of the silver atoms in the crystal?

QUESTION 23

Are the following statements correct (Y) or not (N)?

a) HF boils at a higher temperature than HCl. (Y) (N)

b) HBr boils at a lower temperature than HI (Y) (N)

c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. (Y) (N)

d) Ammonia solutions are buffer solutions because they contain the conjugate pair NH_3 – NH_4^+. (Y) (N)

e) Pure water at 80 °C is acidic. (Y) (N)

f) During electrolysis of an aqueous KI solution with graphite electrodes, the *pH* near the cathode is below 7. (Y) (N)

QUESTION 24

Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1 : 3. How many moles of HNO_3 are consumed by 1 mol of Zn?

a) 2.2 ( )
b) 2.4 ( )
c) 2.6 ( )
d) 2.8 ( )
e) 3.0 ( )
f) 3.2 ( )

SOLUTIONS FOR SECTION A

1: (b); :

2: (b);

3: (e) is not correct;

4: (b);

5: (a);

6: (c);

7: **a)** curve A;
  b) curve B;
  c) curve D;

8: (b);

9: (d);

10: **a)** alpha;
  b) neutron;
  c) beta;
  d) gamma;
  e) gamma;

11: (b);

12: (c);

13: (d);

14: **a)** N;
  b) Y;
  c) Y;
  d) N;

15: **a)** Y;
  b) N;
  c) Y;
  d) N;
  e) N;

16: **a)** 300 nm;
  b) 600 nm;
  c) 5000 nm;
  d) 150 nm;

17: **a)** Curve A;
  b) Curve B;
  c) Curve D;
  d) Curve C;
  e) Curve C;

18: (a);

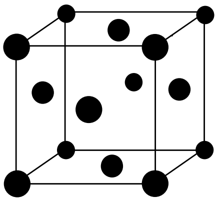
19: (b);

20: (d);

21: (b);

22:

a)



b) 4 atoms,

c) The length of each edge of the unit cell is 0.409 nm,

d) The atomic radius of the silver atoms in the crystal is 0.145 nm.

23: **a)** Y;
  b) Y;
  c) N;
  d) N;
  e) N;
  f) N;

24: (d)

SECTION B: PHYSICAL CHEMISTRY

PROBLEM 25 Muon

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is:

$\mu \rightarrow e + \bar{\nu}_e + v_\mu$,

where $\bar{\nu}_e$ is the electron antineutrino, and v_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + v_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of 1.4846×10^{-11} J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^{1}H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

SOLUTION

a) Energy of a stationary muon:

$E_\mu = m_\mu c^2 = E_e + E_{v,v}$

$m_\mu c^2 = m_e c^2 + (T_e + E_{v,v})$

$$m_\mu = \frac{m_e + (T_e + E_{v,v})}{c^2} = \frac{9.109\times10^{-31} + (1.4846\times10^{-11} + 2.000\times10^{-12})}{(2.998\times10^8)^2} =$$

$$= 1.883\times10^{-28} \text{ kg}$$

b) From Bohr theory:

$$E_n = -\frac{m e^4}{2 n^2 h^2} = -109700 \text{ cm}^{-1} \times \frac{1}{n^2} \times \left(\frac{m}{m_e}\right),$$

where

$$m = \frac{m_{\mu}\, m_{H}}{m_{\mu} + m_{H}}$$

$$\lambda = \frac{1}{E_4 - E_2} = \frac{1}{109700\left(\frac{m}{m_e}\right)\left(\frac{1}{4} - \frac{1}{16}\right)} = 2.615\times10^{-7}\ \text{cm}$$

$$\frac{m}{m_e} = 185.9$$

$$m = 185.9 \times 9.109\times10^{-31} = 1.693\times10^{-28}\ \text{kg}$$

The mass of a proton from Tables attached :

m_H = 1.673×10^{-27} kg

$$m_{\mu} = \frac{m\, m_H}{m_H - m} = \frac{1.693\times10^{-28} \times 1.673\times10^{-27}}{1.673\times10^{-27} - 1.693\times10^{-28}} = 1.884\times10^{-28}\ \text{kg}$$

PROBLEM 26 Spectrum of CO

Rotational energy levels of diatomic molecules are well described by the formula $E_J = B\,J(J+1)$, where J is the rotational quantum number of the molecule and B its rotational constant. Constant B is related to the reduced mass μ and the bond length R of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}\,.$$

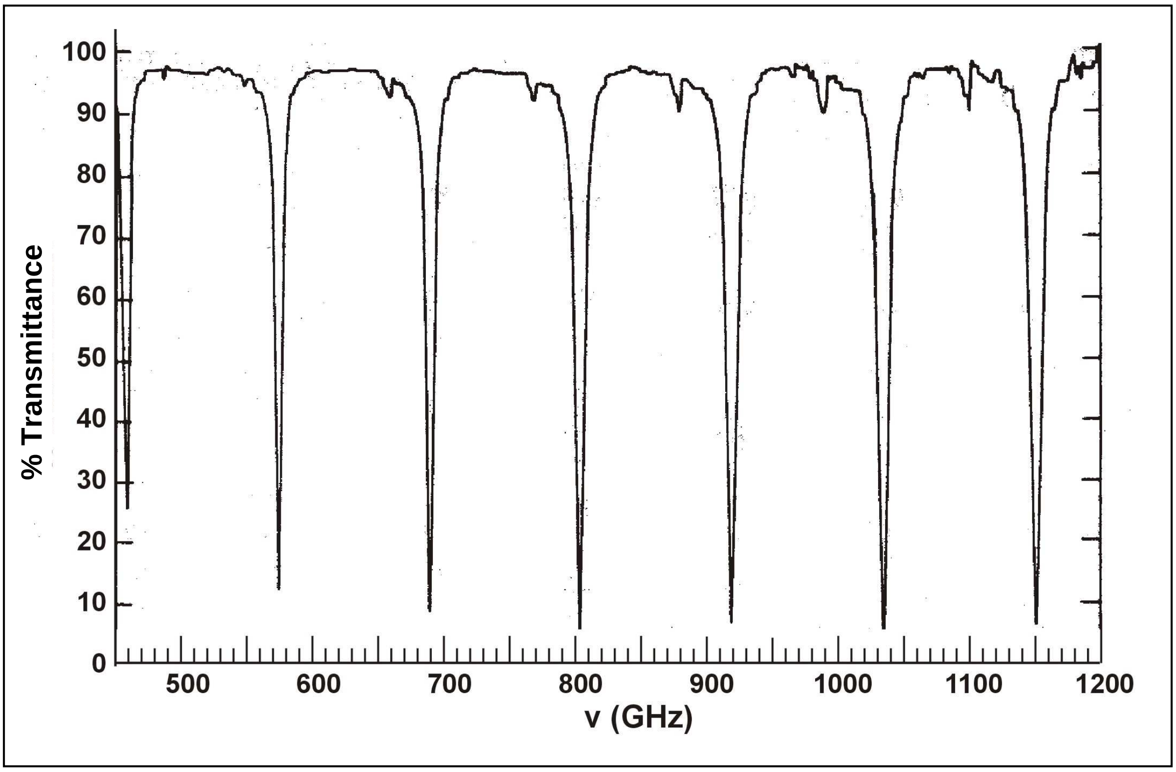
In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h\ \nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2\ B\ (J+1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h\ (\Delta v) = 2\ B$.

By inspecting the spectrum provided, determine the following quantities for $^{12}C^{16}O$ with appropriate units:

a) Δv

b) B

c) R



SOLUTION

a) For example: $\Delta\nu$ = 1150 – 1035 = 115 GHz

b) $$B = \frac{h\,\Delta\nu}{2} = \frac{6.63\times10^{-34}\times115\times10^{9}}{2} = 3.81\times10^{-23}\text{ J}$$

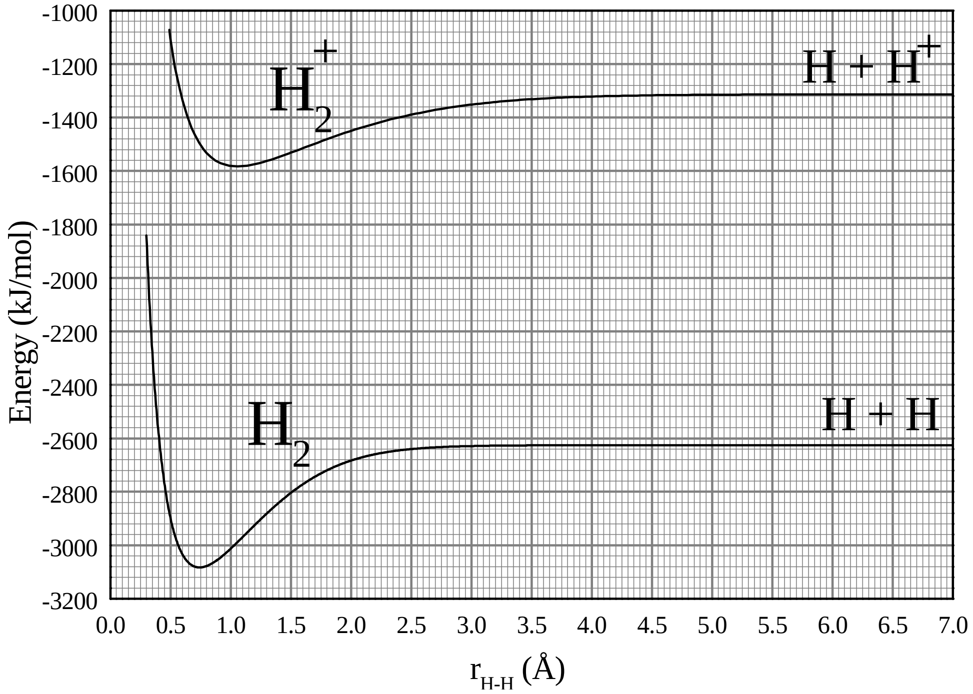
c) $$\mu = \frac{m(\text{C})\times m(\text{O})}{m(\text{CO})} = \frac{12\times16}{28} = 6.86\text{ a.u.} = 1{,}14\times10^{-26}\text{ kg}$$

For interatomic distance R:

$$R = \frac{h}{2\pi\sqrt{2\mu B}} = \frac{6.63\times10^{-34}}{2\times3.14\sqrt{2\times1.14\times10^{-26}\times3.81\times10^{-23}}} = 1.13\times10^{-10}\text{ m} = 1.13\text{ Å}$$

PROBLEM 27 Hydrogen molecule

Using the information provided on this graph, give numerical answers with appropriate units to the following questions:



1. What are the equilibrium bond lengths of H_2 and H_2^+?
2. What are the binding energies of H_2 and H_2^+?
3. What is the ionisation energy of the H_2 molecule?
4. What is the ionisation energy of the H atom?
5. If we use electromagnetic radiation of frequency 3.9×10^{15} Hz in order to ionise H_2, what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

SOLUTION

1. The equilibrium bond lengths of H_2 and H_2^+ can be read from the minimum of the curves: $r(H_2) = 0.75$ Å; $r(H_2^+) = 1.05$ Å

2. The binding energies of H_2 and H_2^+ can be calculated as the differences in the values for infinitive bond lengths and those for minima of the particular curves:

$E_{\text{bond}}(H_2) = -2620 - (-3080) = 460$ kJ mol^{-1}

$E_{\text{bond}}(H_2^+) = -1310 - (-1580) = 270$ kJ mol^{-1}

3. The ionization energy $E_{ion}(H_2)$:

$E_{ion}(H_2)$ = – 1580 – (– 3080) = 1500 kJ mol^{-1}

4. $E_{ion}(H)$ = – 1310 – (– 2620) = 1310 kJ mol^{-1}

5. $H_2 + h\nu \rightarrow H_2^+ + e^-$

$$E(H_2) + h\nu \rightarrow E(H_2^+) + \frac{m_e v_e^2}{2}$$

$$v_e = \sqrt{\frac{2\,(E(H_2) - E(H_2^+) + h\nu}{m_e}} =$$

$$= \sqrt{\frac{2\left(\frac{-3080\times10^3 - (-1510\times10^3)}{6.02\times10^{23}}\right) + 6.63\times10^{-34}\times4.1\times10^{15}}{9.11\times10^{-31}}} = 492\times10^3\ \text{m s}^{-1}$$

PROBLEM 28 Cryoscopy

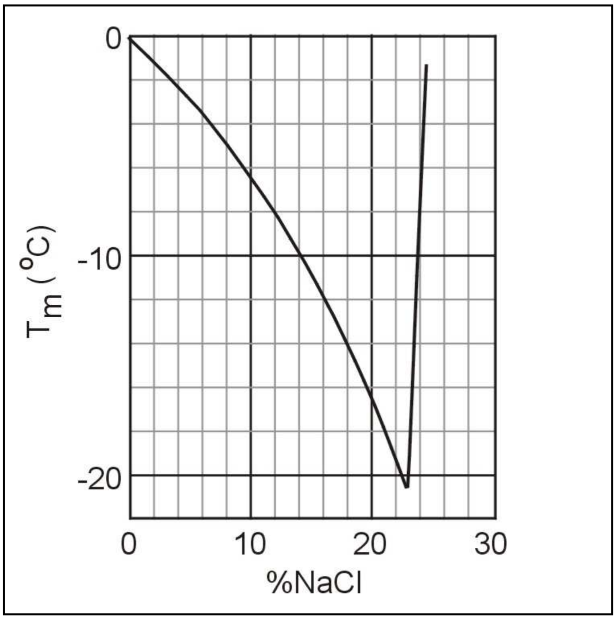
Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 °C) and well above the CO_2 sublimation point (–78 °C) this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as –20 °C can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 °C with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

a) The mixing process is spontaneous. (Y) (N)

b) The change of entropy during the mixing process is negative. (Y) (N)

c) The following diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is is the freezing point of the bath based on the diagram?



d) If an equal mass of $MgCl_2$ were used instead of NaCl, would the freezing point be higher? (Y) (N)

SOLUTION

The correct answers are as follows:

a) Y (Yes)

b) N (No)

c) The freezing point of the bath is –9 °C.

d) Y (Yes)

PROBLEM 29 Pool

A very large swimming pool filled with water of temperature equal to 20 °C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine:

a) The heat delivered to the water.

b) Is the change of entropy of the resistor positive, negative, or zero?

(i) $\Delta S_{res} > 0$ ( )
(ii) $\Delta S_{res} = 0$ ( )
(iii) $\Delta S_{res} < 0$ ( )

c) Is the change of entropy of the water positive, negative, or zero?

i) $\Delta S_{pool} > 0$ ( )
(ii) $\Delta S_{pool} = 0$ ( )
(iii) $\Delta S_{pool} < 0$ ( )

d) Is the change of entropy of the system positive, negative, or zero?

(i) $\Delta S_{total} > 0$ ( )
(ii) $\Delta S_{total} = 0$ ( )
(iii) $\Delta S_{total} < 0$ ( )

e) Is the process reversible? (Y) (N)

SOLUTION

a) $Q = 500\ \text{W} \times 20\ \text{min} \times 60 = 600\ \text{kJ}$

b) $\Delta S_{res} = 0$

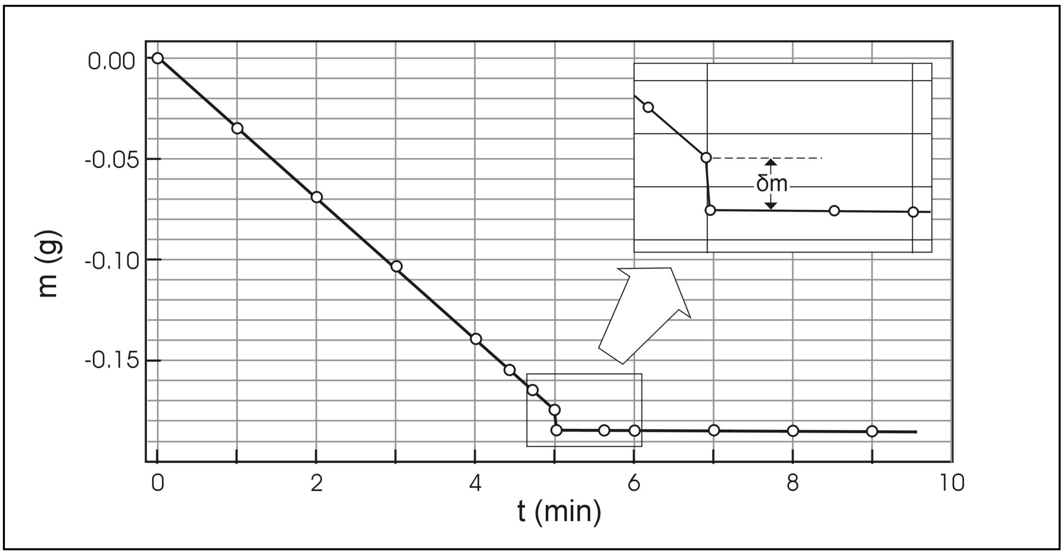
c) $\Delta S_{pool} > 0$

d) $\Delta S_{total} > 0$

e) The answer is No (N).

PROBLEM 30 Gas velocity

The experiment described here gives a simple way to determine the mean velocity *u* of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time *t* = 0. Balance readings are recorded as shown on the diagram.



At *t* = 5 min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δ*m*. Therefore, the force exerted on the lid is *f* = δ*m g*. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., *f* = ½ *u* dm/dt. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume *g* = 9.8 m s^{-2}.

SOLUTION

$$\frac{dm}{dt} = \frac{\Delta m}{\Delta t} = \frac{0.14\ \text{g}}{4\ \text{min}} = 0.035\ \text{g}\,\text{min}^{-1} = 5.8\times10^{-4}\ \text{g}\,\text{s}^{-1}$$

$$\delta m\ g = \frac{1}{2} u \frac{dm}{dt}$$

$$u = \frac{0.01\times 9.81\times 2}{5.8\times10^{-4}} = 338\ \text{m}\,\text{s}^{-1}$$

SECTION C: Organic Chemistry

PROBLEM 31 Ester identification

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 cm^3 of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 cm^3 of a 1.00 M HCl solution to titrate the unused NaOH only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with I_2/NaOH to give a yellow precipitate and C_6H_5COONa. The diacid **B** reacted with Br_2 in CCl_4 to give a single, optically inactive product (compound **D**). Ozonolysis of **B** gave only one product.

a) Determine the molecular mass of compound **A**.

b) Give the structural formulas of **A**, **B**, and **C** without stereochemical information.

c) Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.

d) Give the stereochemical formula for **D**, using a Fischer projection.

e) Give the stereochemical formula for **B**.

The diester **A** also reacted with Br_2 in CCl_4 and was converted to a mixture of two compounds (**E**, **F**) both optically active.

f) Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

If we use Na^{18}OH for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

g) Mark the correct answer:

i) Only **B** ☐

ii) Only **C** ☐

iii) Both **B** and **C** ☐

SOLUTION

a) For reaction with diester A 30 – 6 = 24 cm^3 of 1.00 M NaOH (0.024 mol NaOH)

Reaction:

$ROOC – X – COOR + 2\ NaOH \rightarrow NaOOC – X – COONa + 2\ ROH$

The amount of diester: 0.024 mol / 2 = 0.012 mol

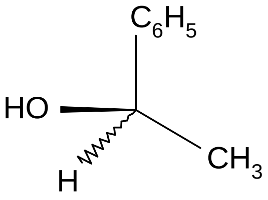
M(A) = 2.81 g / 0.012 mol = 234 g mol^{-1}

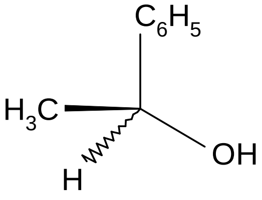
b) **A**: $H_3COCO\text{-}CH{=}CH\text{-}COO(CH_3)C_6H_5$

B: $HOOC\text{-}CH{=}CH\text{-}COOH$

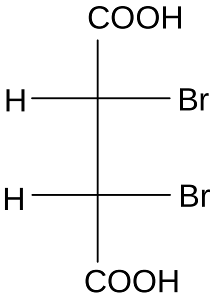
C: $C_6H_5CH(OH)CH_3$

c) Possible stereochemical formulas for **C**:

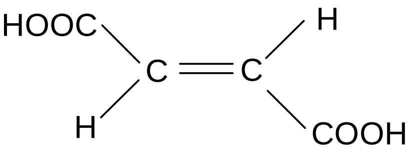




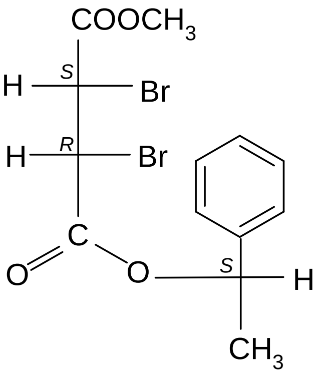
d) Stereochemical formula for **D**:

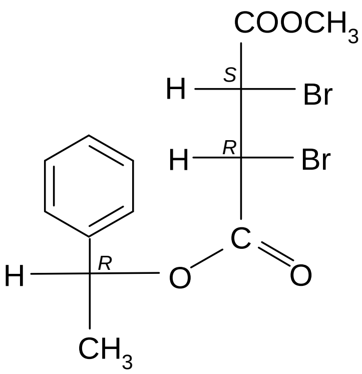


e) Stereochemical formula for **B**:

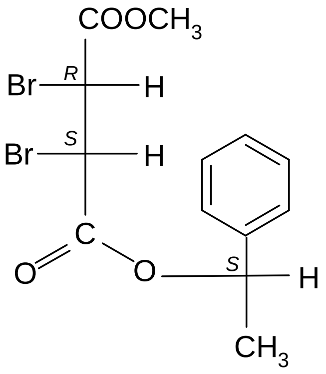


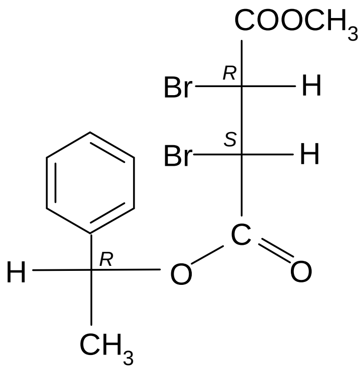
f) Possible stereochemical formula(s) for **E**:





Possible stereochemical formula(s) for **F**:

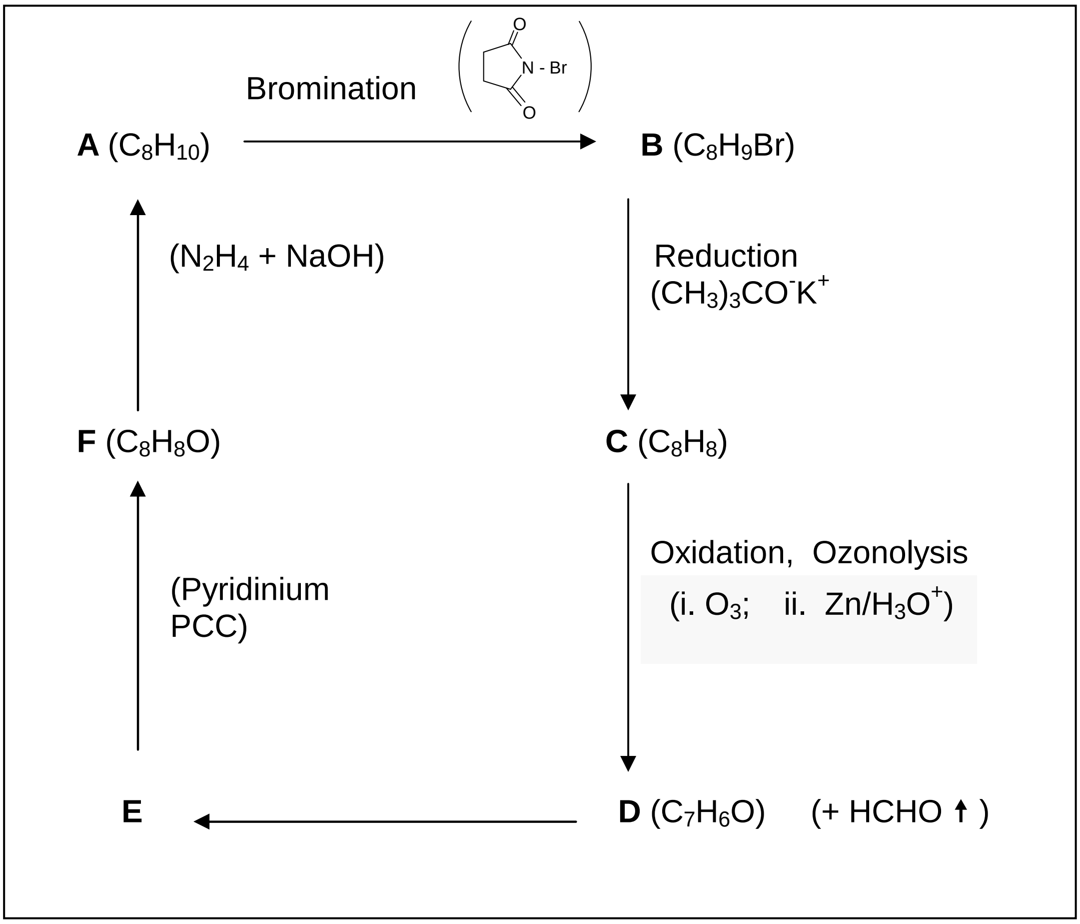




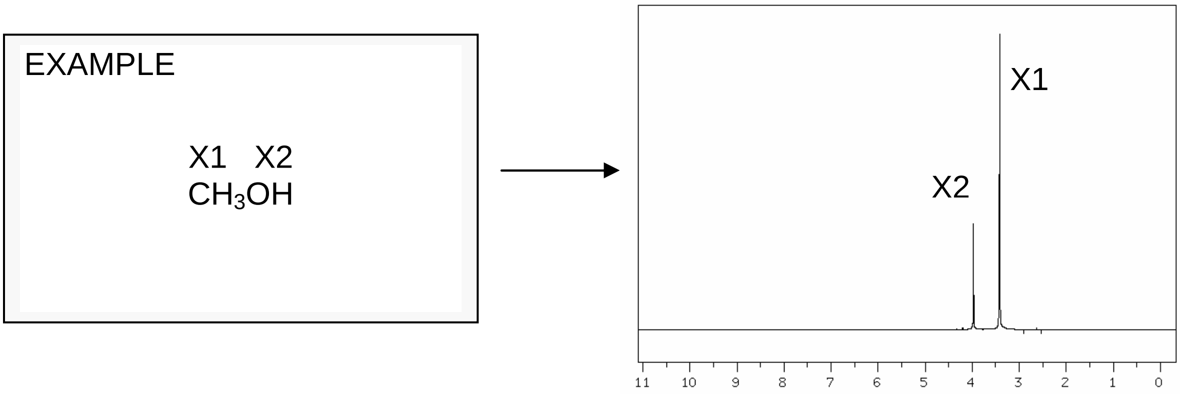
g) Correct answer is ii).

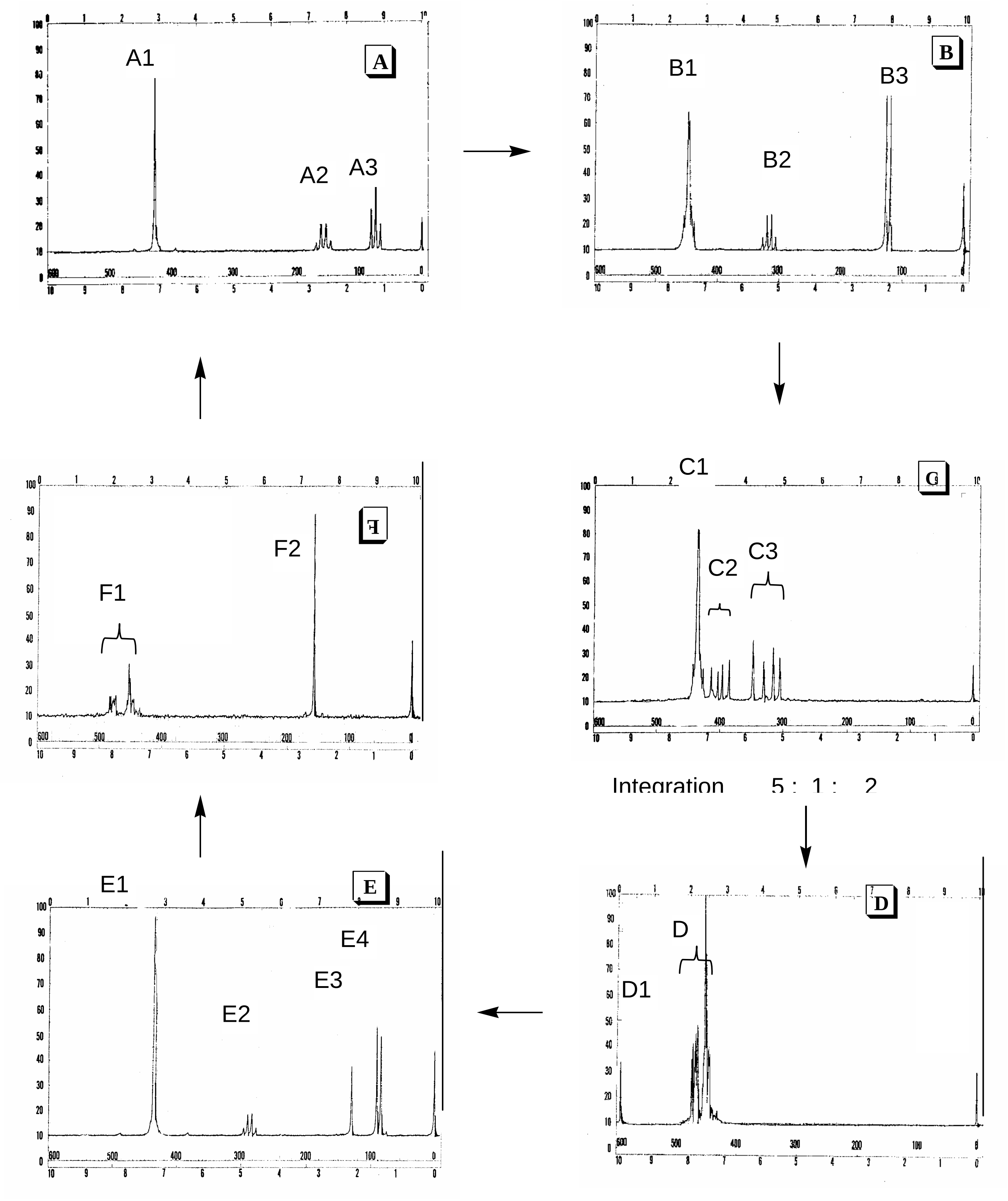
PROBLEM 32 NMR puzzle

An organic compound **A** (C_8H_{10}) gives the following chain of reactions:



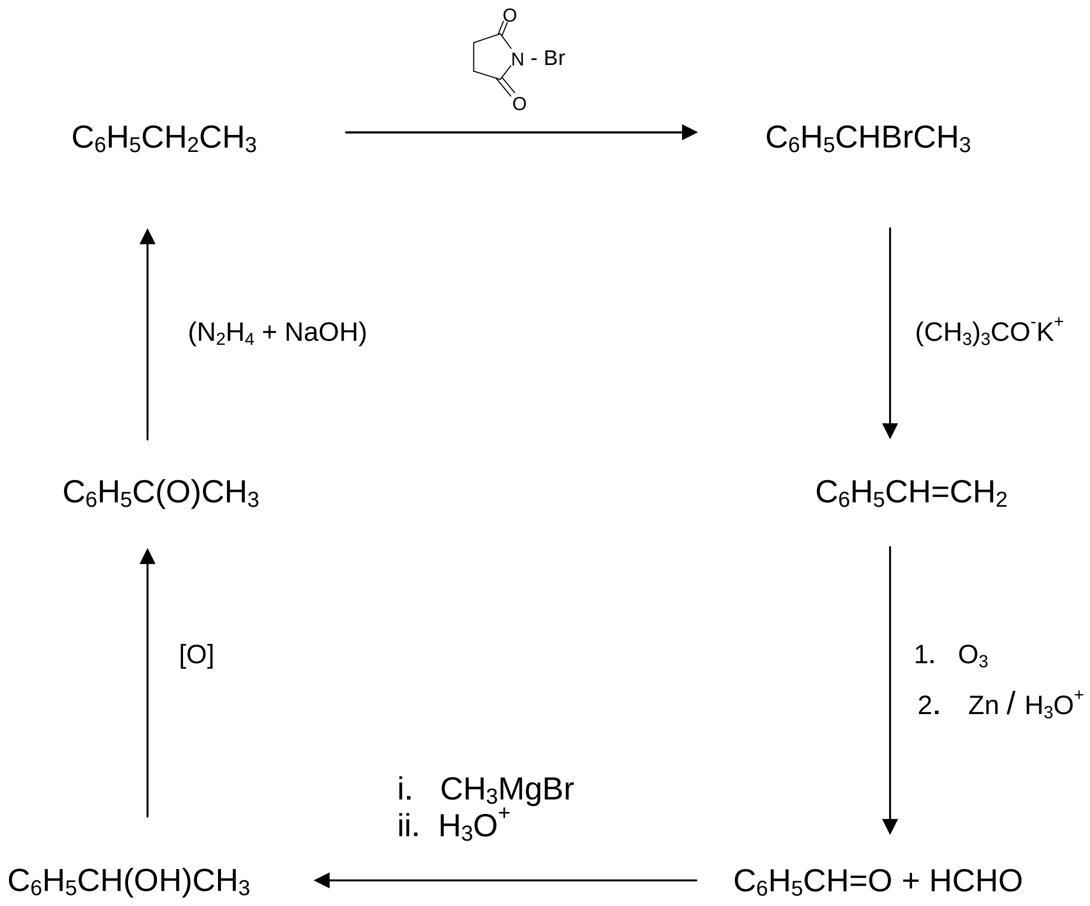
Based on the ^{1}H-NMR spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding ^{1}H-NMR peaks, as shown in the example.

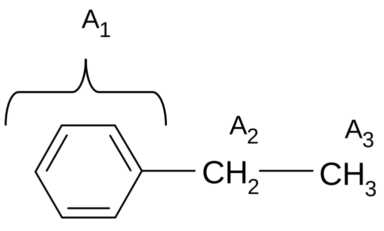




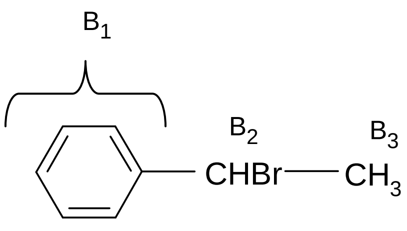
General remarks: NMR spectra were ecorded in $CDCl_3$ on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in $CDCl_3$ solutions and catalyse rapid exchange of some particular protons.

SOLUTION

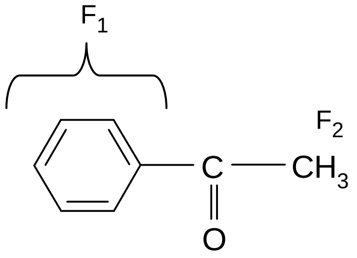




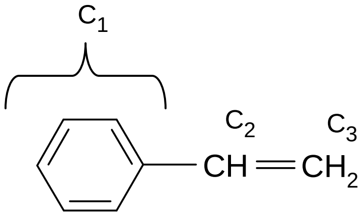
A



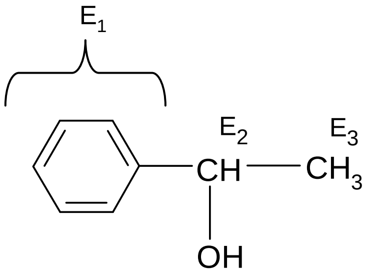
B



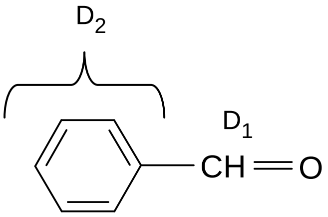
F



C



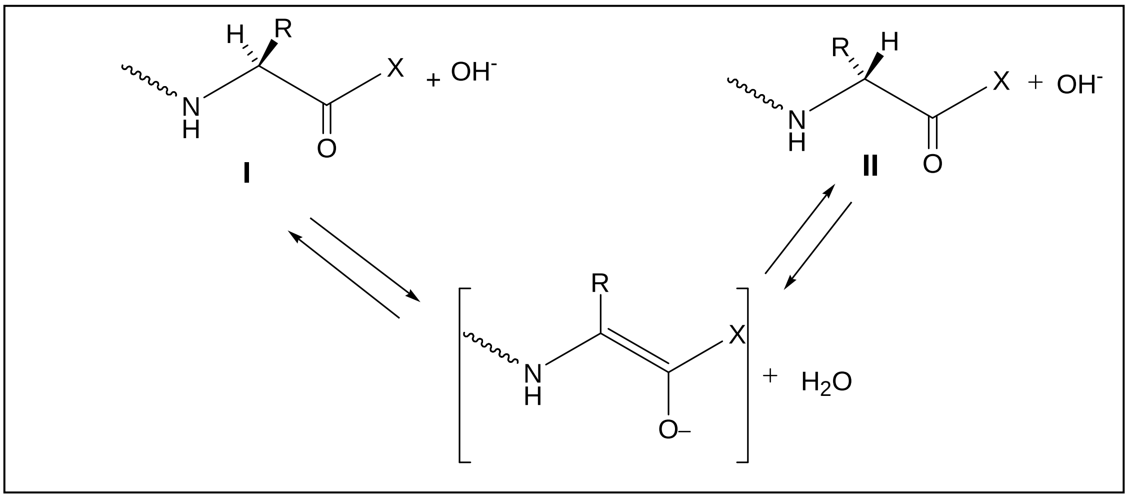
E



D

PROBLEM 33 Peptides

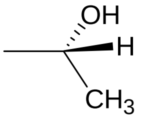
Racemization of α-aminoacids and peptides can occur by an α-enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:



intermediate

1. Draw stereochemical formulas **I** and **II** (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α-enolization mechanism described above operating on each of the following hydroxyaminoacids **A** and **B**:

A: serine (R = $–CH_2OH$)

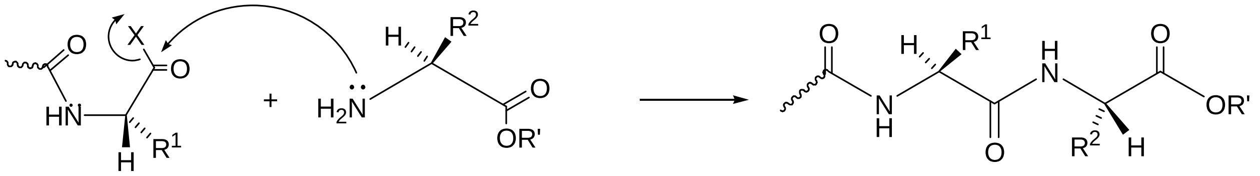
B: (2*S*,3*R*)-threonine (R = )

2. Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

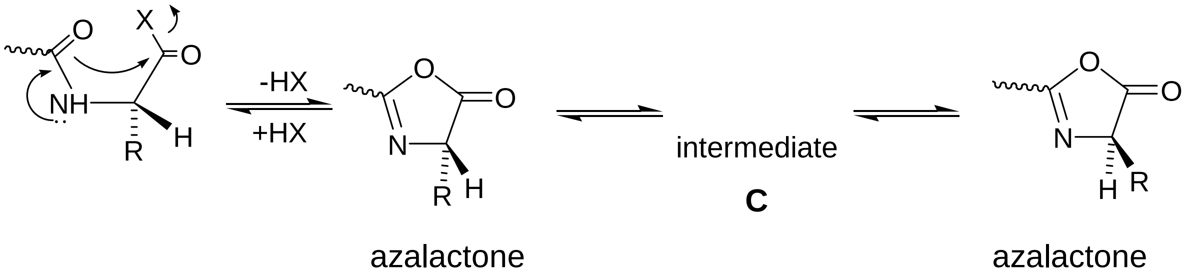
	enantiomers	diastereomers
A $_{I, II}$	☐	☐

	enantiomers	diastereomers
B $_{I, II}$	☐	☐

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:



It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:



3. Write the structural formula for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center.

Azalactones are very reactive substances that can still react with the amino group of an aminoacid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40 ˚C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$ (**P₁**).

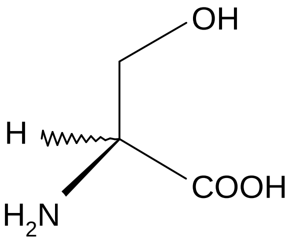
a) Propose a structure for substance **P_1**.

b) Write the reaction product(s) of the substance **P_1** with *S*-alanine ethyl ester (**P_2**) (the side chain R of the aminoacid alanine is a methyl group) using stereochemical formulas (with bold and dashed bonds) for both reactants and product.

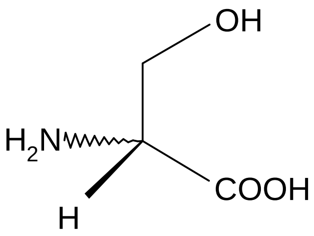
SOLUTION

1.

A:

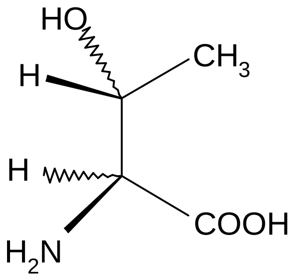


I

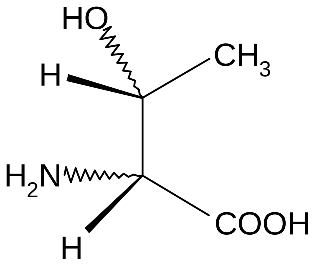


II

B:



I

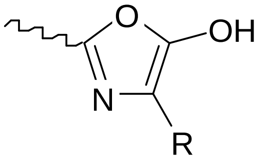


II

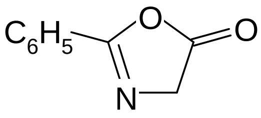
2. **A(I)** and **A(II)** are enantiomers**.**

B(I) and **B(II)** are diastereomers**.**

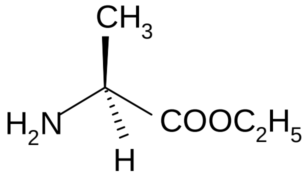
3. Intermediate **C**



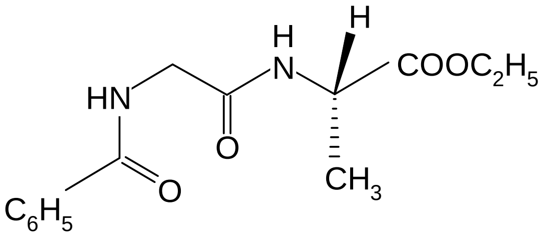
4.



Substance $\mathbf{P_1}$



Ester $\mathbf{P_2}$



Product

SECTION D: Inorganic Chemistry

PROBLEM 34 Aluminium

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al_2O_3) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $AlO_x(OH)_{3-2x}$ where $0<x<1$.

Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al_2O_3 40 – 60 %, H_2O 12 – 30 %, SiO_2 free and combined 1 – 15 %, Fe_2O_3 7 – 30 %, TiO_2 3 – 4 %, F, P_2O_5, V_2O_5, etc., 0.05 – 0.2 %). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200 °C. Complete and balance the following chemical reactions:

$Al_2O_3 + OH^- + \qquad \rightarrow \quad [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + OH^- \quad \rightarrow \quad SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + \qquad \rightarrow \quad CaSiO_3\downarrow +$

$[Al(OH)_4(H_2O)_2]^- \rightarrow \qquad \downarrow + OH^- + H_2O$

$Al(OH)_3 \rightarrow Al_2O_3 +$

ii) Héroult-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6. Typical electrolyte composition ranges are Na_3AlF_6 (80 – 85 %), CaF_2 (5 – 7 %), AlF_3 (5 – 7 %), Al_2O_3 (2 – 8 % intermittently recharged). Electrolysis is carried out at 940 °C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:

$Al_2O_3(l) + C(anode) \rightarrow Al(l) + CO_2(g)$

Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:

$HF + Al(OH)_3 + NaOH \rightarrow Na_3AlF_6 +$

During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

iii) By using the thermodynamic data given below, which are taken to be independent on temperature, determine the thermodynamic quantities Δ*H*, Δ*S* and Δ*G* at 940 °C for the reaction:

$C(graphite) + CO_2(g) \rightarrow 2\ CO(g)$.

	Al(s)	Al_2O_3(s)	C (graphite)	CO(g)	CO_2(g)	O_2(g)
$\Delta_f H^o$ (kJ mol^{-1})	0	–1676	0	–111	–394	
S^o (J.K^{-1} mol^{-1})	28	51	6	198	214	205
$\Delta_{fus}H$ (kJ mol^{-1})	11	109				

iv) At the same temperature and using the data from the table in part (iii) determine the quantities Δ*H* and Δ*G* for the reaction

$2\ Al(l) + 3\ CO_2(g) \rightarrow Al_2O_3(l) + 3\ CO(g)$

given that $\Delta S = -126$ J K^{-1} mol^{-1}. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[Al(H_2O)_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[Al(OH)_4]^-$(aq). In both cases liberation of H_2 occurs. AlF_3 is made by treating Al_2O_3 with HF gas at 700 °C, while the other trihalides, AlX_3, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The $AlCl_3$ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4 °C) the structure changes to a 4-coordinate molecular dimer, Al_2Cl_6. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar $AlCl_3$ molecules.

For the molecular dimer Al_2Cl_6, in the gas phase, two different Al–Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al–Cl distances.

vii) What is the hybridization of the Al atom(s) in Al_2Cl_6 and $AlCl_3$?

SOLUTION

i) $Al_2O_3 + 2\ OH^- + 7\ H_2O \rightarrow 2\ [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + 2\ OH^- \rightarrow SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + Ca^{2+} \rightarrow CaSiO_3\downarrow + H_2O$

$[Al(OH)_4(H_2O)_2]^- \rightarrow Al(OH)_3\downarrow + 2\ OH^- + 2\ H_2O$

$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

ii) $2\ Al_2O_3(l) + 3\ C(anode) \rightarrow 4\ Al(l) + 3\ CO_2(g)$

$6\ HF + Al(OH)_3 + 3\ NaOH \rightarrow Na_3AlF_6 + 6\ H_2O$

iii) $$\Delta_r H^0_{1213} = 2\Delta_f H^0_{1213}(CO) - \Delta_f H^0_{1213}(CO_2) = 2\times(-111) - (-394) = 172\ \text{kJ}$$

$$\Delta_r S^0_{1213} = 2S^0_{1213}(CO) - S^0_{1213}(CO_2) - S^0_{1213}(C) = 2\times(-198) - 214 - 6 = 176\ \text{J K}^{-1}$$

$$\Delta_r G^0_{1213} = \Delta_r H^0_{1213} - T\Delta S^0_{1213} = 172 - 1213\times 0.176 = -\ 41.5\ \text{kJ K}^{-1}$$

iv)

$$\Delta_r H^0_{1213} = 3\Delta_f H^0_{1213}(CO) + \Delta_f H^0_{298}(Al_2O_3) + \Delta_{melt} H(Al_2O_3) - 3\Delta_f H^0_{1213}(CO_2) - 2\Delta H_{melt} H(Al) = \\ = 3\times(-111) - (-1676) + 109 - 3\times(-394) - 2\times 11 = -740\ \text{kJ}$$

$$\Delta_r H^0_{1213} = 3\Delta_f H^0_{1213}(CO) + \Delta_f H^0_{298}(Al_2O_3) + \Delta_{melt} H(Al_2O_3) - 3\Delta_f H^0_{1213}(CO_2) - 2\Delta H_{melt} H(Al) = \\ = 3\times(-111) - (-1676) + 109 - 3\times(-394) - 2\times 11 = -740\ \text{kJ}$$

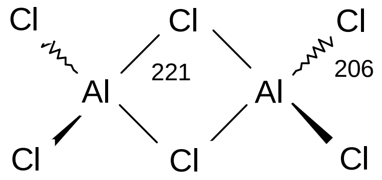
v) $2\ Al + 6\ H^+ + 12\ H_2O \rightarrow 2\ [Al(H_2O)_6]^{3+} + 3\ H_2$

$2\ Al + 2\ OH^- + 6\ H_2O \rightarrow 2[Al(OH)_4]^- + 3\ H_2$

$Al_2O_3 + HF \rightarrow 2\ AlF_3 + 3\ H_2O$

$2\ Al + 3\ X_2 \rightarrow 2\ AlX_3$

vi)



vii) Al_2Cl_6 - *sp*^{3} hybridization

$AlCl_3$ - *sp*^{2} hybridization

PROBLEM 35 Kinetics

The acid-catalyzed reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ was found to be of first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by 0.010 mol dm^{-3} was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

$[CH_3COCH_3]$	$[I_2]$	Time
(mol dm^{-3})	(mol dm^{-3})	(min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	…
1.50	…	…
…	…	0.36

a) Derive the rate law for the reaction and calculate the rate constant.

b) Calculate the time needed for 75 % of CH_3COCH_3 to react in excess I_2.

c) Show graphically the dependence of the rate on $[CH_3COCH_3]$ and on $[I_2]$, for fixed initial concentration of the other reagents.

d) If the rate is doubled by raising the temperature by 10 °C from 298 K, calculate the activation energy for this reaction.

SOLUTION

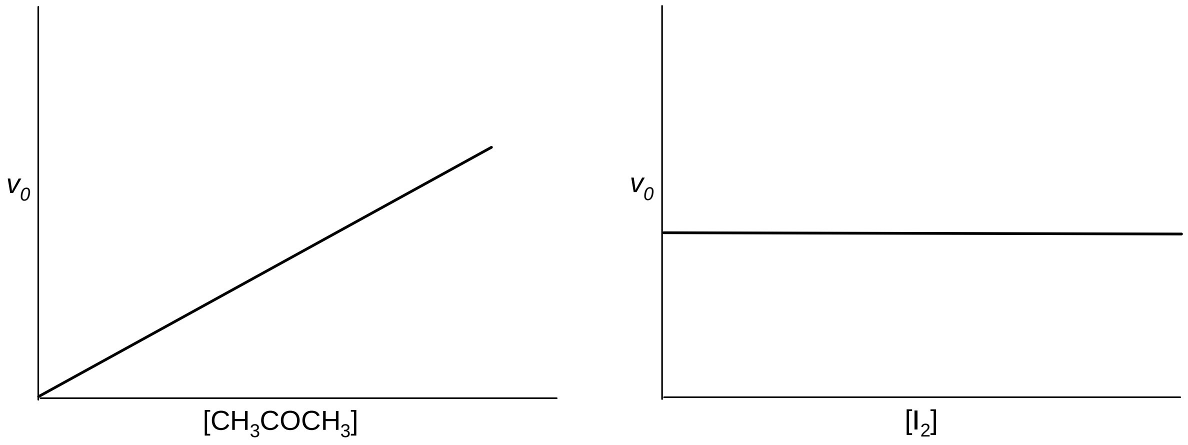
a) $v = k\,[CH_3COCH_3]$

$$k = \frac{v}{[CH_3COCH_3]} = \frac{\frac{0.010}{7.2}}{0.25} = 5.56\times10^{-3}\ \text{min}^{-1} = 9.26\times10^{-5}\ \text{s}^{-1}$$

b) $\tau = \ln 2 / k = 125$ min

$t = 2\ \tau = 250$ min

c)



d)

$$k = A\exp\left(-\frac{E_A}{RT}\right)$$

$$\frac{v_2}{v_1} = \frac{k_2}{k_1} = \frac{\exp\left(-\frac{E_A}{RT_2}\right)}{\exp\left(-\frac{E_A}{RT_1}\right)} = \exp\left(-\frac{E_A}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right)$$

$$\ln\frac{v_2}{v_1} = -\frac{E_A}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$E_A = -R\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}\ln\frac{v_2}{v_1}$$

$$E_A = -8.314\left(\frac{1}{308}-\frac{1}{298}\right)^{-1}\ln\frac{2}{1} = 52.9\ \text{kJ mol}^{-1}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of the Dipeptide *N*-acetyl-*L*-prolinyl-*L*-phenylalanine Methyl Ester (Ac-*L*-Pro-*L*-Phe-OCH$_3$)

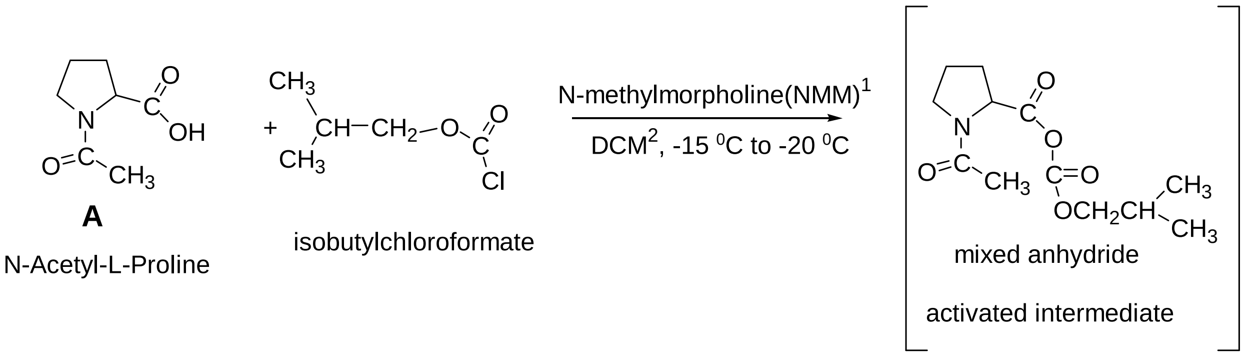
Introduction

Peptide synthesis is now a well-refined art and many of their synthetic procedures can be readily adapted to the elementary laboratory. Interest in peptides, always high, has heightened even more with the recent discovery of the importance of the so-called "opiate" peptides as well as of other biological active peptides.

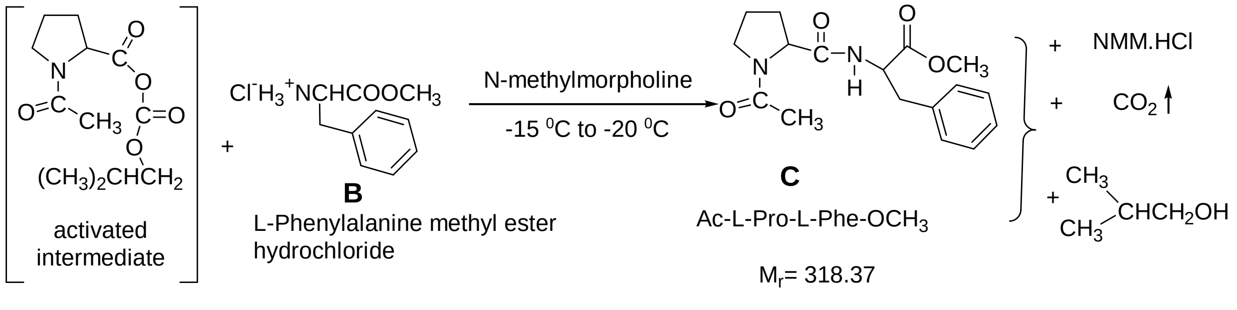
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

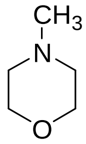
Reactions

STEP 1



STEP 2



[1] *N*-methylmorpholine (NMM) = 

[2] DCM = Dichloromethane

Procedure

STEP 1

Place the 1.50 g (0.0095 mol) sample of *N*-acetyl-*L*-proline (labelled AcPro), which you have been given, into a 50-cm^3 round-bottom flask. Add 20 cm^3 dichloromethane (labelled DCM) in the graduated cylinder. Use some of the 20 cm^3 DCM to wash out the AcPro vial and add the remaining DCM also into the round-bottomed flask. Plug the flask with a septum, clamp it loosely to a support stand and cool it to –15 °C to –20 °C in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled NMM) to the flask, by means of a syringe. Then, slowly add 1.5 cm^3 (0.0116 mol) isobutyl-chloroformate (labelled IBCF) to the flask by means of a second syringe. During the addition, swirl the reaction mixture gently by hand, and continue swirling for another 10 min. The temperature should remain in the range –20 ^{o} to –15 ^{o}C.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled $HCl\cdot H_2NPheOCH_3$) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled NMM) using a third syringe, while the reaction mixture is swirled by hand. *ATTENTION: Leave the needle part of the syringe in the septum for the remainder of the reaction*. Allow the reaction to proceed for 60 min at –15 °C to –20 °C, swirling periodically by hand.

During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.

After 60 min at –20 ^{o}C to –15 ^{o}C, remove the 50 cm^3 round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 cm^3 beaker and let it warm up to room temperature. Transfer the contents of the flask into the 50 cm^3 separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3 – 5 cm^3), which is in a vial (labelled DCM). Wash the organic layer successively with two 20 cm^3 portions of 0.2 M aqueous HCl solution, two 20 cm^3 portions of 1 % aqueous

$NaHCO_3$ solution (read caution comment in next paragraph) and finally one 10 cm^3 portion of saturated solution of sodium chloride (labelled brine).

Important

After each washing allow the separating funnel to stand for enough time, so that the two phases separate completely. Also, take into consideration that the organic phase (DCM) is always the lower layer and contains the product. All the aqueous washings are collected in the same Erlenmeyer flask (empty if necessary).

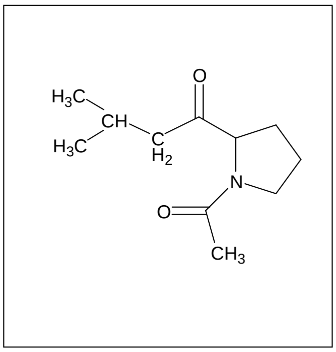
CAUTION: Keep in mind, also, that during washing with 1 % $NaHCO_3$, the CO_2 liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.

Before continuing, wash the glass funnel, the 50 cm^3 cylinder and the 50 cm^3 round-bottom flask with water and then dry them with acetone. Your supervisor will show you where to dispose of the water and the acetone.

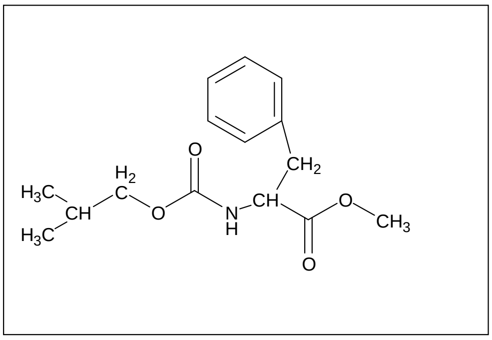
Pour the organic layer into a clean 50 cm^3 Erlenmeyer flask. Add the anhydrous sodium sulphate, which is in a vial labelled Na_2SO_4, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm^3 round-bottom flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3 – 5 cm^3). Removal of the organic solvent is done under reduced pressure, using a rotary evaporator apparatus. This will be done for you by a laboratory supervisor, who will add 20 cm^3 of diethylether to the residue in your flask, which will cause precipitation of your product. After cooling for 5 minutes in the ice bath, scrape the walls of the flask with a spatula, filter by suction the crystallized dipeptide through a fritted glass funnel. Wash twice with diethylether (5 cm^3 each time).

Leave the product on the filter under suction for at least 3 minutes. Then collect it on weighing paper, weigh it in the presence of a supervisor and then transfer it into a sample vial and label it with your student code. Write the mass of your product (**C**) on the label and on your answer sheet (on the next page).

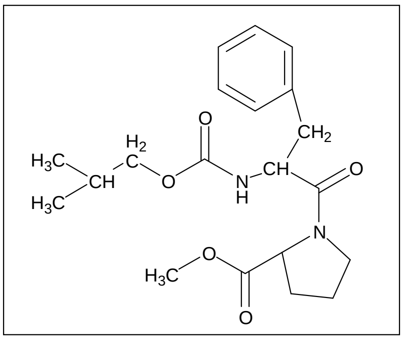
During the reaction between the phenylalanine methylester **B** and the activated mixed anhydride intermediate (step 2) the formation of the desired dipeptide product **C** is usually accompanied by a by-product the correct structure of which is one of the three structures **I**, **II**, **III** given below. Circle the Roman numeral corresponding to the correct structure.



I



II



III

TLC- Analysis

You have two Eppendorfs, one empty and one with a tiny amount of substance **B**. Put a small amount of **C** into the empty Eppendorf, and dissolve both **B** and **C** in a few drops of methanol. Use the supplied capillary tubes to apply small samples of these solutions to the TLC plate. Develop the TLC plate with a solution of chloroform-methanol-acetic acid (7 : 0.2 : 0.2) as eluant. The appropriate amount of eluant has been placed in the proper vial by the supervisor.

After the elution, analyze the TLC-plate using a UV-lamp. Clearly mark the starting line, solvent front and the UV-active spots.

Draw the diagram in the box on the answer sheet. Determine the R_f values.

Finally place the TLC-plate in a small plastic bag with a sealing strip and put it in an envelope provided by the supervisor. Write your student code on the envelope.

The examination committee will check the quality of the *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester that you have prepared by determining its angle of optical rotation and consequently its specific rotation, $[a]^{t}_{D,}$ using an accurate polarimeter apparatus.

SOLUTION

The following values were required to be written in the Answer Sheet

- Mass of Ac-*L*-Pro-*L*-Phe-OCH_3 obtained (product **C**).
- The yield of Ac-*L*-Pro-*L*-Phe-OCH_3 **C.**
- The TLC diagram with indication of the base line and the front of the solvent.
- R_f value of *L*-phenylalanine methyl ester hydrochloride (material B) and that of R_f value of Ac-*L*-Pro-*L*-Phe-OCH_3 (product C).

- Conclusions from the TLC analysis:

  Compound **C:**
  - Is pure,
  - Contains some **B**,
  - Contains several contaminants,
  - No conclusion.

- Specific rotation of the dipeptide Ac-*L*-Pro-*L*-Phe-OCH_3 C (to be measured later by the examination committee)

  $[a]_D^T$ = 45 °

- The correct structure of the by-product: **II.**

36th

IChO

International Chemistry Olympiad

8 theoretical problems
2 practical problems

THE THIRTY-SIXTH

INTERNATIONAL CHEMISTRY OLYMPIAD

18–27 JULY 2004, KIEL, GERMANY

THEORETICAL PROBLEMS

PROBLEM 1

Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0 °C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

The thermodynamic properties and the composition of natural gas can be found in Table 1.

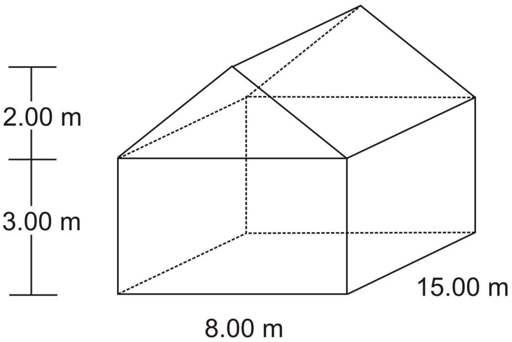
1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

a) Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).

b) Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m^3 of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00 °C and the air temperature in the house (dimensions given in the figure below) is 10.0 °C. Assume a water density of ρ = 1.00 kg dm^{-3} and air behaving like an ideal gas.



1.3 Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0 °C and the energy which is required to heat the initial amount of air (21.0 % of O_2, 79.0 % of N_2) to 30.0 °C at a pressure of 1.013×10^5 Pa.

In February, the outside temperature is about 5 °C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is 1.00 W K^{-1} m^{-1}.

1.4 Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0 °C during the party (12 hours).

1.00 m^3 of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

1.5 What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0 %? What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100 % efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	Δ_fH^0 (kJ mol^{-1})$^{-1}$	S^0 (J mol^{-1} K^{-1})$^{-1}$	C_p^0 (J mol^{-1} K^{-1})$^{-1}$
CO_2 (g)	0.0024	-393.5	213.8	37.1
N_2 (g)	0.0134	0.0	191.6	29.1
CH_4 (g)	0.9732	-74.6	186.3	35.7
C_2H_6 (g)	0.0110	-84.0	229.2	52.5
H_2O (l)	-	-285.8	70.0	75.3
H_2O (g)	-	-241.8	188.8	33.6
O_2 (g)	-	0.0	205.2	29.4

Equation:

$J = E \times (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \times \Delta T \times d^{-1}$

J	energy flow E along a temperature gradient (wall direction z) per area A and time Δt
d	wall thickness
λ_{wall}	heat conductivity
ΔT	difference in temperature between the inside and the outside of the house

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SOLUTION

1.1 Chemical equations:

a) methane: $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

b) ethane: $2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$

Thermodynamic data for the equations:

$\Delta H^0 = [2 \times (-241.8) - 393.5 - (-74.6)]$ kJ mol^{-1} = -802.5 kJ mol^{-1}

$\Delta S^0 = [2 \times (188.8) + 213.8 - 186.3 - 2 \times 205.2]$ J mol^{-1} K^{-1} = -5.3 J mol^{-1} K^{-1}

$\Delta G^0 = -802.5\ \text{kJ mol}^{-1} - 298.15\ \text{K} \times (-5.3\ \text{J mol}^{-1}\ \text{K}^{-1}) = -800.9\ \text{kJ mol}^{-1}$

Methane: $\Delta H^0 = -802.5\ \text{kJ mol}^{-1}$; $\Delta S^0 = -5.3\ \text{J mol}^{-1}\ \text{K}^{-1}$; $\Delta G^0 = -800.9\ \text{kJ mol}^{-1}$

$\Delta H^0 = [6 \times (-241.8) - 4 \times 393.5 - 2 \times (-84.0)]\ \text{kJ mol}^{-1} = -2856.8\ \text{kJ mol}^{-1}$

$\Delta S^0 = [6\times188.8 + 4\times213.8 - 2\times229.2 - 7\times205.2]\ \text{J mol}^{-1}\ \text{K}^{-1} = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G^0 = -2856.8\ \text{kJ mol}^{-1} - 298.15\ \text{K} \times (93.2\ \text{J mol}^{-1}\ \text{K}^{-1}) = -2884.6\ \text{kJ mol}^{-1}$

Ethane: $\Delta H^0 = -2856.8\ \text{kJ mol}^{-1}$; $\Delta S^0 = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$; $\Delta G^0 = -2884.6\ \text{kJ mol}^{-1}$

1.2 a) Amount of methane and ethane in 1 m^3 natural gas:

$m = \rho \times V = 0.740\ \text{g dm}^{-3} \times 1000\ \text{dm}^3 = 740\ \text{g}$

$M_{av} = \sum_i x(i)M(i) = (0.0024 \times 44.01\ \text{g mol}^{-1}) + (0.0134 \times 28.02\ \text{g mol}^{-1})$

$+ (0.9732 \times 16.05\ \text{g mol}^{-1}) + (0.011 \times 30.08\ \text{g mol}^{-1}) = 16.43\ \text{g mol}^{-1}$

$n_{tot} = m\ (M_{av})^{-1} = 740\ \text{g} \times (16.43\ \text{g/mol})^{-1} = 45.04\ \text{mol}$

$n(i) = x(i) \cdot n_{tot}$

$n(CH_4) = x(CH_4) \times n_{tot} = 0.9732 \times 45.04\ \text{mol} = 43.83\ \text{mol}$

$n(C_2H_6) = x(C_2H_6) \times n_{tot} = 0.0110 \times 45.04\ \text{mol} = 0.495\ \text{mol}$

b) Energy of combustion, deviation:

$E_{comb.}(H_2O(g)) = \sum_i n(i)\Delta_c H°(i) =$

$= 43.83\ \text{mol} \times (-802.5\ \text{kJ mol}^{-1}) + 0.495\ \text{mol} \times 0.5 \times (-2856.8\ \text{kJ mol}^{-1})$

$= -35881\ \text{kJ}$

$E_{comb.}(H_2O(g)) = -35881\ \text{kJ}$

Deviation from PUC

$E_{PUC}(H_2O(g)) = 9.981\ \text{kWh m}^{-3} \times 1\ \text{m}^3 \times 3600\ \text{kJ (kWh)}^{-1} = 35932\ \text{kJ}$

Deviation: $\Delta E = (E_{comb.}(H_2O(g)) - E_{PUC}(H_2O(g)) \times 100\ \% \times [E_{comb.}(H_2O(g))]^{-1}$

$= (35881\ \text{kJ} - 35932\ \text{kJ}) \times 100\ \% \times (35881\ \text{kJ})^{-1} = -0.14\%$

1.3 Energy for heating the water:

Volume of water: $V_{water} = 22.5\ \text{m}^3$

$n_{water} = V_{water}\ \rho_{water}\ (M_{water})^{-1} = 22.5\ m^3 \times 10^6\ g\ m^{-3} \times (18.02\ g\ mol^{-1})^{-1} = 1.249\times10^6\ mol$

$E_{water} = n_{water} \times C_p \times \Delta T = 1.249\times10^6\ mol \times 75.30\ J\ K^{-1}\ mol^{-1} \times 14\ K = 1316\ MJ$

Energy for heating the air:

Volume of the house is:

$V_{air} = (15\ m \times 8\ m \times 3\ m) + 0.5 \times (15\ m \times 8\ m \times 2\ m) = 480\ m^3$

$n_{air} = pV\ (RT)^{-1} = 1.013\times10^5\ Pa \times 480\ m^3 \times (8.314\ J\ (K\ mol)^{-1} \times 283.15\ K)^{-1} =$

$= 2.065\times10^4\ mol$

$C_p(air) = 0.21 \times 29.4\ J\ (K\ mol)^{-1} + 0.79 \times 29.1\ J\ (K\ mol)^{-1} = 29.16\ J\ (K\ mol)^{-1}$

$E_{air} = n_{air} \times C_p(air) \times \Delta T = 2.065\times10^4\ mol \times 29.17\ J\ (K\ mol)^{-1} \times 20\ K = 12.05\ MJ$

1.4 Energy for maintaining the temperature:

Surface area of the house:

$A_{house} = 3\ m \times 46\ m + 8\ m \times 2\ m + ((2\ m)^2 + (4\ m)^2)^{1/2} \times 2 \times 15\ m = 288.16\ m^2$

Heat conductivity: $\lambda_{wall} = 1\ J\ (s\ K\ m)^{-1}$

Energy flux along a temperature gradient (wall thickness d = 0.2 m)

$J = E_{loss}\ (A \times \Delta t)^{-1} = \lambda_{wall}\ \ \Delta T\ \ d^{-1}$

$E_{loss} = 288.16\ m^2 \times (12\cdot60\cdot60\ s) \times 1\ J\ (s\ K\ m)^{-1} \times 25\ K \times (0.2\ m)^{-1} = 1556\ MJ$

$E_{loss} = 1556\ MJ$

1.5 Total energy and costs:

Total energy: $E_{tot} = E_{water} + E_{air} + E_{loss} = 1316\ MJ + 12\ MJ + 1556\ MJ = 2884\ MJ$

2884 MJ corresponds to $2.884\times10^6\ kJ \times (3600\ s\ h^{-1} \times 9.981\ kJ\ s^{-1}\ m^{-3} \times 0.9)^{-1} = 89.18\ m^3$

Volume of gas: $V = 89.18\ m^3$

2884 MJ correspond to a cost of:

0.40 € $m^{-3} \times 89.18\ m^3$ = 35.67 €

Rent for equipment: 150.00 €

Total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

$2.884 \cdot 10^6$ kJ × 0.137 € × (3600 s h^{-1} × 1 kJ s^{-1} h)$^{-1}$ = 109.75 €

Rent for equipment: 100.00 €

Total cost of electric heating: 209.75 €

PROBLEM 2

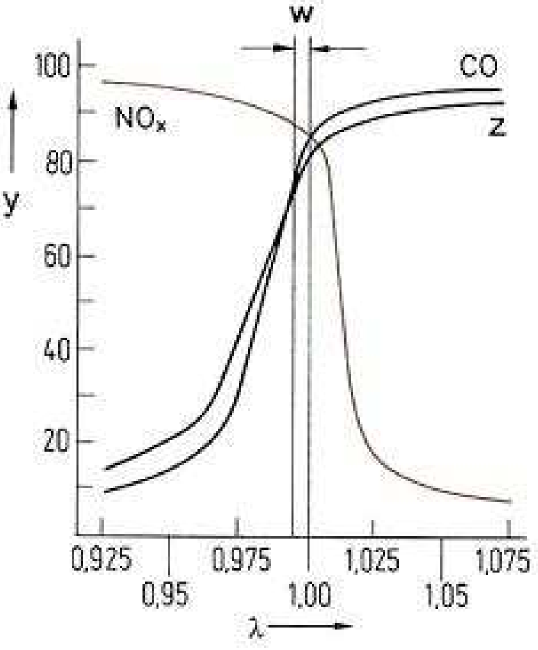
Kinetics at catalyst surfaces

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ-value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as $\lambda = \frac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}$.



w: λ-window
y: conversion efficiency (%)
z: Hydrocarbons

2.2 Decide the questions on the answer sheet concerning the λ probe.

The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 ℃ may be described by using the Langmuir isotherm with $K = 0.85\ \text{kPa}^{-1}$.

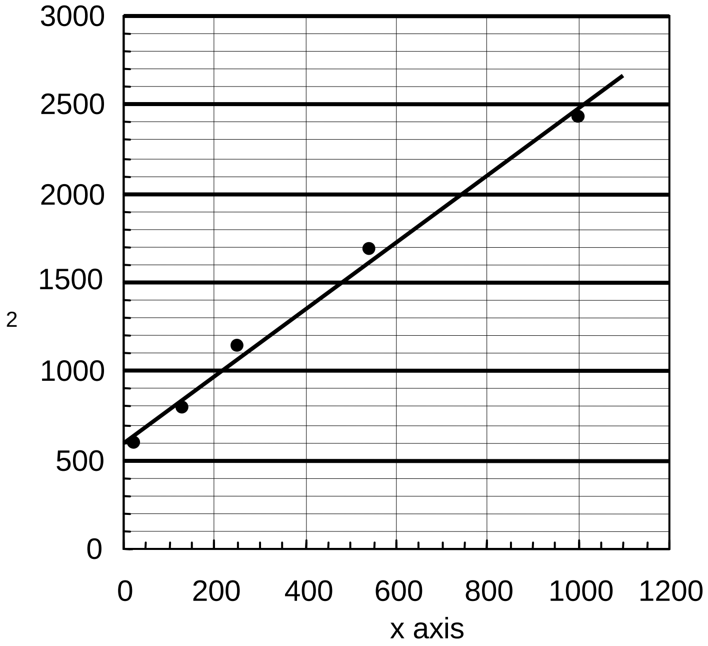
2.3 a) Determine the surface coverage θ at a pressure of 0.65 kPa.

b) Determine the pressure p at which 15 % of the surface is covered.

c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k\ \theta$

Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).

d) Data for the adsorption of another gas on a metal surface (at 25 ℃)



x axis: $p \cdot (\text{Pa})^{-1}$
y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

V_a is the gas volume that has been adsorbed.

If the Langmuir isotherm can be applied, determine the gas volume $V_{a,max}$ needed for a complete coverage of the metal surface and the product $K\ V_{a,max}$.

Hint: Set $\theta = V_a / V_{a,max}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,

$$\text{CO (ads.)} + 0.5\ \text{O}_2\ \text{(ads.)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{CO}_{500\,0}\ \text{(ads.)}$$

In a slow second step, CO_2 is then desorbed from the surface:

$$\text{CO}_2\ \text{(ads.)} \xrightarrow{k_2} \text{CO}_2\ \text{(g)}$$

2.4 Derive the formula for the reaction rate of the CO_2(g) - formation as a function of the partial pressures of the reaction components.

Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta_{\text{i}} = \frac{K_i \times p_i}{1 + \sum_j K_j \times p_j} \qquad \text{j: relevant gas components}$$

SOLUTION

2.1 Reaction equations:

$2\ CO + O_2 \rightarrow 2\ CO_2$

$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$

$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

2.2 Questions concerning the λ probe:

	true	false	no decision possible
If the λ-value is in the range of the λ-window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	☒	☐	☐
With λ > 1, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	☒	☐	☐
With λ < 0.975, nitrogen oxides can be reduced poorly.	☐	☒	☐

2.3 a) Surface coverage:

$$\theta = \frac{0.85\ \text{kPa}^{-1} \times 0.65\ \text{kPa}}{1 + 0.85 \times 0.65}$$

θ = 0.356 or 35.6 %

b) Pressure at which 15 % of the surface is covered:

$$\theta = \frac{K \times p}{1 + K \times p} \quad \Leftrightarrow \quad K \times p = \theta + \theta \times K \times p \quad \Leftrightarrow \quad p \cdot (K - \theta \times K) = \theta \quad \Leftrightarrow$$

$$p = \frac{\theta}{K - \theta \times K}$$

θ = 0.15

p = 0.21 kPa

c) Orders of decomposition:

Order of the decomposition reaction at low gas pressures	1
Order of the decomposition reaction at high gas pressures	0

Notes:

$$r = k \times \theta = k \, \frac{K \times p}{1 + K \times p},$$

p *low* $\Rightarrow \; p << \frac{1}{K} \Rightarrow r = k \; K \; p$ *reaction order 1.*

p *high* $\Rightarrow \; p >> \frac{1}{K} \Rightarrow r = k$ *reaction order 0.*

d) Gas volume $V_{\mathrm{a,max}}$ and product $K \cdot V_{\mathrm{a,max}}$:

$$\frac{1}{\theta} = \frac{1}{K \; p} + 1 = \frac{V_{\mathrm{a,max}}}{V_{\mathrm{a}}} \quad \Rightarrow \quad \frac{1}{K \, V_{\mathrm{a,max}}} + \frac{p}{V_{\mathrm{a,max}}} = \frac{p}{V_{\mathrm{a}}}$$

Slope: $\frac{1}{V_{\mathrm{a,max}}} = 1.9 \text{ cm}^{-3} \;\Rightarrow\; V_{\mathrm{a,max}} = 0.53 \text{ cm}^3$

Intercept: $\frac{1}{K \; V_{\mathrm{a,max}}} = 6 \times 10^2 \text{ Pa cm}^{-3} \quad \Rightarrow \quad K \, V_{\mathrm{a,max}} = 1.7 \times 10^{-3} \text{ Pa}^{-1} \text{ cm}^3$

2.4 Equation for reaction rate:

The information given in the text leads directly to $r = k_2 \; \theta_{\mathrm{CO_2}}$

The law of mass action for the first step of the mechanism is given by

$$\theta_{\mathrm{CO_2}} = \frac{k_1}{k_{-1}} \cdot \theta_{\mathrm{co}} \; \theta_{\mathrm{o_2}}^{\frac{1}{2}}, \;\Rightarrow \qquad r = k_2 \, \frac{k_1}{k_{-1}} \, \theta_{\mathrm{co}} \; \theta_{\mathrm{o_2}}^{\frac{1}{2}}.$$

The Langmuir isotherm gives:

$$\theta_{CO} = \frac{K_{CO}\ p_{CO}}{1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}} \text{ and } \theta_{O_2} = \frac{K_{O_2}\ p_{O_2}}{1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}}$$

$$r = k_2\ \frac{k_1}{k_{-1}}\ \frac{K_{CO}\ p_{CO}\left(K_{O_2}\ p_{O_2}\right)^{\frac{1}{2}}}{\left(1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}\right)^{\frac{3}{2}}}$$

PROBLEM 3

Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these "compounds" was not known but they are still of great interest to solid state chemists.

Attempts to reduce $CaCl_2$ to CaCl have been made with

(a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl.

After an attempt to reduce $CaCl_2$ with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When $CaCl_2$ is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When $CaCl_2$ is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(Ca) : n(Cl) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3.

3.4 a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.

b) What compound is formed by the reaction of $CaCl_2$ with carbon?
(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl. One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^0$ for CaCl
3	Triangular	0.155 – 0.225	BN	–663.8 kJ mol^{-1}
4	Tetrahedral	0.225 – 0.414	ZnS	–704.8 kJ mol^{-1}
6	Octahedral	0.414 – 0.732	NaCl	–751.9 kJ mol^{-1}
8	Cubic	0.732 – 1.000	CsCl	–758.4 kJ mol^{-1}

$\Delta_L H^0$(CaCl) is defined for the reaction $Ca^+(g) + Cl^-(g) \rightarrow CaCl(s)$

3.5 a) What type of structure is CaCl likely to have?

[$r(Ca^+) \approx 120$ pm (estimated), $r(Cl^-) \approx 167$ pm)]

Not only the lattice energy $\Delta_L H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^0$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^0$ (CaCl) with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{fusion}H^0$(Ca)		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1.\ IE}H$(Ca)	$Ca \rightarrow Ca^+$	589.7 kJ mol^{-1}
ionization enthalpy	$\Delta_{2.\ IE}H$(Ca)	$Ca^+ \rightarrow Ca^{2+}$	1145.0 kJ mol^{-1}
heat of vaporization	$\Delta_{vap}H^0$(Ca)		150.0 kJ mol^{-1}
dissociation energy	$\Delta_{diss}H(Cl_2)$	$Cl_2 \rightarrow 2\ Cl$	240.0 kJ mol^{-1}

enthalpy of formation	$\Delta_f H^0(CaCl_2)$		–796.0 kJ mol^{-1}
electron affinity	$\Delta_{EA}H(Cl)$	$Cl + e^- \rightarrow Cl^-$	–349.0 kJ mol^{-1}

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and $CaCl_2$ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

SOLUTION

3.1 Chemical equations:

(a) $CaCl_2 + Ca \rightarrow 2\ CaCl$

(b) $2\ CaCl_2 + H_2 \rightarrow 2\ CaCl + 2\ HCl$

(c) $4\ CaCl_2 + C \rightarrow 4\ CaCl + CCl_4$

3.2

Silvery metallic particles:	Ca
Colourless crystals:	$CaCl_2$

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and $CaCl_2$

3.3 Empirical formula:

100 % –(mass % Ca + mass % Cl) = mass % X

100 % –(52.36 % + 46.32 %) = 1.32 % X

mol % of Ca = 52.36 mass % / M(Ca)

= 52.36 mass % / 40.08 g mol^{-1} = 1.31 mol %

mol % of Cl = 46.32 mass % / M (Cl)

= 46.32 mass % / 35.45 g mol^{-1} = 1.31 mol %

mol % of X = 1.32 % X / M (H)

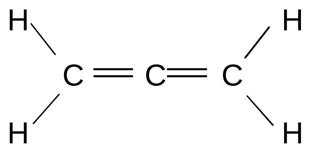
= 1.32 % X / 1.01 g mol^{-1} = 1.31 mol %

$n(Ca) : n(Cl) : n(H) = 1 : 1 : 1$

Empirical formula: CaClH

Notes: The reaction of $CaCl_2$ *with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.*

3.4 a) Structures only:



$H-C\equiv C-CH_3$

b) Empirical formula of the compound formed:

$Ca_3C_3Cl_2$

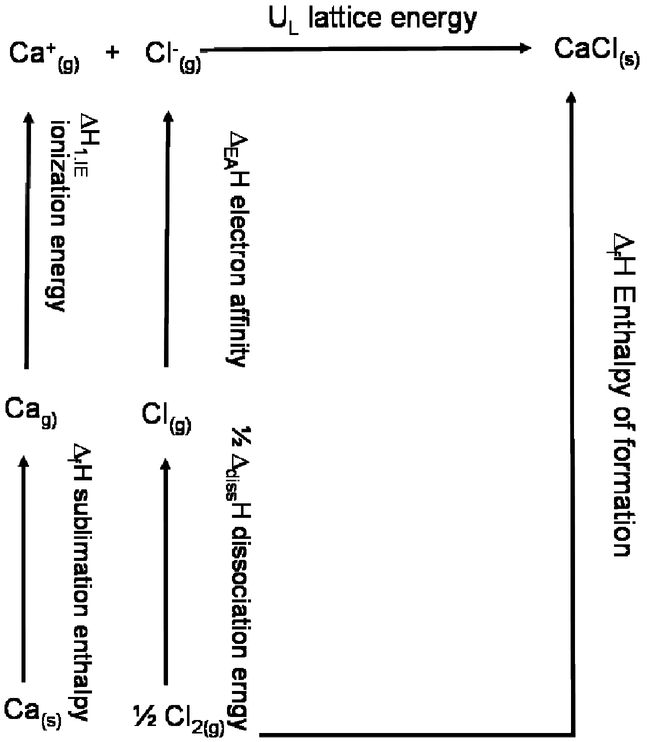
Notes: If the ratio of n(Ca) : n(Cl) = 1.5 : 1 [or better = 3 : 2 which can be rewritten as $CaCl_2 \cdot 2\,Ca^{2+} = Ca_3Cl_2^{4+}$ *] is given and the reduction product must contain a* C_3^{4-} *anion which needs two* Ca^{2+} *cations for electroneutrality, the composition* $Ca_3C_3Cl_2$ *will follow.*

3.5 a) Structure type CaCl likely to have:

$r(Ca^+)/r(Cl^-)$ = 120 pm / 167 pm = 0.719

NaCl	CsCl	ZnS	BN	no decision possible
☒	☐	☐	☐	☐

b) $\Delta_f H^0$(CaCl) with a Born-Haber-cycle:



Summing up of all the single steps of the Born-Haber-cycle:

$$\Delta_f H^0\ (CaCl) = \Delta_{subl}H^0(Ca) + \Delta_{1.\ IE}H(Ca) + \tfrac{1}{2}\ \Delta_{diss}H(Cl_2) + \Delta_{EA}H(Cl) + \Delta_L H(CaCl)$$

$$= (159.3 + 589.7 + 120 - 349.0 - 751.9)\ \text{kJ mol}^{-1}$$

$$= -231.9\ \text{kJ mol}^{-1}$$

3.6 Stability to disproportionation:

$2\ CaCl \rightarrow CaCl_2 + Ca$

$\Delta H = \Delta_f H^0(CaCl_2) - 2\ \Delta_f H^0(CaCl) = -796.0\ \text{kJ mol}^{-1} + 463.8\ \text{kJ mol}^{-1} = -332.2\ \text{kJ mol}^{-1}$

Disproportionation:	yes	no	no decision possible, more information needed
	☐	☒	☐

PROBLEM 4

Determining atomic masses

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2 : 1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

4.1 Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is m(Ag) : m(Y) = 11.88 : 1. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S. To convert 10.0 g of Argyrodite completely, 0.295 dm^3 of hydrogen are needed at 400 K and 100 kPa.

4.2 Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties. To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$ - vibrational frequency of the bond, in wavenumbers (cm^{-1})

c - speed of light

k - force constant, indicating the strength of the bond (N m^{-1}= kg s^{-2})

μ reduced mass in AB_4, which is given by $\mu = \dfrac{3\,m(A)\,m(B)}{3\,m(A) + 4\,m(B)}$

m(A), m(B) - the masses of the two bond atoms

The vibrational frequency of the C-H bond of methane is known to be 3030.00 cm^{-1}. The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1}. The bond enthalpy of a C-H bond in methane is 438.4 kJ mol^{-1}. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be 450.2 kJ mol^{-1}.

4.3 Determine the force constant *k* of a C-H bond using Hooke's law.

Estimate the force constant *k* of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

SOLUTION

4.1 Atomic mass of X, symbol of X, structures:

1) $X + 2\ H_2 \rightarrow XH_4$

2) $2\ X + 3\ H_2 \rightarrow X_2H_6$

i) $5.0\ \text{g} = [n_1(X) + n_2(X)] \cdot M(X)$

ii) $5.628\ \text{g} =$

$= n_1(XH_4) \times [M(X) + 4 \times 1.01\ \text{g mol}^{-1}] + n_2(X_2H_6)y \times [2\ M(X) + 6 \times 1.01\ \text{g mol}^{-1}]$

iii) $n_1(XH_4) = 2\ n_2(X_2H_6)$

iii,i) → i') $2\ n_1(X) \times M(X) = 5.0\ \text{g}$

iii,ii) → ii') $n_1(X) \times [2M(X) + 7.07\ \text{g mol}^{-1}] = 5.628\ \text{g}$

i',ii') → vi) $(5.0\ \text{g}) \times [2\ M(X)]^{-1} = (5.628\ \text{g}) \times [2\ M(X) + 7.07\ \text{g mol}^{-1}]^{-1}$

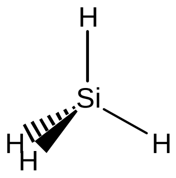
$M(X) = 3.535\ \text{g mol}^{-1} \times (5.628\ \text{g})^{-1} \times [(5.0\ \text{g})^{-1} - (5.628\ \text{g})^{-1}]^{-1}$

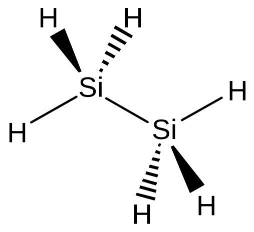
$M(X) = 28.14\ \text{g mol}^{-1}$

Atomic mass of X: $M(X) = 28.14\ \text{g mol}^{-1}$

Chemical symbol of X: Si

3D structures of the two products:





4.2 Atomic mass of Y and empirical formula of Argyrodite:

$Ag_aY_bS_{0.5\cdot a + 2\cdot b}$ + b H_2 $\rightarrow$ 0.5a Ag_2S + b YS + b H_2S

i) 10 g = $n(Ag_aY_bS_{0.5\cdot a+2\cdot b}) \times$ [a 107.87 g mol^{-1} + b M(Y) +
+ (0.5 a + 2 b) $\times$ 32.07 g mol^{-1}]

ii) $n(H_2) = \dfrac{pV(H_2)}{RT}$ $\qquad$ $n(H_2) = \dfrac{100\ \text{kPa} \times 0.295 \times 10^{-3}\ \text{m}^3}{8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 400\ \text{K}}$

$n(H_2) = 8.871 \times 10^{-3}$ mol $\qquad$ $n(Ag_aY_bS_{0.5\cdot a + 2\cdot b}) = b^{-1} \times 8.871\cdot10^{-3}$ mol

iii) $11.88 = \dfrac{a \times 107.87\ \text{g mol}^{-1}}{b \times M(Y)}$ $\qquad$ a 107.87 g mol^{-1} = 11.88 $\times$ b $\times$ M(Y)

ii,i) $\rightarrow$ ii')

b $\times$10 g $\times$ (8.871·10^{-3} mol)$^{-1}$ =

= a 107.87 g mol^{-1} + b M(Y) + (0.5 a + 2 b) $\times$32.07 g mol^{-1}

b 1127 g mol^{-1} = a 107.87 g mol^{-1} + b M(Y) + (0.5 a + 2 b) $\times$32.07 g mol^{-1}

iii,ii')$\rightarrow$iv)

b·1127 g mol^{-1} = 11.88·b·M(Y) + b·M(Y) + (0.5·a + 2b)·32.07 g mol^{-1}

b·1127 g mol^{-1} =

$$= 11.88\ b\ M(Y) + b\ M(Y) + \left(0.5\ \frac{11.88 \times b \times M(Y)}{107.87\ \text{gmol}^{-1}} + 2\ b\right) \times 32.07\ \text{g mol}^{-1}$$

M(Y) = 72.57 g mol^{-1} $\rightarrow$ iii $\qquad$ a : b = 8 : 1

Chemical symbol of Y: Ge

Empirical formula of Argyrodite: Ag_8GeS_6

4.3 The force constants of a C-H bond:

$$k(\text{C-H}) = [2\pi\, c\ \tilde{\nu}\ (\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3\,M(\text{C}) \times M(\text{H})}{3\,M(\text{C}) + 4\,M(\text{H})}$$

$$= [2\pi \times\ 3{\cdot}10^{10}\ \text{cm s}^{-1} \times 3030\ \text{cm}^{-1}]^2 \frac{1}{6.022 \times 10^{23}\ \text{mol}^{-1}} \times \frac{3 \times 12.01 \times 1.01}{3 \times 12.01 + 4 \times 1.01}\ \text{g mol}^{-1}$$

$k(\text{C-H}) = 491.94\ \text{N m}^{-1}$

The force constants of a Z-H bond:

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(\text{Z-H})}{\Delta_b H(\text{C-H})}$$

$$= 491.94\ \text{N m}^{-1}{\cdot}450.2\ \text{kJ mol}^{-1}{\cdot}[438.4\ \text{kJ mol}^{-1}]^{-1} = 505.18\ \text{N m}^{-1}$$

The atomic mass and symbol of Z:

$$\frac{3\,M(\text{Z}) \times M(\text{H})}{3\,M(\text{Z}) + 4\,M(\text{H})} = \frac{k(\text{Z-H}) \times N_A}{[2\pi\, c\, \tilde{\nu}(\text{Z-H})]^2}$$

$$M(\text{Z}) = \frac{4}{3}\left(\frac{[2\pi\, c\, \tilde{\nu}(\text{Z-H})]^2}{k(\text{Z-H}) \cdot N_A} - \frac{1}{M(\text{H})}\right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3}\left(\frac{[2\pi \times 3 \cdot 10^{10} \times 2938.45]^2}{505180 \times 6.022 \cdot 10^{23}} - \frac{1}{1.01}\right)^{-1} \text{g mol}^{-1}$$

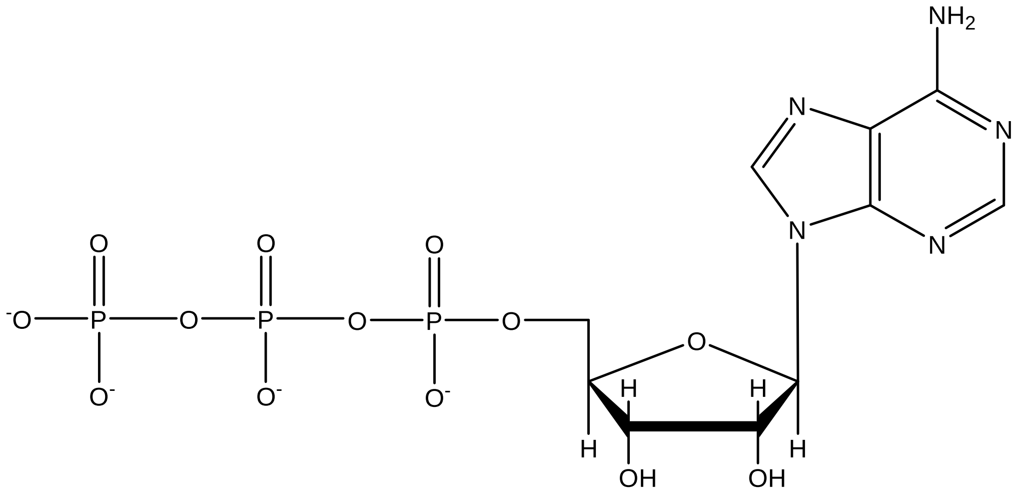
Atomic mass of Z: $M(\text{Z}) = 72.68\ \text{g mol}^{-1}$

Chemical symbol of Z: Ge

PROBLEM 5

Biochemistry with Thermodynamics

Structure of ATP^{4-}



Shifting chemical equilibria with ATP:

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$$c(ATP^{4-}) = 2.25 \text{ mmol dm}^{-3}$$
$$c(ADP^{3-}) = 0.25 \text{ mmol dm}^{-3}$$
$$c(HPO_4^{2-}) = 1.65 \text{ mmol dm}^{-3}$$

Free energy stored in ATP can be released according to the following reaction:

$$ATP^{4-} + H_2O \rightleftarrows ADP^{3-} + HPO_4^{2-} + H^+ \qquad \Delta G^o = -30.5 \text{ kJ mol}^{-1} \qquad (1)$$

As the pH is close to 7 in most living cells, biochemists use ΔG^o instead of ΔG°. The standard state of ΔG^o is defined as having a constant pH of 7. In equations with ΔG^o and K' for reactions at $pH = 7$ the concentration of H^+ is therefore omitted. Standard concentration is 1 mol dm^{-3}.

5.1 Calculate the actual Δ*G'* of reaction (1) in the red blood cell at 25 ℃ and *pH* = 7.

In living cells many so-called “anabolic” reactions take place, which are at first sight thermodynamically unfavourable because of a positive Δ*G*. The phosphorylation of glucose is an example:

glucose + $HPO_4^{2-} \rightleftharpoons$ glucose 6-phosphate^{2-} + H_2O $\Delta G°' = +13.8$ kJ mol^{-1} (2)

5.2 Calculate first the equilibrium constant *K*' of reaction (2) and then the ratio *c*(glucose 6-phosphate) / *c*(glucose) in the red blood cell in chemical equilibrium at 25 ℃ and *pH* = 7.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:

$$\text{glucose} + \text{ATP}^{4-} \overset{\text{hexokinase}}{\rightleftharpoons} \text{glucose 6-phosphate}^{2-} + \text{ADP}^{3-} + \text{H}^+ \qquad (3)$$

5.3 Calculate Δ*G*° and *K*' of reaction (3).

What is now the ratio c(glucose 6-phosphate) / c(glucose) in the red blood cell in chemical equilibrium at 25 ℃ and *pH* = 7?

ATP synthesis:

An adult person ingests about 8000 kJ of energy (Δ*G*') per day with the food.

5.4 a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a Δ*G*' of –52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.

b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?

c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.

In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

5.5 a) How many protons (H^+) are in a spherical mitochondrium with a diameter of 1 μm at $pH = 7$?

b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.

SOLUTION

5.1 Actual $\Delta G'$ of reaction (1):

$$\Delta G' = \Delta G^{o\prime} + R\ T\ \ln \frac{[ADP^{3-}]\,[HPO_4^{2-}]}{[ATP^{4-}]}$$

$$= -30500\ \text{J mol}^{-1} + 8.314\ \text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\ \text{K} \times \ln \frac{0.00025 \times 0.00165}{0.00225}$$

$$= -30.5\ \text{kJ mol}^{-1} - 21.3\ \text{kJ mol}^{-1} = -51.8\ \text{kJ mol}^{-1}$$

5.2 Equilibrium constant K' of reaction (2), ratio c(glucose 6-phosphate) / c(glucose):

$$\Delta G^{o\prime} = -R\ T\ lnK'$$

$$K' = e^{-\Delta G^{o\prime}/RT} = e^{-13800\ \text{J/mol} / (8.314\ \text{J/(mol K)}\ \cdot\ 298.15\ \text{K})} = 0.0038$$

$$K' = \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]\,[HPO_4^{2-}]}$$

$$\frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]} = K' \cdot [HPO_4^{2-}]$$

$$= 0.0038 \cdot 0.00165$$

$$= 6.3 \cdot 10^{-6}$$

5.3 $\Delta G^{o\prime}$ and K' of reaction (3), ratio c(glucose 6-phosphate) / c(glucose):

$$\Delta G^{o\prime}(3) = \Delta G^{o\prime}(1) + \Delta G^{o\prime}(2) = -30.5\ \text{kJ mol}^{-1} + 13.8\ \text{kJ mol}^{-1} = -16.7\ \text{kJ mol}^{-1}$$

$$\Delta G^{o\prime} = -R\ T\ lnK'$$

$$K' = e^{-\Delta G^{o\prime}/RT} = e^{16700\ \text{J/mol} / (8.314\ \text{J/(mol K)}\ \cdot\ 298.15\ \text{K})} = 843$$

$$K' = \frac{c(\text{glucose 6-phosphate}) \times c(\text{ADP}^{3-})}{c(\text{glucose}) \times c(\text{ATP}^{4-})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K'\,\frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})}$$

$$= 843 \times (2.25 \text{ mmol dm}^{-3} / 0.25 \text{ mmol dm}^{-3}) = 7587$$

5.4 a) Mass of ATP produced per day:

Energy available for ATP synthesis: 8000 kJ day^{-1} × 0.5 = 4000 kJ day^{-1}

Energy required for synthesis of ATP: 52 kJ mol^{-1}

Amount of ATP produced: 4000 kJ day^{-1} / 52 kJ mol^{-1} = 76.9 mol day^{-1}

Mass of ATP produced: 76.9 mol day^{-1} × 503 g mol^{-1} = 38700 g day^{-1}

$\underline{m_{\textbf{day-1}} = 38.7 \text{ kg day}^{-1}}$

b) Mass of ATP in the human body:

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day

Mass of ATP in the body: 38.7 kg day^{-1} / (1440 min day^{-1}) · 1 min = 26.9 g

m_{body} **=** 26.9 g

c) What happens to the rest of the free energy? Mark one correct answer:

- It is used to reduce the entropy of the body. ☐
- It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule. ☐
- It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP. ☐
- It heats the body of the person. ☒

5.5 a) How many protons are in a spherical mitochondrium with a diameter of 1 m at *pH* = 7?

$V = 4/3\ \pi\ r^3 = 4/3\ \pi\ (0.5\times10^{-6} \text{ m})^3 = 5.2\times10^{-19} \text{ m}^3 = 5.2\times10^{-16} \text{ dm}^3$

$c = 1\times10^{-7} \text{ mol dm}^{-3}$

$n = V\,c\cdot N_A = 5.2\times10^{-16} \text{ dm}^3 \times 1\times10^{-7} \text{ mol dm}^{-3} \times 6.022\times10^{23} \text{ mol}^{-1} = 31$

b) How many protons have to enter a mitochondrium?

Number of ATP molecules:

$$n(ATP) \quad = \quad \frac{m(\text{ATP})\, N_A}{M(\text{ATP})} \quad = \quad \frac{0.2 \times 10^{-15}\, g \times 6.022 \times 10^{23}\, \text{mol}^{-1}}{503\ \text{g mol}^{-1}} \quad = \quad 239400$$

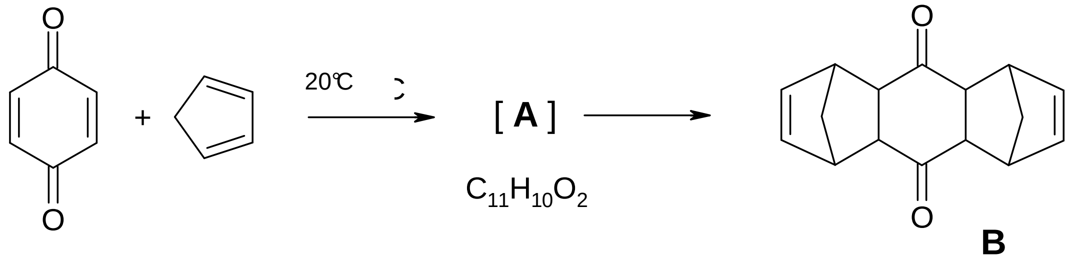
Number of H^+ per cell: $n(H^+_{\text{per cell}}) = n(\text{ATP}) \times 3 = 718300$

Number of H^+ per mitochondrium: $n(H^+_{\text{mit}}) = n(H^+_{\text{per cell}}) / 1000 = 718$

PROBLEM 6

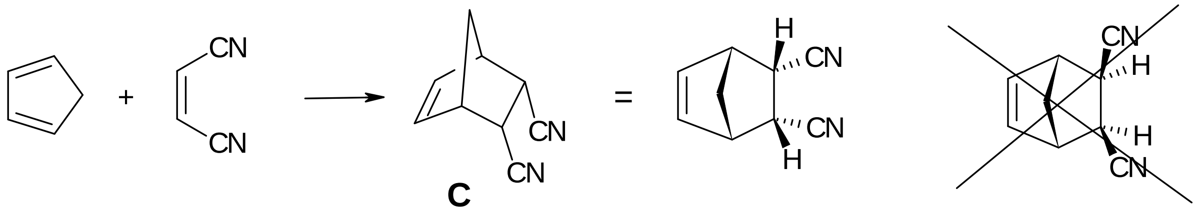
Diels-Alder Reactions

The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:



6.1 Draw the structure of **A** (without stereochemical information).

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



Not formed

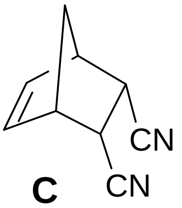
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

6.2 Give the structures of **D1** and **D2**.

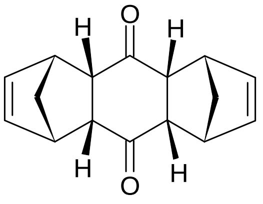
Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

Hints:

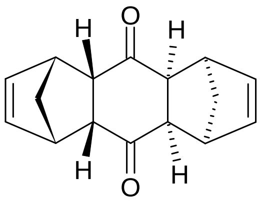
- keep the stereospecific formation of **C** in mind and
- the sterically less hindered isomer forms.



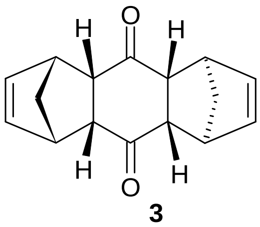
C



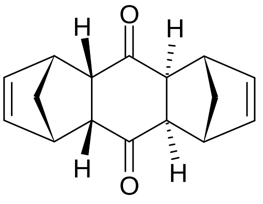
1



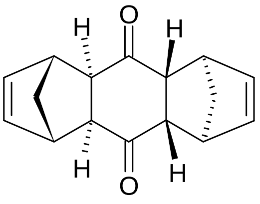
2



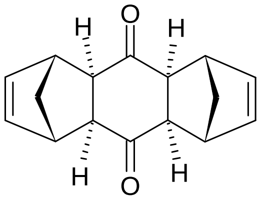
3



4



5



6

6.3 Which single isomer of the six stereoisomers 1-6 of B shown above did they isolate?

After prolonged heating (15h, 120 ℃) of the originally isolated stereoisomer **B** (melting point mp: 157 ℃), Diels and Alder obtained two new stereoisomers **E** (mp: 153 ℃) and **F** (mp: 163 ℃). Equilibration of **B** with a catalytic amount of a strong base at 25 ℃ gave a further stereoisomer **G** (mp: 184 ℃).

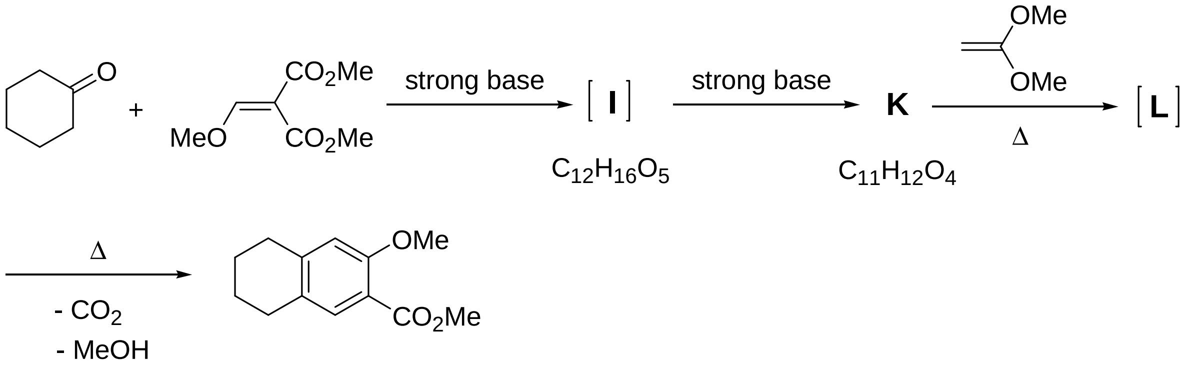
$$\underset{10\%}{\mathbf{B}} \rightleftharpoons \underset{20\%}{\mathbf{E}} + \underset{70\%}{\mathbf{F}}$$

$$\underset{60\%}{\mathbf{B}} \rightleftharpoons \underset{40\%}{\mathbf{G}}$$

6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.

Hint: You do not need to know, which of the six stereoisomers 1 – 6 (shown above) corresponds to either **E**, **F** or **G** in order to answer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.



6.5 Draw the structures for **I**, **K** and **L**.

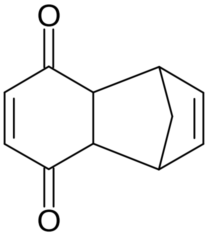
Hints: - **K** has only one methyl group.

- **L** is the Diels-Alder adduct of K and the alkene shown.

SOLUTION

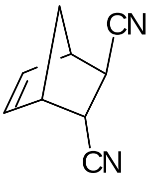
6.1 Structure of **A** only:

[**A**] :

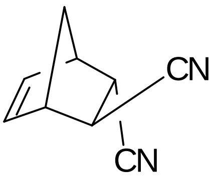


6.2 Structures of **D1, D2 only:**

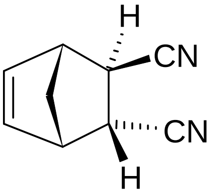
D1:

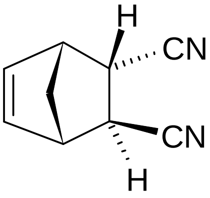


D2:



alternatively, the following structures are also correct:





Note: The two compounds are enantiomers

6.3 Correct structure of **B** (circle only one):

1 [✓ **2**] **3** **4** **5** **6**

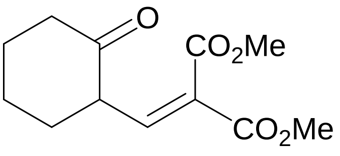
Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure ***C****. As shown in structure* ***C*** *this endo- configuration is characterized by the two H atoms and the* CH_2*-bridge of the bicyclic system being on the same side of the ring. Only structures* ***1*** *and* ***2*** *of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure* ***1*** *the three rings form a U-shaped molecule which is sterically more hindered than structure* ***2*** *which has a zig-zag structure.*

6.4 Decide the questions concerning the Diels-Alder reaction.

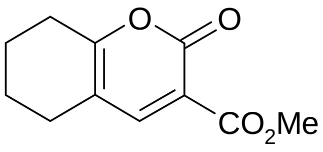
	true	false	no decision possible
• The Diels-Alder reaction is reversible	☒	☐	☐
• The formation of **B** in the original reaction is thermodynamically controlled	☐	☒	☐
• **B** is thermodynamically more stable than **E**	☐	☒	☐
• **E** is thermodynamically less stable than **F**	☒	☐	☐
• **G** is an enantiomer of **B**	☐	☒	☐
• **G** is thermodynamically more stable than **F**	☐	☐	☒

6.5 Structures of **I**, **K**, **L** only:

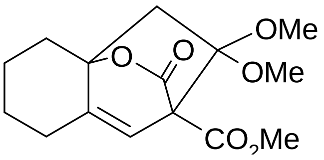
I



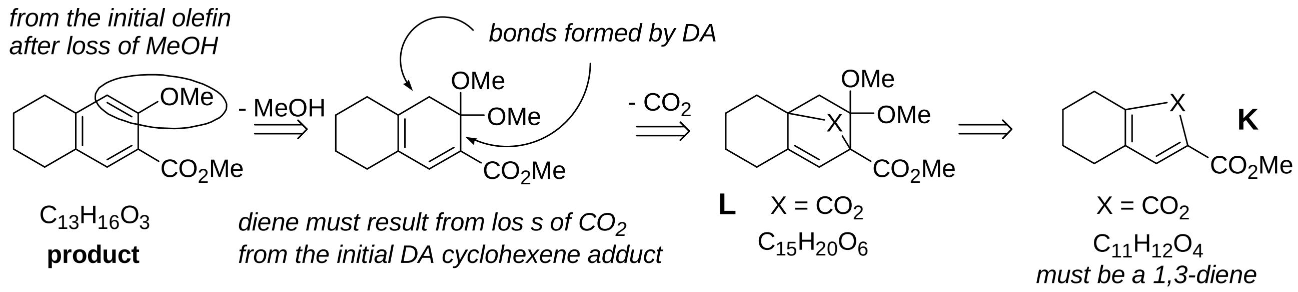
K

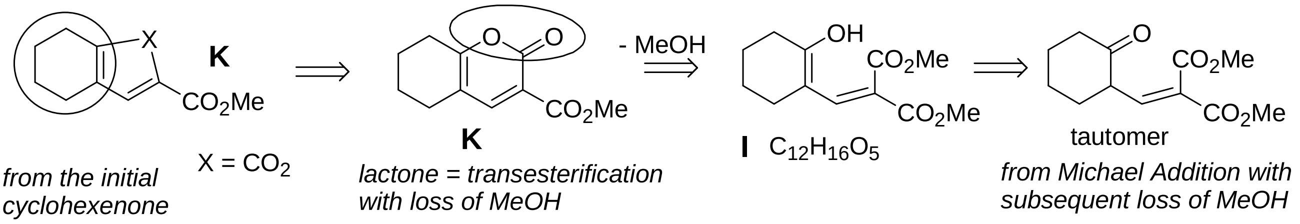


L



Notes:


from the initial olefin after loss of MeOH
OMe
CO2Me
C13H16O3
product
- MeOH
bonds formed by DA
OMe
OMe
CO2Me
diene must result from los s of CO2 from the initial DA cyclohexene adduct
- CO2
OMe
X
OMe
CO2Me
L
X = CO2
C15H20O6
X
K
CO2Me
X = CO2
C11H12O4
must be a 1,3-diene


X
K
CO2Me
X = CO2
from the initial cyclohexenone
O
O
CO2Me
K
lactone = transesterification with loss of MeOH
- MeOH
OH
CO2Me
CO2Me
I
C12H16O5
O
CO2Me
CO2Me
tautomer
from Michael Addition with subsequent loss of MeOH

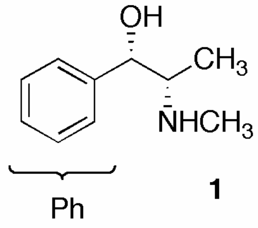
PROBLEM 7

Stereochemistry in Drugs

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system.

Pseudoephedrine (**1**) is a constituent in many common drugs against colds, e.g. in nasal sprays.



1

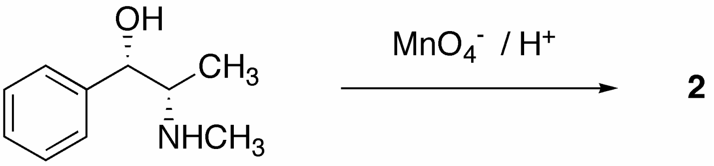
7.2 Mark the stereocenters in **1** with an asterisk * on the answer sheet.

Order the substituents on each stereocenter in **1** according to their priority and determine their absolute configuration (*R* or *S*).

7.3 Draw a Newman or a sawhorse representation of **1**.

Draw a Fischer representation of **1**.

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:



1

7.4 Draw the stereochemically correct structure of compound **2** and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on <u>all</u> atoms which undergo a change in their formal oxidation numbers.

The treatment of **2** with $LiAlH_4$ results exclusively in compound **3**, which differs from **1** in its melting point.

$$\mathbf{2} \xrightarrow{LiAlH_4} \mathbf{3}$$

7.5 a) Draw the stereochemically correct structure of **3**.

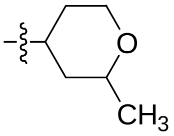
b) Decide the statements on the answer sheet concerning isomers.

c) Draw a structural model to rationalize the exclusive formation of **3** from **2**.

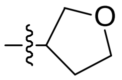
SOLUTION

7.1 Fill in < or > (A < B means A has a priority lower than B) :

-§-SCH_3 $\boxed{>}$ -§-$P(CH_3)_2$

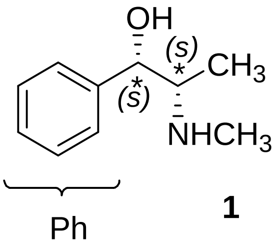


$\boxed{<}$



-§-CCl_3 $\boxed{<}$ -§-CH_2Br

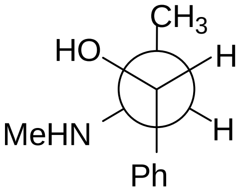
7.2



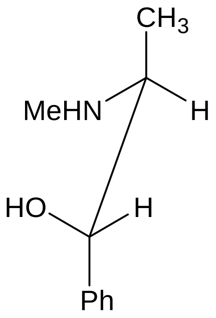
1

highest priority →			lowest priority
OH	$CH(NHCH_3)CH_3$	Ph	H
$NHCH_3$	CH(OH)Ph	CH_3	H

7.3 Newman projection or sawhorse projection of **1**:

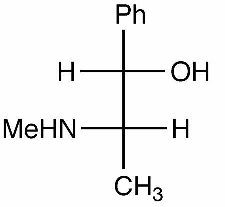


or

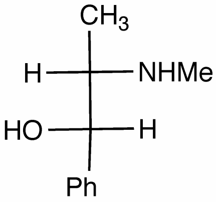


(Me = CH_3)

Fischer projection of **1**:

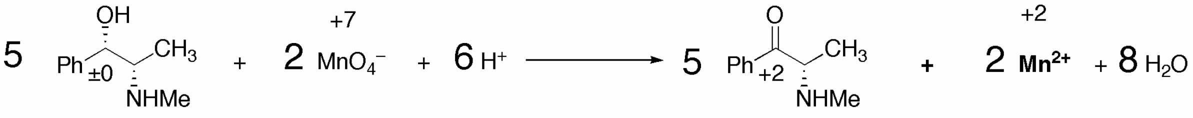


or



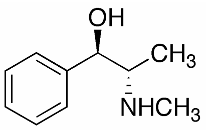
(Me = CH_3)

7.4 Equation with oxidation numbers and stereochemically correct structure of **2**:



1 **2**

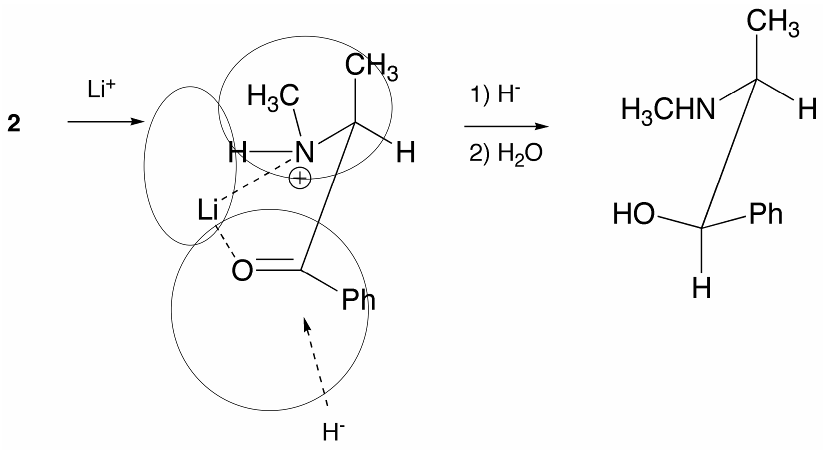
7.5 a) Structure of **3** (correct stereochemistry)**:**



b) Statements concerning isomers:

	true	false
1 and **3** are stereo-isomers	☒	☐
1 and **3** are enantiomers	☐	☒
1 and **3** are diastereomers	☒	☐
1 and **3** are conformational isomers	☐	☒

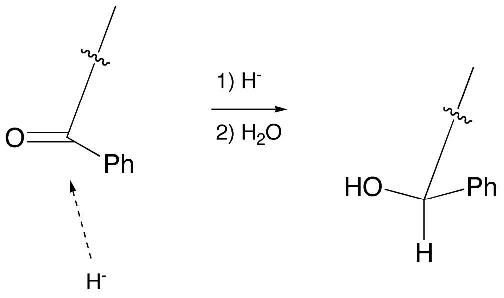
c) Draw a structural model to rationalize the exclusive formation of **3** from **2**



Notes: Attack of hydride occurs from the sterically least hindered side.

Full points will also be given for an explanation using the formation of a hydrogen bond.

1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.



PROBLEM 8

Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

(T = 298.15 K throughout whole problem)

Solution **A** is an aqueous solution of $CaCl_2$ with a concentration of 1.780 g dm^{-3}. Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3}.

$pK_{a1}(H_2CO_3) = 6.37$ $pK_{a2}(HCO_3^-) = 10.33$

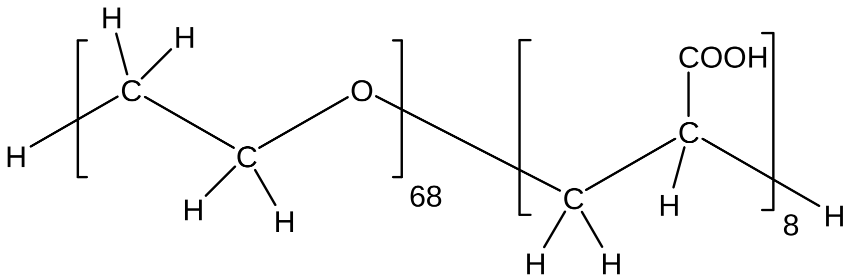
8.1 Calculate the pH of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**. Solution **C** is adjusted to pH 10. A precipitate forms.

$K_{sp}(Ca(OH)_2) = 6.46\times10^{-6}$ $K_{sp}(CaCO_3) = 3.31\times10^{-9}$

8.2 Show by calculation for each of the compounds $Ca(OH)_2$ and $CaCO_3$ whether it can be found in the precipitate or not.

In a similar experiment 100 cm^3 of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (**A**+**B**) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3 Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 cm^3 of an aqueous NaOH solution (c(NaOH) = 0.19 mol dm^{-3}). The solution is diluted by the addition of 200 cm^3 of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a *pH* of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8$ g mol^{-1}
- The charge of the particles is found to be Z = –800 (number of unit charges).
  (pK_a(COOH, copolymer) = 4.88)

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

8.5 Calculate which modification of calcium carbonate has been formed.

Modification	density
Calcite	2.71 g cm^{-3}
Vaterite	2.54 g cm^{-3}
Aragonite	2.95 g cm^{-3}

SOLUTION

8.1 pH of solution **B**:

$$K_{b2} = \frac{c(\text{HCO}_3^-)/(1\text{ mol dm}^{-3}) \times c(\text{OH}^-)/(1\text{ mol dm}^{-3})}{c(\text{CO}_3^{2-})/(1\text{ mol dm}^{-3})} \qquad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$$K_{b2} = 2.14\times10^{-4}$$

$K_{b1} = 2.34\times10^{-8}$

Since $K_{b2} >> K_{b1}$, only one protonation step of the CO_3^{2-} has to be considered.

$c(HCO_3^-) = c(OH^-) = x$ and $c(CO_3^{2-}) = c_0(CO_3^{2-}) - x$

$$c_0(Na_2CO_3) = \frac{1.700\text{ g dm}^{-3}}{105.99\text{ g mol}^{-1}}$$

$c_0(Na_2CO_3) = c_0(CO_3^{2-}) = 0.016\text{ mol dm}^{-3}$

$$K_{b2} = \frac{x^2/(1\text{ mol dm}^{-3})}{(c_0(CO_3^{2-}) - x)} \qquad x = c(OH^-) = 1.75\times10^{-3}\text{ mol dm}^{-3}$$

$pH = 11.2$

8.2 $Ca(OH)_2$, $CaCO_3$ in the precipitate?

$M(CaCl_2) = 110.98\text{ g mol}^{-1}$ $pH = 10$, $c(OH^-) = 1\times10^{-4}\text{ mol dm}^{-3}$

$$c_0(Na_2CO_3) = \frac{1.700\text{ g cm}^{-3}}{105.99\text{ g mol}^{-1}\times 2} \qquad c(CaCl_2) = \frac{1.780\text{ g dm}^{-3}}{110.98\text{ g mol}^{-1}\times 2}$$

$c_0(Na_2CO_3) = 8.0\times10^{-3}\text{ mol dm}^{-3}$ $c(CaCl_2) = c_0(Ca^{2+}) = 8.0\times10^{-3}\text{ mol dm}^{-3}$

Calculations for $Ca(OH)_2$:

$c(OH^-)^2 \times c_0(Ca^{2+}) = 8\times10^{-11} < 6.46\times10^{-6} = K_{sp}(Ca(OH)_2)$ no precipitate

Calculations for $CaCO_3$:

$$K_{b2} = \frac{c(HCO_3^-)\times c(OH^-)}{c(CO_3^{2-})}, \qquad c(HCO_3^-) = \frac{K_{b2}}{c(OH^-)} \times c(CO_3^{2-})$$

$c(HCO_3^-) = 2.14 \times c(CO_3^{2-})$ and $c(HCO_3^-) + c(CO_3^{2-}) = c_0(Na_2CO_3)$

$2.14 \times c(CO_3^{2-}) + c(CO_3^{2-}) = 8.0\times10^{-3}\text{ mol dm}^{-3}$

Initial concentration of CO_3^{2-} in solution **C**: $c(CO_3^{2-}) = 2.55\times10^{-3}\text{ mol dm}^{-3}$

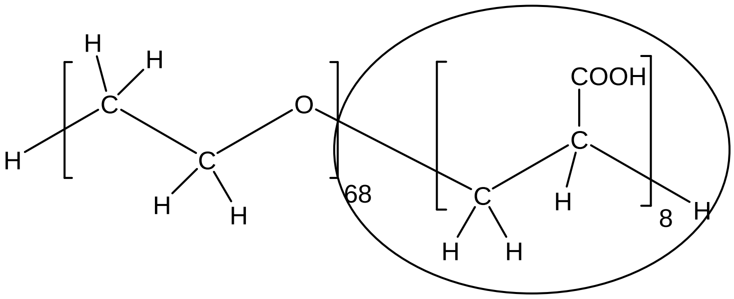
Initial concentration of Ca^{2+} in solution **C**: $c(Ca^{2+}) = 8.0\times10^{-3}\text{ mol dm}^{-3}$

hence $c(\mathrm{CO_3^{2-}}) \times c(\mathrm{Ca^{2+}}) = 2.04\times10^{-5} > 3.3\times10^{-9} = K_{sp}(\mathrm{CaCO_3})$ precipitate

$Ca(OH)_2$ will be found in the precipitate yes ☐ no ☒

$CaCO_3$ will be found in the precipitate yes ☒ no ☐

8.3 Circle the <u>block</u> that attaches to the $CaCO_3$ crystal:



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

$$\mathrm{RCOOH + OH^- \rightleftarrows RCOO^- + H_2O} \qquad pK_b = 9.12$$

pH and *pK$_a$* lead to the total concentration of COOH groups in the solution:

$c(\mathrm{COO^-}) = \mathrm{x}$ $\qquad c(\mathrm{COOH}) = c_0(\mathrm{COOH}) - \mathrm{x}$ $\qquad \mathrm{x} = c_0(\mathrm{OH^-}) - c(\mathrm{OH^-})$

$c_0(\mathrm{OH^-}) = \dfrac{50\ \mathrm{cm^3}}{250\ \mathrm{cm^3}}\ 0.19\ \mathrm{mol\ dm^{-3}}$ $\qquad c_0(\mathrm{OH^-}) = 0.038\ \mathrm{mol\ dm^{-3}}$

$c(\mathrm{OH^-}) = 10^{-1.7}\ \mathrm{mol\ dm^{-3}} = 0.02\ \mathrm{mol\ dm^{-3}}$ $\qquad \mathrm{x} = 0.018\ \mathrm{mol\ dm^{-3}}$

$$K_b = \frac{(c_0(\mathrm{COOH})\ \text{-x}) / (1\ \mathrm{mol\ dm^{-3}}) \times c(\mathrm{OH^-}) / (1\ \mathrm{mol\ dm^{-3}})}{\mathrm{x} / (1\ \mathrm{mol\ dm^{-3}})}$$

$$c_0(\text{COOH}) = \frac{K_b\ \text{x} \times (1\ \text{mol dm}^{-3})}{c(\text{OH}^-)} + \text{x}$$

$$c_0(\text{COOH}) = \left(\frac{0.018 \times 10^{-9.12}}{0.02} + 0.018\right) \text{mol dm}^{-3}$$

c_0(COOH) = 0.018 mol dm^{-3}

(Or as pH >> pK_a : c_0(COOH) = c(COOH) + x ≈ x)

T*otal concentration of polymer chains* $c(\text{polymer}) = \dfrac{c_0(\text{COOH})}{8}$

M(polymer) = $M(C_{160}O_{84}H_{306})$ = 3574.66 g mol^{-1}

m(polymer) = c(polymer) × V × M(polymer)

$$m(\text{polymer}) = \frac{c_0(\text{COOH}) \times V \times M(\text{polymer})}{8} = \frac{0.018 \times 0.250 \times 3574.66}{8}\text{g} = 2.0\ \text{g}$$

8.5 Modification of CaCO$_3$:

The charge of the particles is caused by the number of protolized COOH groups per particle.

$c(\text{COO}^-) \approx c_0(\text{COOH})$, $\alpha \approx 1$

Number of COOH groups per particle: $N_{\text{COOH}} = \dfrac{|Z|}{\alpha}$ $N_{\text{COOH}} = 800$

Number of polymer chains per particle: $N_{\text{polymer}} = \dfrac{N_{\text{COOH}}}{8} = 100$

The number of polymers per particle indicates the mass of polymer per particle. Thus, the mass of the calcium carbonate particle can be calculated:

M(CaCO$_3$ particle) = M(total particle) – N_{polymer} M(polymer)

M(CaCO$_3$ particle) = 8.01×10^8 g mol^{-1} – 100 × 3574.66 g mol^{-1}

M(CaCO$_3$ particle) = 8.01×10^8 g mol^{-1}

Mass of one CaCO$_3$ particle: m(CaCO$_3$ particle) = M(CaCO$_3$ particle) · N_A^{-1}

and with the volume of the spherical particle ($V = \frac{4}{3}\pi r^3$) the density can be calculated:

$$\rho(\text{CaCO}_3) = \frac{m(\text{CaCO}_3\text{ particle})}{V(\text{CaCO}_3\text{ particle})} = \frac{3\,m(\text{CaCO}_3\text{ particle})}{4\pi r^3}$$

$$= \frac{3\,(M\ (\text{total particle}) - N_{\text{polymer}}\ M(\text{polymer})\,)}{N_a 4\pi\, r^3}$$

$$= \frac{3 \times 8.01\times10^8\ \text{g mol}^{-1}}{N_A \cdot 4\pi\,(5\times10^{-6}\text{cm})^3} = 2.54\ \text{g cm}^{-3}$$

The modification of calcium carbonate is Calcite ☐ Vaterite ☒ Aragonite ☐

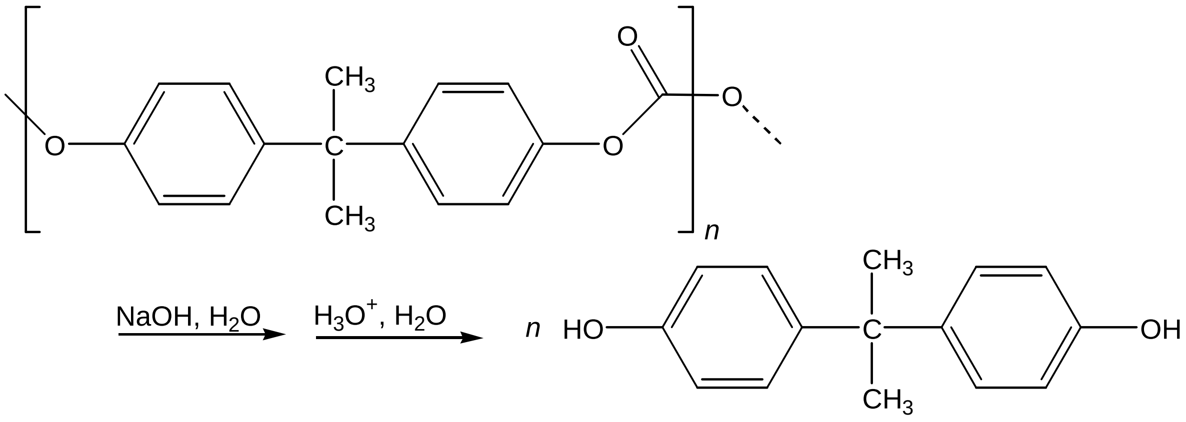
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

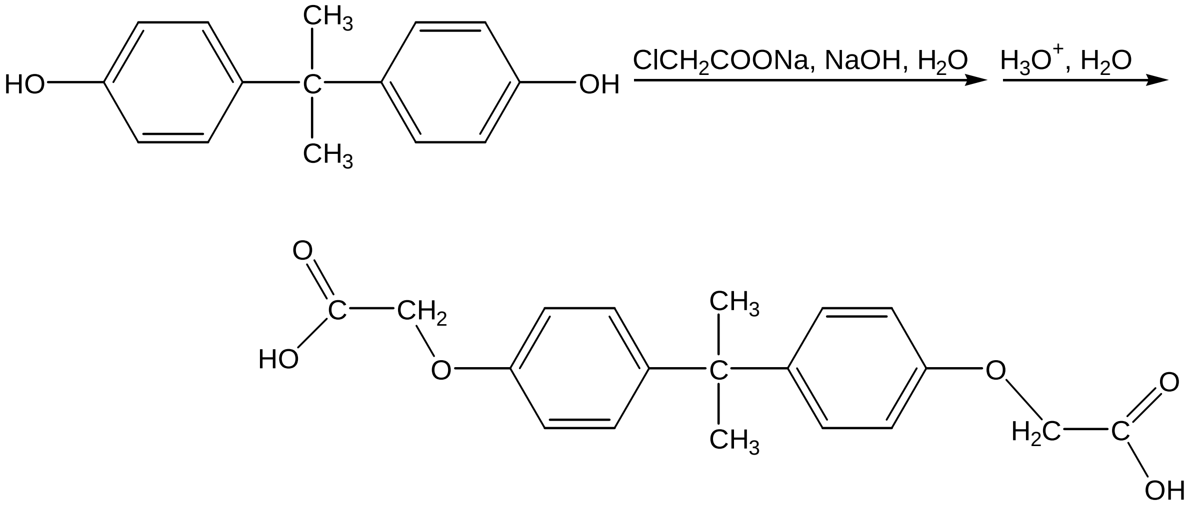
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyaceticacid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
  (Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
  (Filling of the melting point tubes in step 1 will be done by the organizer.)
  (The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1: Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. **1**), 4.0 g of sodium hydroxide (No. **5**) and 3 cm^3 of demineralized water into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 cm^3 of ethanol (No. **2**) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 cm^3 of demineralized water and transfer the reaction mixture into a 400 cm^3 beaker. Rinse the Erlenmeyer flask with 25 cm^3 of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm^3 with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 cm^3 of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- For drying and weighing deliver your labelled beaker A into the instructor room.
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. 28), your starting material of the second step.
- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

Step 2: Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(p-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Add 10 cm^3 of an aqueous sodium-hydroxide solution (No. **6**), 1 cm^3 of demineralized water and a magnetic stirring bar.

- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating must be stopped.
- After that, 50 cm^3 of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 cm^3 of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 cm^3 of ethanol (No. **2**). The precipitate is washed twice with 10 cm^3 portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 cm^3 of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 cm^3 of hydrochloric acid (No. **3**) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.

- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.

SOLUTION

1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

$M_1(\text{polycarbonate}) = M_1(C_{16}H_{14}O_3)_nH_2 \approx M_1(C_{16}H_{14}O_3) = 254.30\ \text{g mol}^{-1}$

$m_1 = 2.54$ g

$M_2\ (C_{15}H_{16}O_2) = 228.31$ g/mol

$m_2 = m_1 \times M_1^{-1} \times M_2$

Theoretical yield of bisphenol A: 2.28 g

1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A.

$M_2\ (C_{15}H_{16}O_2) = 228.31$ g/mol

$m_2 = 2.00$ g

$M_3\ (C_{19}H_{20}O_6) = 344.39$ g/mol

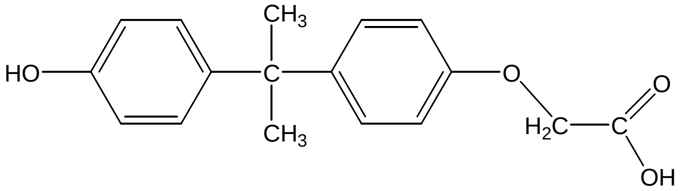
$m_3 = m_2 \times M_2^{-1} \times M_3$

Theoretical yield of bisphenol A bis(carboxymethyl)ether: 3.02 g

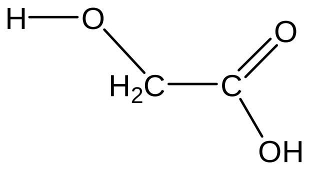
1.3

Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products.

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



2. Alkaline hydrolysis of sodium chloroacetate:



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.

Answer the additional questions and write the results with adequate accuracy.

The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 *Qualitative determination of the alkaline earth metal(s)*

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).

At the beginning, lanthanum has to be separated as an insoluble residue.

All steps must be carried out in the hood!

Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.

Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

  1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3. From now on this solution is called “parent solution”.

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of about 75 cm^3. The *pH*-value has to be about ***pH* 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 *Quantitative determination of the copper content*

Transfer 25.00 cm^3 of your parent solution (No. **13**) into the 100 cm^3 volumetric flask and fill up with demineralized water to a volume of 100.0 cm^3. For each titration, transfer 25.00 cm^3 of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm^3 of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

Ca ☐ Sr ☐ Ba ☒

Ca and Sr ☐ Ca and Ba ☐ Sr and Ba ☐

Ca and Sr and Ba ☐

Complete the following reaction equations:

$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$

$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$

$2\ Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ BaCrO_4 + 2\ H^+$

2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm^{-3} EDTA solution: V = 11.60 cm^3

(accoding to 100 cm^3 of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution: V = 10.50 cm^3

(according to 100 cm^3 of superconductor solution)

Complete the following reaction equations:

$2\ Cu^{2+} + 4\ I^- \rightleftharpoons I_2 + 2\ CuI$

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

2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

[M(Cu) = 63.55 g mol^{-1}; M(La) = 138.91 g mol^{-1}]

Amount of copper:

10,50 cm^3 × 0.01 mol dm^{-3} × 4 × 10 × 63.55 g mol^{-1} = 266.9 mg

Amount of lanthanum:

[11.60 – (10.50 / 10 × 4)] cm^3 × 0.1 mol dm^{-3} × 10 × 138.91 g mol^{-1} = 1028 mg

Mass Cu: m(Cu) = 266.9 mg
Mass La: m(La) = 1028 mg

2.5 Assume a fictive consumption of 39.90 cm^3 of 0.1000 mol dm^{-3} EDTA solution and 35.00 cm^3 of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution. Calculate the coefficient x in the formula $La_xM_{(2-x)}CuO_4$ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = [39.90 – (35.00/10 × 4)] cm^3 = 25.90 cm^3

Consumption for copper = (39.90 – 25.90) cm^3 = 14.00 cm^3

n(La) : n(Cu) = 25.90 : 14.00 = 1.85 : 1

coefficient x: 1.85 formula: $La_{1.85}Ba_{0.15}CuO_4$

37th

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International Chemistry Olympiad

8 theoretical problems
2 practical problems

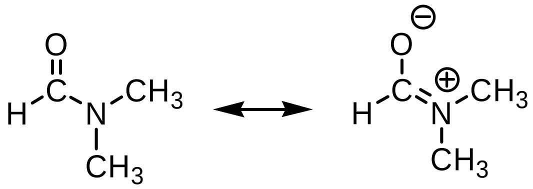
THE THIRTY-SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
16–25 JULY 2005, TAIPEI, TAIWAN

THEORETICAL PROBLEMS

PROBLEM 1

Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms N,N-dimethylformamide (DMF), which can be described as the following resonance structures.



1.1 Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide ($CH_3CONHCH_3$, compound **B**), and propionamide (compound **C**, $CH_3CH_2CONH_2$,). Express your answer from high to low melting point as follows:

____ > ____ > ____ (Insert compound codes **A**, **B**, **C**)

1.2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.

(a) 1660 cm^{-1} because of the shorter carbonyl bond length.

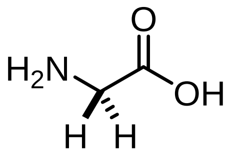
(b) 1660 cm^{-1} because of the longer carbonyl bond length.

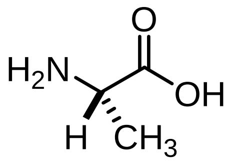
(c) 1740 cm^{-1} because of the shorter carbonyl bond length.

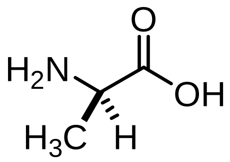
(d) 1740 cm^{-1} because of the longer carbonyl bond length.

1.3 Glycine (H_2N-CH_2-COOH) is an α-amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

1.4 When an α-amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?


Glycine (Gly)


L-Alanine (L-Ala)


D-Alanine (D-Ala)

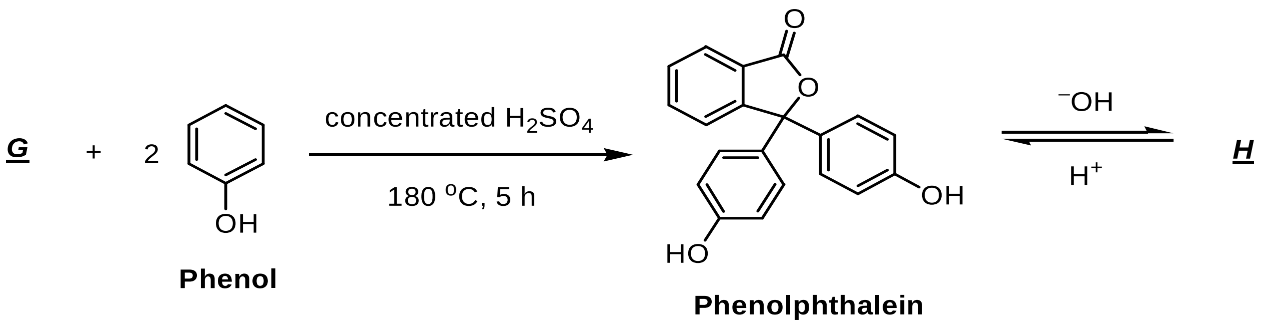
1.5 Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

1.6 Predict the binding affinity of phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) with a polyamide gel. Express your answer from high to low binding affinity as follows:

______>______>_ (Insert compound codes **D**, **E**, and **F**)

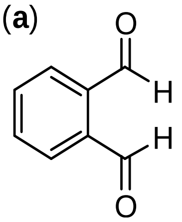
The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary colour. For example, phenolphthalein is a commonly used acid-base indicator, which is colourless in acidic and neutral solutions, but reddish pink in basic solutions (*pH* 8.3 – 10.0).



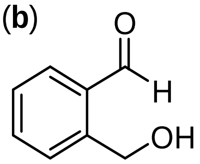
1.7 Draw the structural formula of **H** derived from phenolphthalein that is attributable to the reddish pink colour in aqueous NaOH solution.

1.8 A simple way to prepare phenolphthalein is via condensation of compound **G** with 2 equivalents of phenol. What is the most effective reagent for **G** to accomplish this transformation? Select your answer from the following compounds.

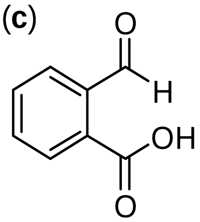
(**a**)



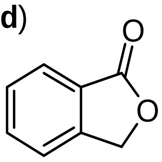
(**b**)



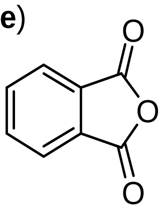
(**c**)



(**d**)



(**e**)



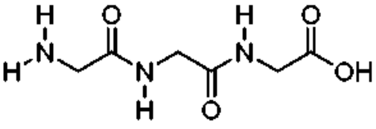
SOLUTION

1.1 The order of the melting points is: **C** > **B** > **A**

The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bonding, but not tertiary amide.
Propionamide, m.p. = 79 ℃; *N*-methylacetamide, m.p. = 28 ℃;
N,*N*-dimethylformamide, m.p. = -61 ℃.

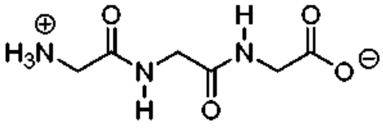
1.2 Correct: (b), 1660 cm^{-1} due to a longer carbonyl bond length.

1.3



Gly-Gly-Gly

or



Gly-Gly-Gly

1.4 There are 27 possible tripeptides.

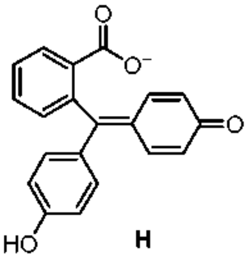
1.5 Among them, 26 tripeptides are optically active.

Optically inactive tripeptide: H_2N-GGG-OH

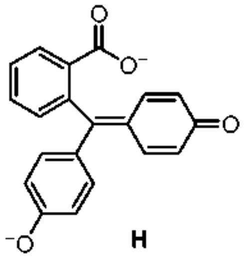
Optically active tripeptides: H_2N-GG^{L}A-OH, H_2N-GG^{D}A-OH, H_2N-G^{L}AG-OH, H_2N-^{L}AG^{D}A-OH, H_2N-^{L}A^{L}A^{D}A-OH, and so on.

1.6 The relative binding strength with polyamide gel for phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) is: **F** > **D** > **E**

1.7



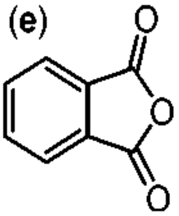
H



H

The range *pH* 8.3 – 10.0 for colour change of phenolphthalein.

1.8

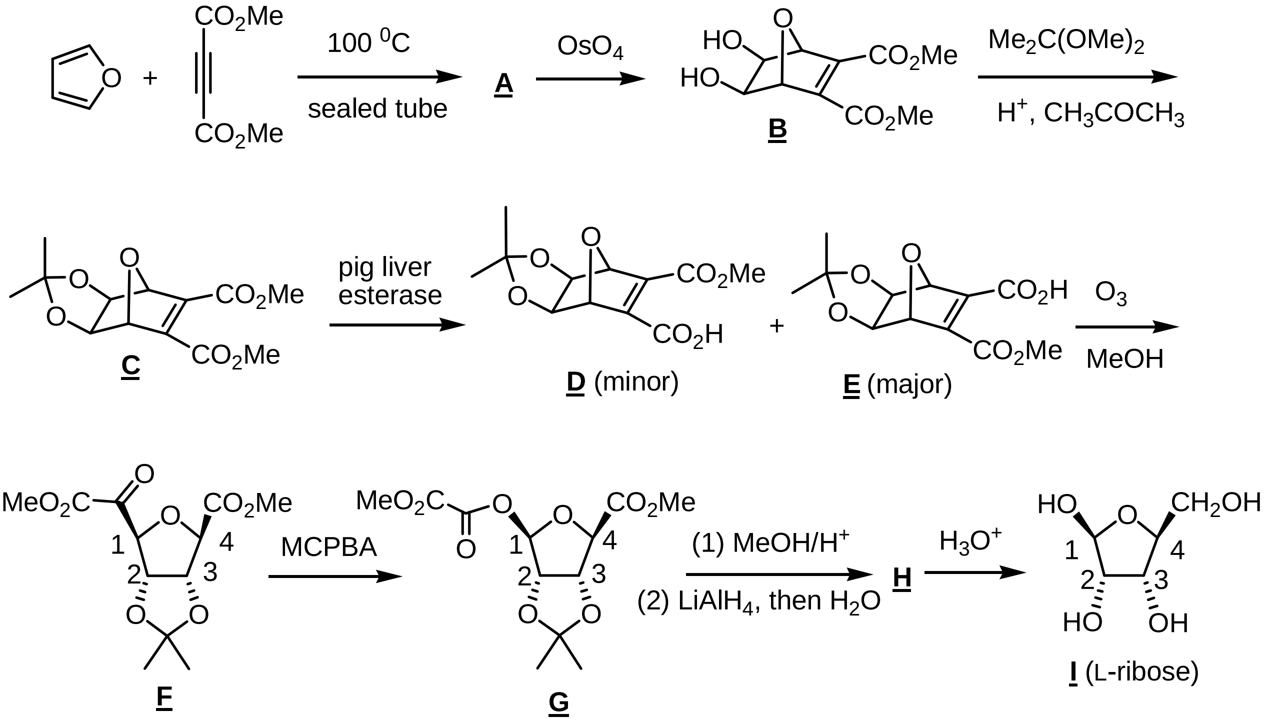


(e)

PROBLEM 2

Organic Synthesis and Stereochemistry

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound I).



2.1 Compound **A** has the molecular formula of $C_{10}H_{10}O_5$. Draw the structural formula of **A**.

2.2 Given the chemistry described for reaction sequence **A** to **C**, indicate whether the following statements are true or false (Use T to represent true and F to represent false).

___ (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.

___ (b) MeOH is generated as a by-product in the reaction of **B** to **C**.

___ (c) Protons act as the catalyst in the transformation of **B** to **C**.

___ (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$.

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20} = -37.1^o$. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20} = -49.0^o$.

2.3 What is the molar ratio of **D**/**E** in the product mixture before the recrystallization? Show your work.

2.4 Reaction of **F** with meta-chloroperbenzoic acid (MCPBA) afforded **G** as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

____ (a) The reaction was to oxidize compound **F**.

_____ (b) The oxygen atom inserted originated from MCPBA.

____ (c) The *R*/*S* notation of C-1 remained unchanged before and after the reaction.

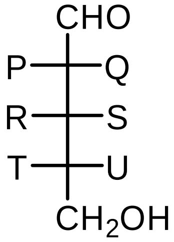
The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows: ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, J = 6 Hz, 1H), 4.74 (d, J = 6 Hz, 1H), 4.89 (s, 1H).

2.5 Draw the configurational formula of **H**.

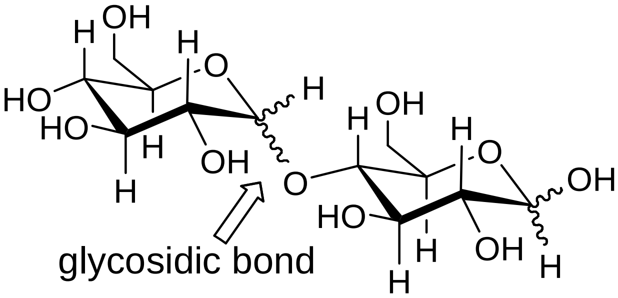
2.6 Assign R/S notations for compound I at C-1, C-2, C-3 and C-4. Give your answers as follows:

C-1: ____; C-2: ____; C-3: ____; C-4: ____.

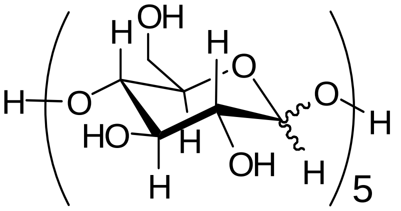
2.7 What are the identities of P, Q, R, S, T and U in the Fischer projection of compound I (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



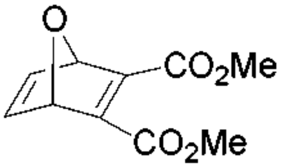
2.8 How many diastereoisomers would be obtained for pentasaccharide **J**, if it is derived from five units of D-glucose?



pentasaccharide **J** derived from D-glucose

SOLUTION

2.1



2.2 T or F

T (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.

T (b) MeOH is generated as a by-product in the reaction of **B** to **C**.

T (c) Protons act as the catalyst in the transformation of **B** to **C**.

T (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$

2.3 12.1 : 87.9 or 12.2 : 87.8

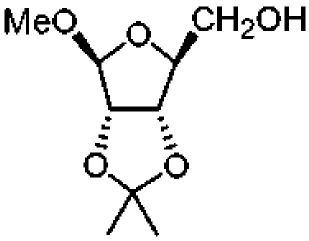
2.4 T or F

T (a) The reaction was to oxidize compound **F**.

T (b) The oxygen atom inserted originated from MCPBA.

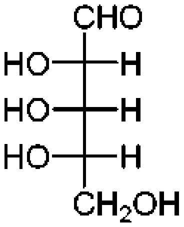
F (c) The *R*/*S* notation of C-1 remained unchanged before and after the reaction

2.5



2.6 C-1: *S*; C-2: *S*; C-3: *R*; C-4: *S*.

2.7



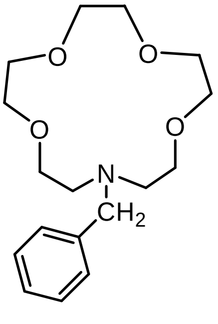
OH group for P, R, and T and H atom for Q, S, and U.

2.8 The number of stereoisomers = 2^5

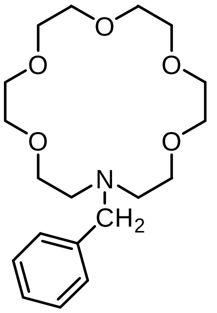
PROBLEM 3

Organic Photochemistry and Photophysics

Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns A and B exhibit different binding constants for Na^+, K^+, and Cs^+.



A

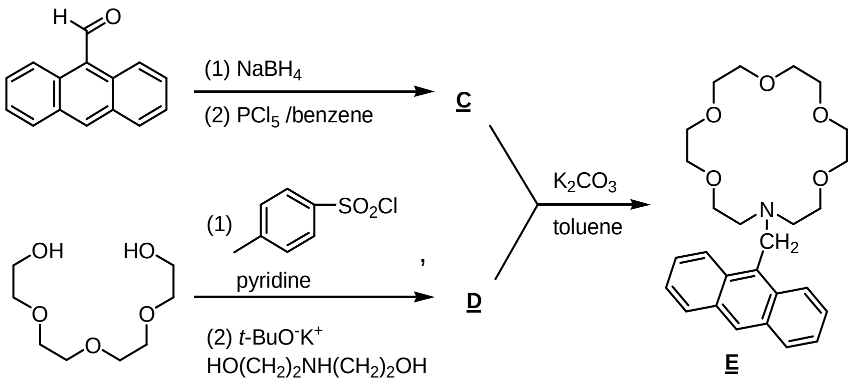


B

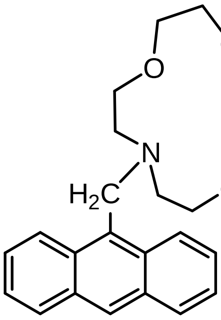
		Binding constant ($\log_{10}$ K)	
Metal ion	Radius (pm)	Compound **A**	Compound **B**
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

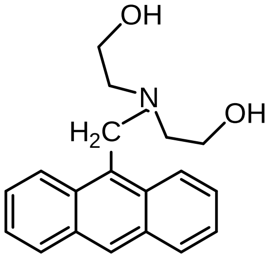
3.1 Provide the structural formula of **C** and **D** in the following synthesis.



For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E**, **F**, and **G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



F



G

3.2 Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.

(a) none of them (b) **E** and **F** only (c) **G** only (d) all of them

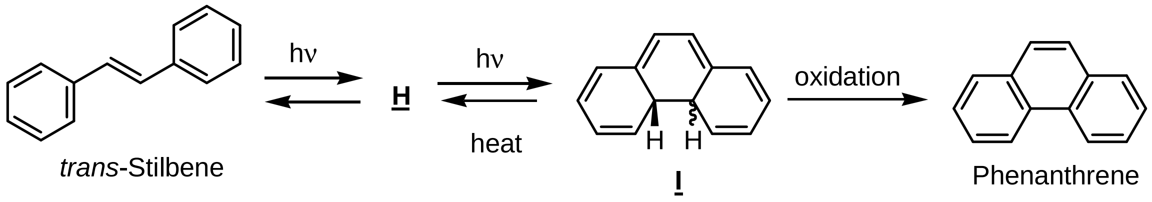
3.3 By adding one equivalent of potassium acetate into a dilute solution (1×10^{-5} M) of **E**, **F**, and **G** in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.

(a) **E** (b) **F** (c) **G**

3.4 Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.

(a) sodium acetate (b) potassium acetate (c) cesium acetate (d) doesn't make any difference

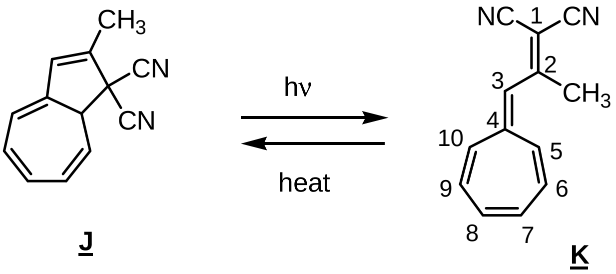
Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of I gives phenanthrene.



3.5 Draw the structural formula of compound **H**?

3.6 What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound I?

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



3.7 Which compound will absorb light with longer wavelength? Select your answer from the following choices: (a) **J** (b) **K**

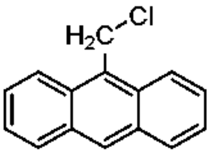
3.8 Compound **K** can react with one equivalent of CF_3CO_2H to generate a stable aromatic salt. Which position of **K** is most likely protonated? Select your answer from the following choices.

(a) C-2 (b) C-3 (c) C-4 (d) C-5

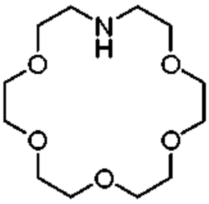
SOLUTION

3.1

C:



D:



3.2 Correct is (d): All of them

3.3 Correct is (a): **E**

3.4 Correct is (a): sodium acetate

3.5

H:

3.6 Trans

3.7 Correct is (b): **K**

3.8 Correct is (b): C-3

PROBLEM 4

A

Gold Capital of Asia

Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines In Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN^-) solutions in the presence of air to form $Au(CN)_2^-$, which is stable in aqueous solution.

$$4\ Au(s) + 8\ CN^-\ (aq) + O_2(g) + 2\ H_2O\ (l) \rightleftharpoons 4\ Au(CN)_2^-(aq) + 4\ OH^-\ (aq)$$

4.A-1 Draw a structure for $Au(CN)_2^-$ showing the spatial arrangements of the atoms.

4.A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to “dissolve” gold. The process is actually a redox reaction with the following simplified chemical equation:

$$Au(s) + NO_3^-(aq) + Cl^-\ (aq) \rightleftharpoons AuCl_4^-(aq) + NO_2(g)$$

4.A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4.A-4 What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion $AuCl_4^-$ forms. Consider the following half-reactions:

$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$ $\qquad E^0 = + 1.50\ V$

$AuCl_4^-(aq) + 3\ e^- \rightarrow Au(s) + 4\ Cl^-$ $\qquad E^0 = + 1.00\ V$

An electrochemical cell can be formed from these two redox couples.

4.A-5 Calculate the formation constant for $AuCl_4^-$ at 25 °C:

$$K = \frac{[AuCl_4^-]}{[Au^{3+}]\,[Cl^-]^4}$$

4.A-6 The function of HCl is to provide Cl^-. What is the purpose of the Cl^- for the above reaction. Select your answer from the following choices.

(a) Cl^- is an oxidizing agent
(b) Cl^- is a reducing agent
(c) Cl^- is a complexing agent
(d) Cl^- is a catalyst

____

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of $HAuCl_4$ is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of $NaBH_4$. Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4.B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

(a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
(b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

4.B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry $AlCl_4^-$ from an aqueous phase to an organic phase. Which property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

(a) one side of the molecule is electropositive, the other side is electronegative.
(b) one side of the molecule is hydrophilic, the other side is hydrophobic.
(c) one side of the molecule is acidic, the other side is basic.

4.B-3 What is the function of $NaBH_4$ in this preparation? Select your answer from the following choices.

(a) reducing agent
(b) oxidizing agent
(c) neutralization agent
(d) complexing agent

4.B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

(a) 10^2
(b) 10^3
(c) 10^4
(d) 10^5

4.B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

(a) 20 – 30 %
(b) 40 – 50 %
(c) 60 – 70 %
(d) 80 – 90 %

SOLUTION

4.A-1 $|N\equiv C-Au-C\equiv N|^{(-)}$

The structure of $Au(CN)_2^-$ is linear.

4.A-2 $4\ Au + 8\ KCN + O_2 + 2\ H_2O \rightleftharpoons 4\ KAu(CN)_2 + 4\ KOH$

$20\ g \div 197\ g\ mol^{-1} \approx 0.10\ mol\ (Au)$

$0.10\ mol \times (8/4) \times 65.12\ g\ mol^{-1} = 13.024\ g\ KCN$

4.A-3 Oxidation: $Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$

Reduction: $3\ NO_3^-(aq) + 6\ H^+(aq) + 3\ e^- \rightarrow 3\ NO_2(g) + 3\ H_2O(l)$

$Au(s) + 3\ NO_3^-(aq) + 6\ H^+(aq) + 4\ Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + 3\ NO_2(g) + 3\ H_2O(l)$

4.A-4 Oxidizing agent: HNO_3 or nitric acid

Reducing agent: Au

4.A-5 $Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$ $E° = 1.50\ V$

$Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$ $E° = 1.00\ V$

$- 3\ e^-$

$Au(s) + Au^{3+}(aq) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + Au(s)$ $E° = +0.50\ V$

$+ 3\ e^-$

$E = E° – (0.059 / n) \log Q$

At equilibrium, $Q = K$, $E = 0$, $K = [AuCl_4\ ] / [Au^{3+}]\ [Cl^-]^4$

$E = (0.059 / n) \log K$, $0.50 = (0.059 / 3) \log K$, $K = 10^{25.42} = 2.6\times10^{25}$

$\Delta G^0_1 + \Delta G^0_2 = \Delta G^0_3$

$(–n\ F\ E^0_1) + (–n\ F\ E^0_2) = –RT \ln K$

$E° = (RT / nF) \ln K = (0.059 / n) \log K$,

$0.50 = (0.059 / 3) \log K$,

$K = 10^{2542} = 2.6\times10^{25}$

4.A-6 Answer for multiple choice question: (c)

4.B-1 Answer for multiple choice question: (b)

4.B-2 Answer for multiple choice question: (b)

4.B-3 Answer for multiple choice question: (a)

4.B-4 Answer for multiple choice question**:** (b)

Calculation:

$$V_{\text{AuNPs}} = \frac{4}{3}\pi\, r^3_{\text{AuNPs}}$$

$$V_{\text{Au}} = \frac{4}{3}\pi\, r^3_{\text{Au}}$$

$$N_{\text{Au}} = \frac{V_{\text{AuNPs}}}{V_{\text{Au}}} = \frac{\frac{4}{3}\pi\, r^3_{\text{AuNPs}}}{\frac{4}{3}\pi\, r^3_{\text{Au}}} = \left(\frac{r^3_{\text{AuNPs}}}{r^3_{\text{Au}}}\right)^3 = \left(\frac{15\text{ A}}{1{,}44\text{ A}}\right)^3 \approx 1000$$

4B-5 Calculation:

Method 1:

$4/3 \times \pi \times r_{\text{AuNPs}}{}^3 = 4/3 \times \pi \times r_{\text{Au}}{}^3 \times N_{\text{Au}}$

$r_{\text{AuNPs}}{}^3 = \mathrm{r}_{\text{Au}}{}^3 \times N_{\text{Au}}$

Surface area of a gold nanoparticle: $\mathrm{S}_{\text{AuNPs}} = 4\,\pi\, r_{\text{AuNPs}}{}^2$

$\mathrm{S}_{\text{AuNPs}} = 4\,\pi\, r_{\text{Au}}{}^2\, \mathrm{N}_{\text{Au}}{}^{2/3}$

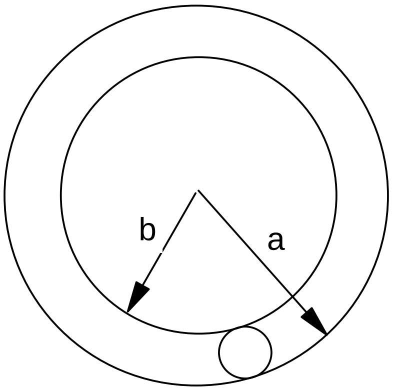
$N_{\mathrm{S}} \approx \mathrm{S}_{\text{AuNPs}} / \pi\, r_{\text{Au}}{}^2 = 4\; N_{\text{Au}}{}^{2/3}$

$\mathrm{P} \approx N_{\mathrm{S}} / N_{\text{Au}} = 4/ N_{\text{Au}}{}^{1/3}$

$\mathrm{N}_{\text{Au}} \approx 1000$

$\mathrm{P} \approx 40\ \%$

or Method 2:



$a = r_{AuNPs}$

$b = r'_{AuNPs} = r_{AuNPs} - 2\, r_{Au}$

$$P\ \% = \frac{\dfrac{V_{AuNPs}}{V_{Au}} - \dfrac{V'_{AuNPs}}{V_{Au}}}{\dfrac{V_{AuNPs}}{V_{Au}}} \times 100\ \% = \frac{\left(\dfrac{r_{AuNPs}}{r_{Au}}\right)^3 - \left(\dfrac{r'_{AuNPs}}{r_{Au}}\right)^3}{\left(\dfrac{r'_{AuNPs}}{r_{Au}}\right)^3} \times 100\ \% =$$

$$= \frac{(15\ \text{A})^3 - (12.12\ \text{A})^3}{(15\ \text{A})^3} \times 100\ \% = 47\ \%$$

PROBLEM 5

Lewis Structure

5.1 Draw one Lewis structure for each of the following molecules.

a) N_2

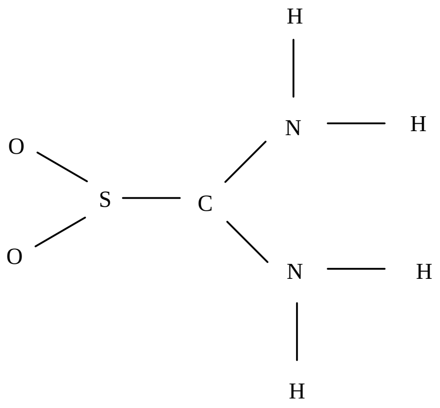
b) NH_3

c) O_3

d) SO_3

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, $O_2SC(NH_2)_2$, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

5.4a What is the geometry around the sulfur atom? Select your answer from the following choices.

a) trigonal pyramidal

b) triangular planar

c) T-shape

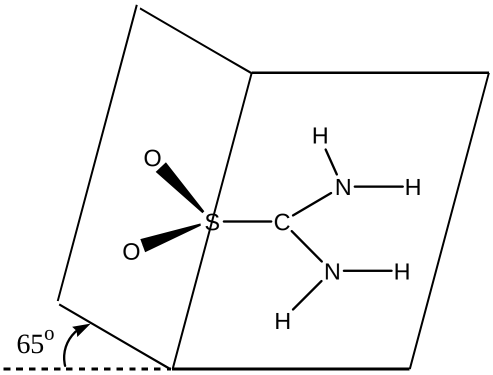
5.4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

a) trigonal pyramidal
b) triangular planar
c) T-shape

5.4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

a) trigonal pyramidal
b) triangular planar
c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



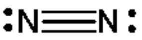
All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the $SC(NH_2)_2$ plane is 65°.

5.5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

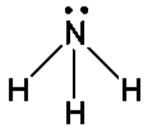
SOLUTION

5.1

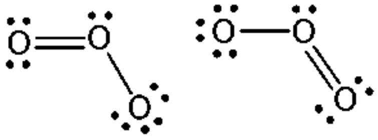
(a)



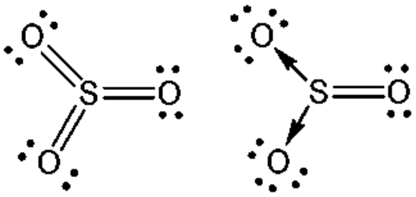
(b)

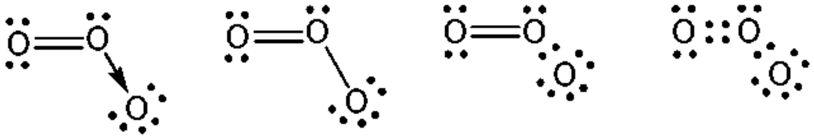


(c)



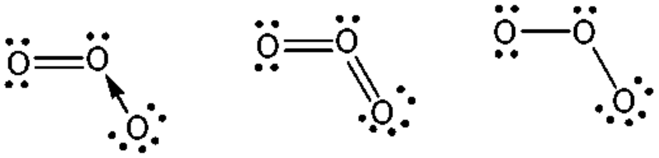
(d)



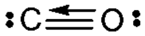


are all correct answers

But



are incorrect answers



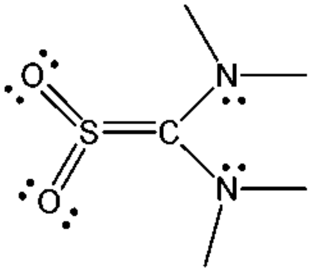
acceptable

5.2

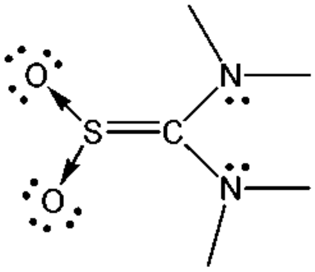
Formal charge C^{-1} ; O^{+1}

Oxidation state C^{2+} ; O^{2-}

5.3



The structure is correct.



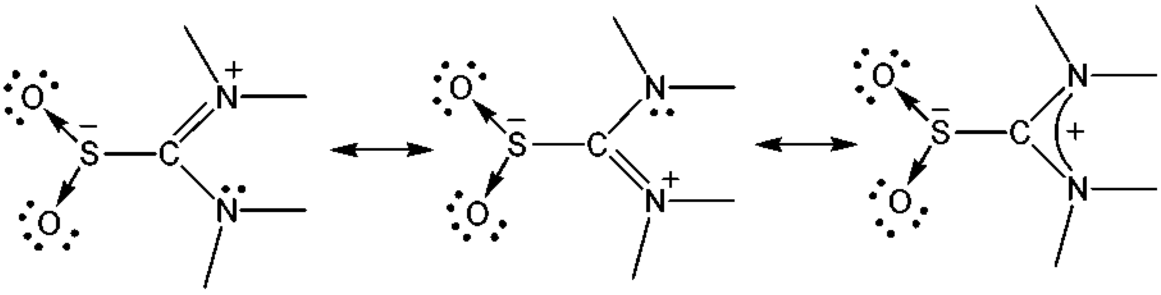
The structure would have a formal charge and is incorrect.

5.4 Sulphur: (b) trigonal planar

Carbon: (b) trigonal planar

Nitrogen: (a) trigonal pyramidal

5.5



PROBLEM 6

Alkalinity of Water and Solubility of CO_2

The capacity of water to accept H^+ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO_3^-, CO_3^{2-}, and OH^-. At *pH* values below 7, H^+ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO_3^-, CO_3^{2-}, and OH^- are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$$

The contributions made by different species to alkalinity depend upon pH. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \quad K_{CO_2} = 3.44\times10^{-2}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \quad K_{H_2CO_3} = 2.00\times10^{-3}$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad K_{a1} = 2.23\times10^{-4}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad K_{a2} = 4.69\times10^{-11}$$

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 4.50\times10^{-9}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = 1.00\times10^{-14}$$

Note: Calculations must be shown.

6.1 Natural waters (river or lake water) generally contain dissolved CO_2. The ratio of $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}]$ in a water at $[H^+] = 1.00\times10^{-7}$ M will be:

_(a)_ : 1.00 : _(b)_. Calculate (a) and (b).

6.2 Gaseous CO_2 in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of $CO_{2\,(aq)}$ (mol dm^{-3}) in pure water that is in equilibrium with the unpolluted air at 1.01×10^5 Pa and 298 K containing 0.0360 % (molar ratio) CO_2. (assuming standard pressure = 1.01×10^5 Pa).

If you are unable to solve this problem, assume that concentration of $CO_{2\ (aq)}$ is equal to 1.11×10^{-5} M for further calculations.

The solubility (S) of CO_2 in water can be defined as

$S = [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$.

The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01×10^5 Pa will vary with alkalinity.

6-3 Find the solubility of atmospheric CO_2 in pure water (mol dm^{-3}). Neglect dissociation of water.

6.4 Find the solubility of atmospheric CO_2 (mol dm^{-3}) in a 1.00×10^{-3} mol dm^{-3} NaOH solution.

At 298 K, 1.01×10^5 Pa unpolluted air is in equilibrium with natural water saturated with $CaCO_3$. The following main equilibrium may exist:

$$CaCO_{3(s)} + CO_{2\ (aq)} + H_2O \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$$

6.5 Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant $K_{eq} = 5.00\times10^{-5}$ for further calculations.

6.6 Calculate the concentration of Ca^{2+} (mg dm^{-3}) in $CaCO_3$-saturated natural water that is in equilibrium with atmospheric CO_2.

If you are unable to solve this problem, assume that concentration of $Ca^{2+}_{(aq)}$ = 40.1 mg dm^{-3} for further calculations.

6.7 Find the alkalinity (mol/L) of the above solution.

6.8 In an underground lake saturated with $CaCO_3$, the water has a high content of CO_2. The concentration of Ca^{2+} in this lake was found to be as high as 100 mg dm^{-3}. Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

SOLUTION

6.1 $[H^+] = 1.00\times10^{-7}$

$K_{a1} = [HCO_3^-]\,[H^+] / [H_2CO_3] = 2.23\times10^{-4}$,

$[HCO_3^-] / [H_2CO_3] = 2.23\times10^{3}$

$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69\times10^{-11}$,

$[CO_3^{2-}] / [HCO_3^-] = 4.69\times10^{-4}$

$[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = \mathbf{4.48\times10^{-4}} : 1.00 : \mathbf{4.69\times10^{-4}}$

6.2 $p(CO_2(aq)) = 1.01\times10^{5}\ \text{Pa} \times 3.60\times10^{-4} = 36.36\ \text{Pa}$

$[CO_2(aq)] = K_{CO_2} \times p(CO_2) = 0.0344 \times (36.36\ \text{Pa} / 1.01\times10^{5}\ \text{Pa}) = \mathbf{1.24\times10^{-5}}$

(If you are unable to solve this problem, for further calculations assume that $[CO_2(aq)] = 1.11\times10^{-5}$.)

6.3

(a) Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-]$

$([H_2CO_3] = [CO_2(aq)] \times K_{H_2CO_3} = 2.48\times10^{-8}$

and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$

both can be neglected.)

$[H^+][HCO_3^-] / [CO_2(aq)] = K_{a1}\ K_{H_2CO_3} = (2.23\times10^{-4})\ (2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6-2: $[CO_2(aq)] = 1.24\times10^{-5}$,

$[H^+] = \mathbf{[HCO_3^-] = 2.35\times10^{-6}}$

Solubility = $[CO_2(aq)] + [HCO_3^-] = 1.24\times10^{-5} + 2.35\times10^{-6} = 1.48\times10^{-5}\ \text{mol dm}^{-3}$

(b) (Using $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-]$

$([H_2CO_3] = [CO_2(aq)] \times \boldsymbol{K_{H_2CO_3}} = 2.22\times10^{-8}$ and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$ both can be neglected.)

$[H^+][HCO_3^-] / [CO_2(aq)] = K_{a1}\ K_{H_2CO_3} = (2.23\times10^{-4})\ (2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6.2: $[CO_2(aq)] = 1.11\times10^{-5}$

$[H^+] = [\mathbf{HCO_3^-}] = 2.225\times10^{-6}$

Solubility = $[CO_2(aq)] + [HCO_3^-] = 1.11\times10^{-5} + 2.225\times10^{-6} = 1.34\times10^{-5}$

6.4 (Using $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

In 1.00×10^{-3} mol dm^{-3} NaOH solution the solubility of CO_2 will be much higher because of the following reactions:

(1) $CO_2(aq) + 2\,OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad K = K_{H_2CO_3} \times K_{a1} \times K_{a2} / (1.00\times10^{-14})^2 = 2.09\times10^{11}$

(2) $CO_2(aq) + CO_3^{2-} + H_2O \rightleftharpoons 2\,HCO_3^- \quad K = K_{H_2CO_3} \times K_{a1} / K_{a2} = 9.37\times10^3$

Combining (1) and (2): $CO_2(aq) + OH^- \rightleftharpoons HCO_3^- \quad K = 4.43\times10^7$

With such a large *K* value all OH^- will finally be converted to HCO_3^-.

$$[HCO_3^-] = 1.00\times10^{-3}$$

$[OH^-] = 1.82\times10^{-6}$

$[H^+] = 5.49\times10^{-9} \quad [CO_3^{2-}] = 8.54\times10^{-6}$

Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] =$

$= 1.24\times10^{-5} + 1.00\times10^{-3} + 8.54\times10^{-6} = 1.02\times10^{-3}$ mol dm^{-3}

6.5 $K_{eq} = K_{sp} \times K_{H_2CO_3} \times K_{a1} / K_{a2} = (4.50\times10^{-9}) \times (2.00\times10^{-3}) \times (2.23\times10^{-4}) / (4.69\times10^{-11}) = 4.28\times10^{-5}$

(If you are unable to solve this problem, assume that $K_{eq} = 5.00\times10^{-5}$ for further calculations.)

6.6

(a) (Using $K_{eq} = 4.28\times10^{-5}$ and $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-] / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.24\times10^{-5}$

$[Ca^{2+}] = 0.510\times10^{-3} = 20.5$ mg dm^{-3}

(b) (Using $K_{eq} = 5.00\times10^{-5}$ and $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.11\times10^{-5}$

$[Ca^{2+}] =$

0.5177×10^{-3} = 20.75 mg dm^{-3}

(c) (Using $K_{eq} = 5.00\times10^{-5}$ and $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.24\times10^{-5}$

$[Ca^{2+}] =$

0.5372×10^{-3} = 21.53 mg dm^{-3}

(d) (Using $K_{eq} = 4.28\times10^{-5}$ and $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.11\times10^{-5}$

$[Ca^{2+}] =$

0.4916×10^{-3} = 19.70 mg dm^{-3}

(If you are unable to solve this problem, assume that $[Ca^{2+}]_{(aq)}$ = 40.1 for further calculations.)

6.7 HCO_3^- is the major species in solution.

The *pH* of the solution can be estimated as $pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33) / 2 =$ $= 6.99 \approx 7.00$,

where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3.

At pH 7.00, both $[OH^-]$ and $[H^+]$ can be neglected. Besides, $[CO_3^{2-}] << [HCO_3^-]$ (from **6.1**)

Alkalinity $= [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \approx [HCO_3^-]$

From 6-6, mass balance, $[HCO_3^-] = 2\ [Ca^{2+}]$

(a) 1.02×10^{-3} (using $[Ca^{2+}]_{(aq)}$ from 6.6 (a))

(b) 1.035×10^{-3} (using $[Ca^{2+}]_{(aq)}$ from 6.6 (b))

(c) 1.0744×10^{-3} (using $[Ca^{2+}]_{(aq)}$ from 6-6 (c))

(d) 0.9831×10^{-3} (using $[Ca^{2+}]_{(aq)}$ from 6-6 (d))

(e) 2.00×10^{-3} (assuming $[Ca^{2+}]_{(aq)} = 40.1$)

Alkalinity = (a) or (b) or (c) or (d) or (e)

6.8

(a) (Using $K_{eq} = 4.28\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\ [Ca^{2+}]$

$[Ca^{2+}] = 100\ mg\ dm^{-3} = 2.50\times10^{-3}\ mol\ dm^{-3}$

Inserting into $K_{eq} = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = 4\ [Ca^{2+}] / [CO_2(aq)]$

$[CO_2(aq)] = 1.46\times10$

$p_{CO_2} = ([CO_2(aq)] / K_{CO_2}) \times 1.01\times10^5\ Pa = 4.28\times10^3\ Pa$

(b) (Using $K_{eq} = 5.00\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\ [Ca^{2+}]$

$[Ca^{2+}] = 100\ mg\ dm^{-3} = 2.50\times10^{-3}\ mol\ dm^{-3}$

Inserting into $K_{eq} = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = 4\ [Ca^{2+}] / [CO_2(aq)]$

$[CO_2(aq)] = 1.25\times10^{-3}$

$p_{CO_2} = ([CO_2(aq)] / K_{CO_2}) \times 1.01\times10^5\ Pa = 3.67\times10^3\ Pa$

PROBLEM 7

Kinetic Behaviour of Ozone

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,

$2\ O_3 \rightarrow 3\ O_2$.

One of the proposed mechanisms is expressed as

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2 \qquad (1)$$

$$O_3 + O \xrightarrow{k_2} 2\ O_2 \qquad (2)$$

where k_1, k_{-1}, and k_2 are the rate constants.

7.1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3, O_2, and O at time t, assuming step 2 is irreversible.

7.2 Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.

7.3 Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is d[O]/dt = 0, show that the rate equation is:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \rightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:

$$CCl_2F_2 \xrightarrow{h\nu} CF_2Cl + Cl \qquad (3)$$

7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)} \qquad (4)$$

Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ mol^{-1}, while the activation energy for the reaction without the presence of catalyst is 14.0 kJ mol^{-1}. Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25 ^{o}C. Assume the frequency factor is the same for each reaction.

SOLUTION

7.1 $-\dfrac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O][O_2] + k_2[O_3][O]$

$-\dfrac{d[O_2]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] - 2k_2[O_3][O]$

$-\dfrac{d[O]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O]$

7.2 Equilibrium constant K is expressed as

$$K = \frac{[O][O_2]}{[O_3]} = \frac{k_1}{k_{-1}}$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$-\frac{d[O_3]}{dt} = k_2[O_3][O] = \frac{k_1\,k_2\,[O_3]^2}{k_{-1}\,[O_2]}$$

7.3 $-\dfrac{d[O]}{dt} = 0$

$$-k_1\,[O_3] + k_{-1}\,[O][O_2] + k_2\,[O_3][O] = 0$$

Thus $$-\frac{d[O_3]}{dt} = 2k_2\,[O_3][O] = \frac{2\,k_1\,k_2\,[O_3]^2}{k_{-1}\,[O_2] + k_2\,[O_3]}$$

7.4 $ClO(g) + O_3(g) \rightarrow Cl(g) + 2\,O_2(g)$

7.5 According to equation $k = A\exp(-E_a / RT)$,

the ratio of rate constants yields

Ratio = exp[(14.0 – 2.1) ×1000 / (8.314 ×298)] = 122.

PROBLEM 8

Protein Folding

Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:

$$\mathbf{N} \overset{K(T)}{\rightleftharpoons} \mathbf{U}$$

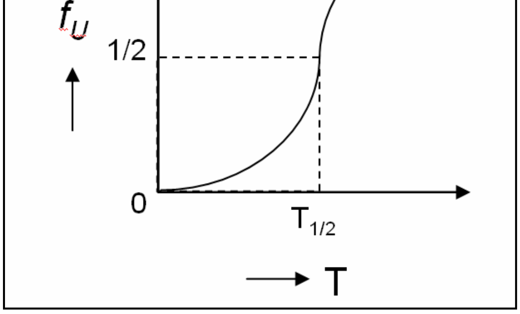
where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. K(*T*) is the equilibrium constant for the process at absolute temperature *T*.

8.1 What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?

8.2 What is the standard free energy change of the process ($\Delta G°(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.

8.3 If $(C_N)_{eq}$ and $(C_U)_{eq}$ denote the equilibrium concentrations of *N* and *U* in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{eq}/C$. Deduce an expression for f_U in terms of the equilibrium constant *K*. Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by $f_U = ½$ and $T = T_{½}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{½}$, f_U increases above ½, but at temperatures lower than $T_{½}$, f_U decreases below ½.

8.4 What is the sign of $\Delta G°(T)$ at temperatures below and above $T_{½}$? Select your answer from the following choices.

a) Negative both below and above $T_{½}$.

b) Positive both below and above $T_{½}$.

c) Positive below $T_{½}$, but negative above $T_{½}$.

d) Negative below $T_{½}$, but positive above $T_{½}$..

8.5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{½}$ and (ii) decreases below $T_{½}$? Select your answer from the following choices.

a) Decrease in both cases.

b) Increase in both cases.

c) Increases above $T_{½}$, but decreases below $T_{½}$.

d) Decreases above $T_{½}$, but increases below $T_{½}$.

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:

$$\mathbf{N} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{U}$$

where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8.6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b?

8.7 Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{eq}$.

SOLUTION

8.1 Answer: 1

8.2 Answer: 0 kJ mol^{-1}

8.3 $$f_U = \frac{C_U^{eq}}{C_N^{eq} + C_U^{eq}} = \frac{\dfrac{C_U^{eq}}{C_N^{eq}}}{1 + \dfrac{C_U^{eq}}{C_N^{eq}}} = \frac{K}{1+K}$$

8.4 Correct answer is (c). Positive below $T_{1/2}$, but negatíve above $T_{1/2}$

8.5 Correct answer is (d). Decreases above $T_{1/2}$, but increases below $T_{1/2}$.

8.6 Answer: $K = k_f / k_b$

8.7 $dC_U/dt = k_f C_N - k_b C_U$

$= k_f(C - C_U) - k_b C_U = k_f C - k_f C_U - k_b C_U = k_f C - (k_f + k_b)\, C_U$ (1)

$K = k_f / k_b = (C_U)_{eq} / (C_N)_{eq}$

$1 / K = k_b / k_f = (C_N)_{eq} / (C_U)_{eq}$

$\Rightarrow \quad k_b / k_f + 1 = (C_N)_{eq} / (C_U)_{eq} + 1$

$\Rightarrow \quad (k_b + k_f) / k_f = [(C_N)_{eq} + (C_U)_{eq}] / (C_U)_{eq}$

$\Rightarrow \quad (k_b + k_f) / k_f = C/(C_U)_{eq}$

$C = [(k_b + k_f)\, (C_U)_{eq}\,] / k_f$ (2)

Now substitute C obtained from eq (2) to eq (1).

We get $k_f \{ [(k_b + k_f)\, (C_U)_{eq}] / k_f \} - (k_f + k_b)\, C_U$

$\Rightarrow \quad [(k_b + k_f)\, (C_U)_{eq}] - (k_f + k_b)\, C_U$

$\Rightarrow \quad - (k_f + k_b)\, [C_U - (C_U)_{eq}]$

So we get

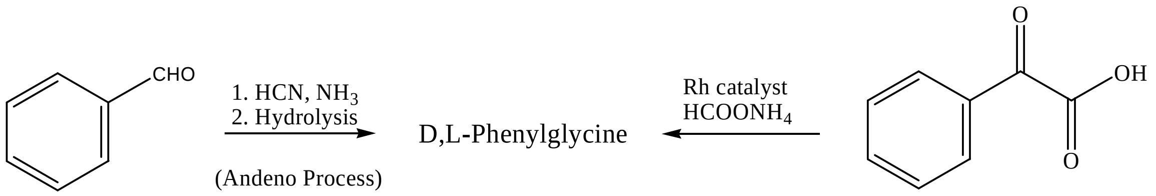
$dC_U/dt = - (k_f + k_b)\, [C_U - (C_U)_{eq}]$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β-lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH_3 following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



Benzaldehyde D,L-phenylglycine Benzoylformic acid

In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as *R*- and *S*-isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H_2O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H_2O at 25 ℃. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

1. To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass

on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (NOTE: irritant, do not contact with skin), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and 22 cm^3 of the pre-mixed solvents at ambient temperature.

2. Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (NOTE: the solvent is air cooled, so there is no tap water running through the condenser.) The temperature of the water bath needs to be maintained in the range of 68 to 72 ℃ by adjusting the thermostat of the hot plate/stirrer.
3. The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.
4. Add 15 cm^3 of deionized water to the resulting mixture and stir for 10 minutes.
5. Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 cm^3 each). For each washing, **break the aspirator pressure**, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.
6. For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 ℃ for 1.5 hour.

During the drying period you can start working on Experiment 2 (analytical experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

7. Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by ^{1}H NMR spectrum

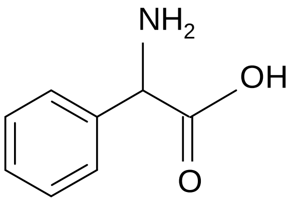
analysis. Turn in the product in a vial (**blue label** with ^{1}H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

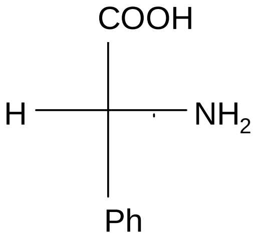
Step 2. Enantiomeric Resolution of D,L-phenylglycine by (+)-Camphorsulfonic Acid [(+)-CSA]

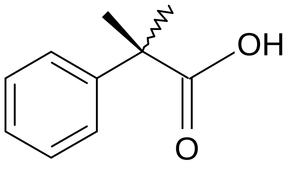
1. To a 25 cm^3 round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 cm^3) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 ℃. Keep the mixture at this temperature for 10 minutes until it turns clear.
2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.
3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 cm^3 each).
4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 ℃ for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).
5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (pink label labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant**.** The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

SOLUTION

1.4 Structural formula (A) and stereochemical formula (B) of the isolated phenylglycine: (Task appeared in the answer sheet only.)







A

B

PROBLEM 2 (Practical)

Identification of Unknown Inorganic Samples

Note

(1) This practical exercise is a kind of “spot test”. You can do it on the pallet or on a sheet of black film (for white precipitate).

(2) Please check all items written in the equipment and reagent list.

(3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.

(4) The volume of each unknown solution is about 1.5 cm^3 (about 30 drops). No more reagents or samples will be provided.

(5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.

(6) Make sure the switch on the battery box is closed.

(7) You will get 8 points for each correct identification.

Introduction

There are 12 unknown samples in your plastic bag□9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the List of Unknown Inorganic Samples carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 cm^3 solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol dm^{-3}).

The unknown samples are as follows:

HCl H_2O_2 H_2SO_4 $ZnCl_2$ NH_4SCN

NaOH Na_2CO_3 Na_2SO_3 $BaCl_2$ $K_4Fe(CN)_6$

Note

1) Two unknown samples are duplicates.

2) The crystal water (. H_2O) is omitted in the formulas listed above.

2.1 Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

2.2 In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is $ZnCl_2$.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).

SOLUTION

2.2A $Zn^{2+}(aq) + 2\ Cl^{-}(aq) \rightarrow Cl_2(g)$ (anode) + $Zn(s)$ (deposit on cathode)

2.2B $Zn(s) + 2\ H^{+}(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$

or

$Zn(s) + 2\ OH^{-}(aq) + 2\ H_2O(l) \rightarrow H_2(g) + [Zn(OH)_4]^{2-}(aq)$

38th

11 theoretical problems
3 practical problems

THE THIRTY-EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 2006, GYEONGSAN, KOREA

THEORETICAL PROBLEMS

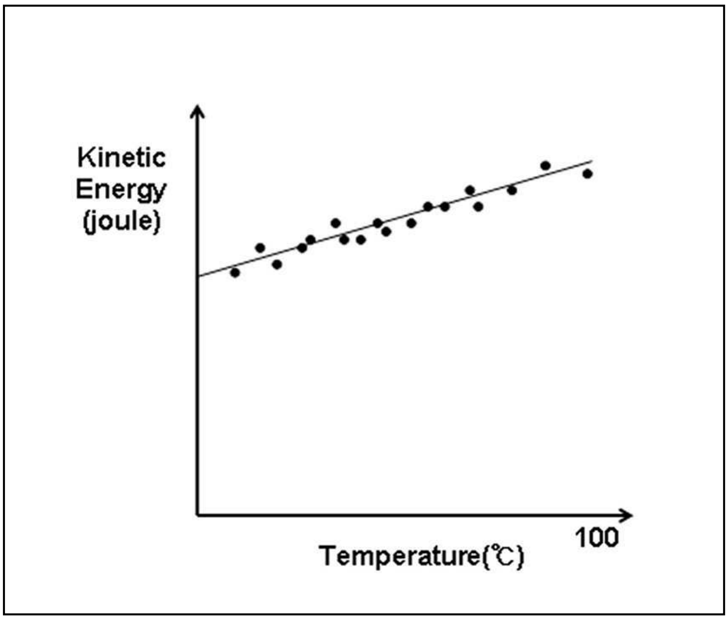
PROBLEM 1

Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27 °C, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm s^{-1} at 27 °C. The density of a water droplet is 1.0 g cm^{-3}.

1.1 Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27 °C. The volume of a sphere is given by (4/3) π r^3 where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0 °C and 100 °C as a function of temperature is found to be linear. Assume that it remains linear below 0 °C.



At thermal equlibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).

The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is 0.31 J g^{-1} K^{-1}.

1.2. Calculate Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

SOLUTION

1.1 The mass of a water droplet:

$m = V\rho = [(4/3)\ \pi\ r^3]\ \rho = (4/3)\ \pi\ (0.5\times10^{-6}\ \text{m})^3\ (1.0\ \text{g cm}^{-3}) = 5.2\times10^{-16}\ \text{kg}$

Average kinetic energy at 27°C:

$$E_k = \frac{m\,v^2}{2} = \frac{(5.2\times10^{-16}\ \text{kg})\times(0.51\times10^{-2}\ \text{m/s})^2}{2} = 6.9\times10^{-21}\ \text{kg m}^2/\text{s}^2 = \underline{6.9\times10^{-21}\ \text{J}}$$

1.2 The average kinetic energy of an argon atom is the same as that of a water droplet. E_k becomes zero at –273 °C.

From the linear relationship in the figure, $E_k = a\,T$ (absolute temperature) where a is the increase in kinetic energy of an argon atom per degree.

$$a = \frac{E_k}{T} = \frac{6.9\times10^{-21}\ \text{J}}{(27+273)\ \text{K}} = 2.3\times10^{-23}\ \text{J K}^{-1}$$

S: specific heat of argon N: number of atoms in 1g of argon

$S = 0.31\ \text{J g}^{-1}\ \text{K}^{-1} = a\times N$

$$N = \frac{S}{a} = \frac{0.31\ \text{J g}^{-1}\ \text{K}^{-1}}{2.3\times10^{-23}\ \text{J K}^{-1}} = 1.4\times10^{22}\ \text{g}^{-1}$$

Avogadro's number (N_A) : Number of argon atoms in 40 g of argon

$N_A = 40\ \text{g mol}^{-1}\times1.4\times10^{22}\ \text{g}^{-1} = \underline{5.6\times10^{23}\ \text{mol}^{-1}}$

PROBLEM 2

Detection of hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

2.1 There are about 1×10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g cm^{-3}; 3/4 hydrogen and 1/4 helium by mass). Estimate the number of stellar protons in the universe to one significant figure.

In the 1920s Cecilia Payne discovered by spectral analysis of starlight that hydrogen is the most abundant element in most stars.

2.2 The electronic transition of a hydrogen atom is governed by $\Delta E(n_i \rightarrow n_f) =$ $= - C(1/n_f^2 - 1/n_i^2)$, where n is principle quantum number, and C is a constant. For detection of the $\Delta E(3 \rightarrow 2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the $n = 2$ state. Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1 \rightarrow 2)$ transition.

2.3 According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $\lambda T = 2.9\times10^{-3}$ m K. Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the $n = 1 \rightarrow n = 2$ excitation of hydrogen.

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

2.4 Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7 K, can cause the hyperfine transition. Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.

2.5 Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the "proton". Fill in the blank.

____

SOLUTION

2.1 Mass of a typical star = $(4/3) \times (3.1) \times (7\times10^{8}\text{ m})^{3} \times (1.4\times10^{6}\text{ g m}^{-3}) = 2\times10^{33}$ g

Mass of protons of a typical star = $(2\times10^{33}\text{ g}) \times (3/4 + 1/8) = 1.8\times10^{33}$ g

Number of protons of a typical star = $(1.8\times10^{33}\text{ g}) \times (6\times10^{23}\text{ g}^{-1}) = 1\times10^{57}$

Number of stellar protons in the universe = $(1\times10^{57}) \times (10^{23}) = \underline{1\times10^{80}}$

2.2 $\Delta E(2\rightarrow3) = C(1/4 - 1/9) = 0.1389\ C$ $\lambda(2\rightarrow3) = 656.3$ nm

$\Delta E(1\rightarrow2) = C(1/1 - 1/4) = 0.75\ C$

$\lambda(1\rightarrow2) = (656.3) \times (0.1389 / 0.75) = 121.5$ nm

2.3 $T = 2.9\times10^{-3}$ m K / 1.215×10^{-7} m = 2.4×10^{4} K

2.4 $\lambda = 3\times10^{8}$ m / 1.42×10^{9} = 0.21 m

$T = 2.9\times10^{-3}$ m K / 0.21 m = 0.014 K

2.5 $^{14}N + ^{4}He \rightarrow ^{17}O + ^{1}H$

PROBLEM 3

Interstellar chemistry

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either be desorbed from the surface or further react through surface migration with adsorbed H atoms to form CH_2, CH_3, etc.

Depending on how energetically a molecule "jumps" from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

3.1 Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1\times10^{12}$ s^{-1} and E_{des} = 12 kJ mol^{-1}.

3.2 Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1}, and the IIG is a sphere with a 0.1 µm radius. Each migratory jump laterally advances the molecule by 0.3 nm. Show work and choose your answer from (a) – (e) below.

(a) $t \le 1$ day (b) 10 days $\le t \le 10^2$ yr c) 10^3 yr $\le t \le 10^6$ yr

(d) 10^7 yr $\le t \le 10^{10}$ yr (e) $t \ge 10^{11}$ yr

3.3 Consider the reaction of CO with H_2 to form H_2CO. The activation energy on a metal catalyst is 20 kJ mol^{-1} that is produced by formaldehyde at a rate of 1 molecule/s per site at 300 K. Estimate the rate of formaldehyde formation per site if the reaction takes place at 20 K.

3.4 Which is a set of all true statements? Circle one.

(a) Most CH species are desorbed from the IIG surface before encountering other reactants by surface migration.

(b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.

(c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

☐ (a) ☐ (b) ☐ (c) ☐ (a, b) ☐ (a, c) ☐ (b, c) ☐ (a, b, c)

SOLUTION

3.1 $k_{des} = A \exp(-E_{des}/RT) = (1\times10^{12}\ s^{-1}) \times (5\times10^{-32}) = 5\times10^{-20}\ s^{-1}$ at $T = 20$ K

surface residence time, $T_{residence} = 1 / k_{des} = 2\times10^{19}$ s $= \underline{6\times10^{11}\ yr}$

(full credit for $T_{half\text{-}life} = \ln 2 / k_{des} = 1\times10^{19}$ s $= 4\times10^{11}$ yr)

residence time = 2×10^{19} s

3.2 The distance to be traveled by a molecule: $x = \pi r = 300$ nm.

$k_{mig} = A \exp(-E_{mig} / RT) = (1\times10^{12}\ s^{-1}) \times (2\times10^{-16}) = 2\times10^{-4}\ s^{-1}$ at $T = 20$ K

Average time between migratory jumps, $T = 1 / k_{mig} = 5\times10^{3}$ s

Time needed to move 300 nm = (300 nm / 0.3 nm) jumps × (5×10^{3} s/jump) =

= 5×10^{6} s = 50 days

The correct answer is (b).

(Full credit for the calculation using a random-walk model. In this case:

$t = T\,(x/d)^{2} = 5\times10^{9}$ s = 160 yr. The answer is still (b).)

3.3 $k(20\text{ K}) / k(300\text{ K}) = \exp[(E/R)\,(1/T_1 - 1/T_2)] = e^{-112} = \sim 1\times10^{-49}$ for the given reaction

The rate of formaldehyde production at 20 K = = ~ 1×10^{-49} molecule/site/s =

= ~ 1×10^{-42} molecule/site/ yr

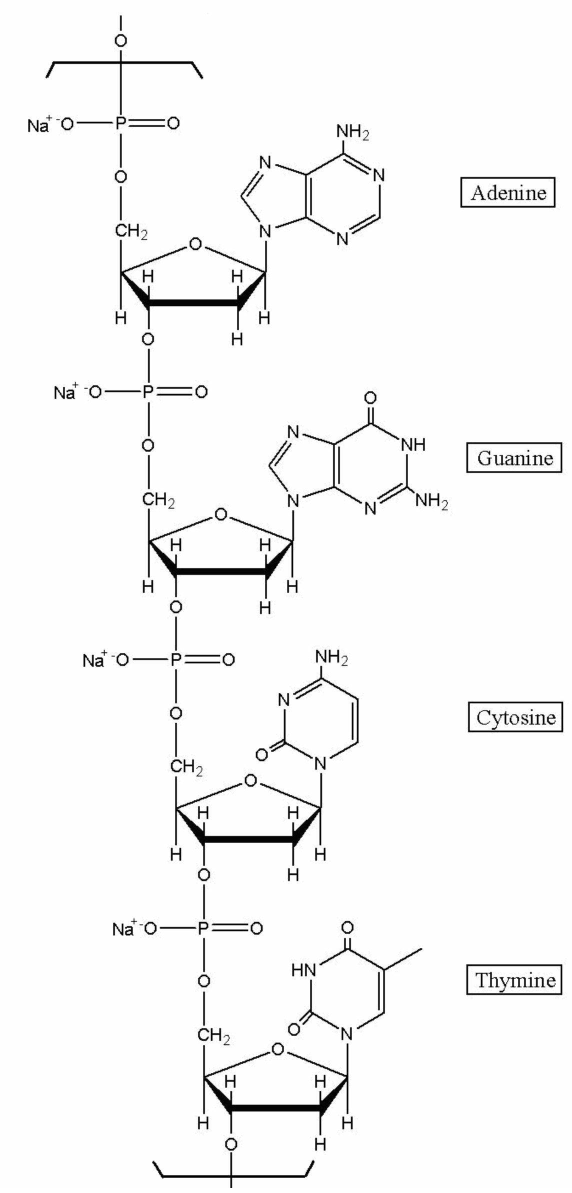
(The reaction will not occur at all during the age of the universe (1×10^{10} yr).)

3.4 The correct answer is (b, c).

PROBLEM 4

The Chemistry of DNA

4.1 In 1944 Oswald Avery isolated a genetic material and showed by elemental analysis that it was a sodium salt of deoxyribonucleic acid. A segment of DNA with formula mass of 1323.72 is shown.



Assuming that equimolar amounts of the four bases are present in DNA, write the number of H atoms per P atom. Calculate (to 3 significant figures) the theoretical weight percentage of H expected upon elemental analysis of DNA.

4.2 Chargaff extracted the separated bases and determined their concentrations by measuring UV absorbance. The Beer-Lambert law was used to obtain the molar concentration. Chargaff discovered the following molar ratio for bases in DNA:

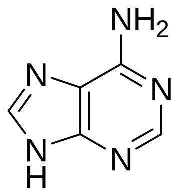
adenine to guanine = 1.43 thymine to cytosine = 1.43
adenine to thymine = 1.02 guanine to cytosine = 1.02

Chargaff's discovery suggested that the bases might exist as pairs in DNA. Watson and Crick mentioned in their celebrated 1953 paper in *Nature*: "It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material."

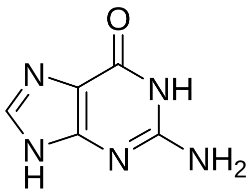
Draw structures of the specific pairing found in DNA. Indicate hydrogen bonds. Omit the sugar-phosphate backbone.

4.3 Mutation can occur through base pairings different from the above. Draw structures of any three alternative base pairs.

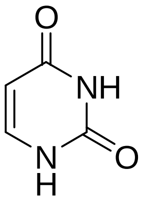
4.4 The plausibility of the formation of purine and pyrimidine bases in the prebiotic atmosphere of the Earth from HCN, NH_3, and H_2O has been demonstrated in the laboratory. Write the minimum number of HCN and H_2O molecules required for formation of the following compounds.



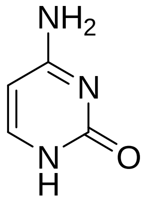
adenine



guanine



Uracil



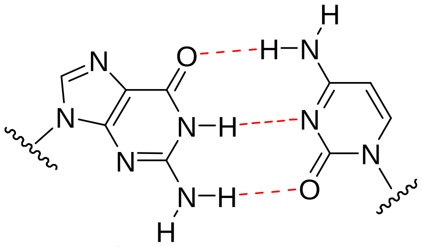
cytosine

SOLUTION

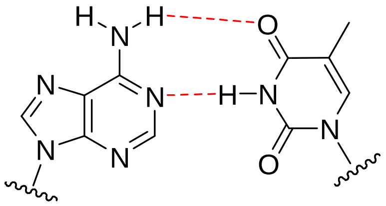
4.1

	H	P
Number of atoms:	11.3	1
theoretical wt %:	3.43	

4.2

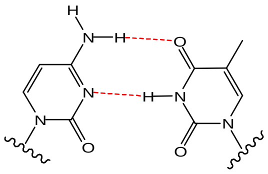


guanine cytosine

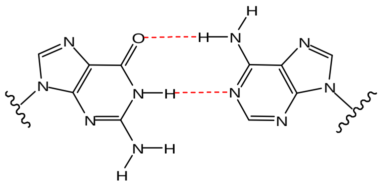


adenine thymine

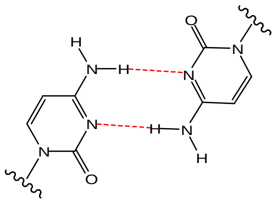
4.3



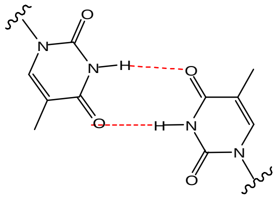
cytosine thymine



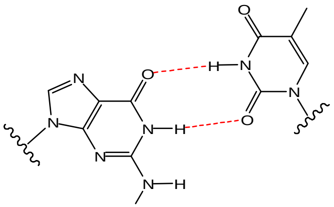
guanine adenine



cytosine cytosine



thymine thymine



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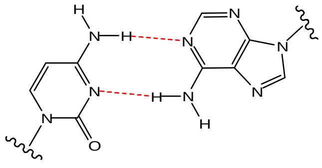
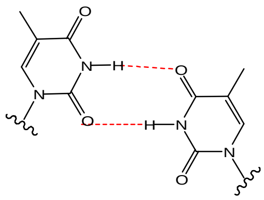
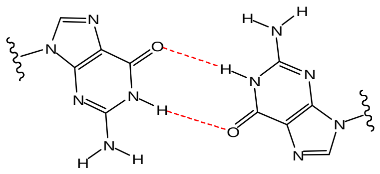


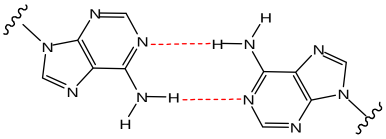
cytosine adenine



thymine thymine

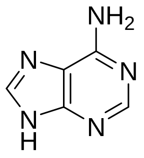


guanine guanine

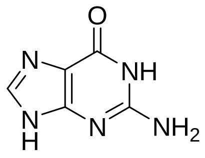


adenine adenine

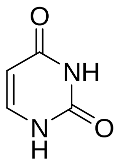
4.4



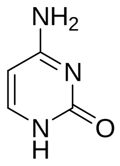
adenine



guanine



Uracil



cytosine

HCN	**(5)**	**(5)**	**(4)**	**(4)**
H_2O	**(0)**	**(1)**	**(2)**	**(1)**

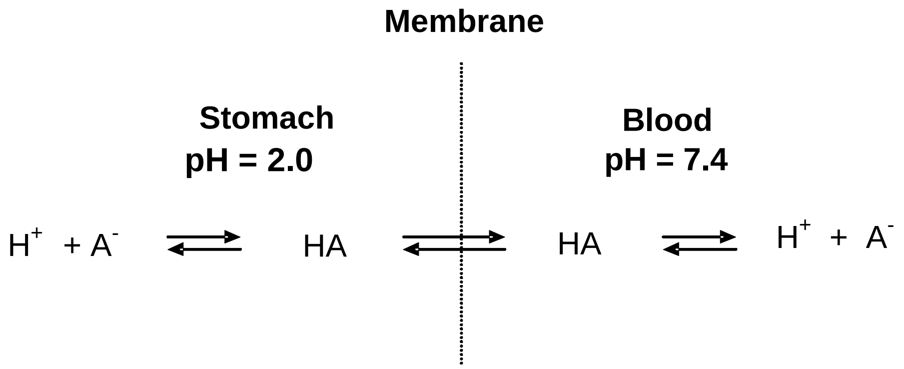
PROBLEM 5

Acid-Base Chemistry

5.1 Calculate $[H^+]$, $[OH^-]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in a 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0 \times 10^{-14}$, $K_2 = 1.2 \times 10^{-2}$ at 25 °C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.

5.2 Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm^3 aqueous solution containing 3.48 cm^3 of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm^3, M_r = 98.00) (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.44).

5.3 The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ($[HA] + [A^-]$) of aspirin (acetylsalicylic acid, pK = 3.52) in the blood to that in the stomach.

SOLUTION

5.1 1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$[H_2SO_4] = 0$

2nd ionization: $[H^+][SO_4^{2-}]\ /\ [HSO_4^-] = K_2 = 1.2\times10^{-2}$ (1)

Mass balance: $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}] = 1.0\times10^{-7}$ (2)

Charge balance: $[H^+] = [HSO_4^-] + 2\,[SO_4^{2-}] + [OH^-]$ (3)

Degree of ionization is increased upon dilution.

$[H_2SO_4] = 0$

Assume $[H^+]_{H_2SO_4} = 2\times10^{-7}$

From (1): $[SO_4^{2-}]\ /\ [HSO_4^-] = 6\times10^4$ (2nd ionization is almost complete)

$[HSO_4^-] = 0$

From (2): $[SO_4^{2-}] = 1.0\times10^{-7}$

From (3): $[H^+] = (2\times10^{-7}) + 10^{-14}\ /\ [H^+]$

$[H^+] = 2.4\times10^{-7}$ (pH = 6.6)

$[OH^-] = 1\times10^{-14}\ /\ (2.4\times10^{-7}) = 4.1\times10^{-8}$

From (1):

$[HSO_4^-] = [H^+]\,[SO_4^{2-}]\ /\ K_2 = (2.4\times10^{-7}) \times (1.0\times10^{-7})\ /\ (1.2\times10^{-2}) = 2.0\times10^{-12}$

Check charge balance:

$2.4\times10^{-7} \approx (2.0\times10^{-12}) + 2\,(1.0\times10^{-7}) + (4.1\times10^{-8})$

Check mass balance:

$0 + 2.0\times10^{-12} + 1.0\times10^{-7} \approx 1.0\times10^{-7}$

5.2 $n(H_3PO_4) = 0.85 \times 3.48\ cm^3 \times 1.69\ g\ cm^{-3} \times 1\ mol\ /\ 98.00\ g \times 1000 = 51.0\ mmol$

The desired pH is above pK_2.

A 1:1 mixture of $H_2PO_4^-$ and HPO_4^{2-} would have *pH* = *p*K_2 = 7.20.

If the *pH* is to be 7.40, there must be more HPO_4^{2-} than $H_2PO_4^-$.

We need to add NaOH to convert H_3PO_4 to $H_2PO_4^-$ and to convert to the right amount of $H_2PO_4^-$ to HPO_4^{2-}.

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$$

The volume of 0.80 NaOH needed to react with to convert H_3PO_4 to $H_2PO_4^-$ is:

51.0 mmol / 0.80 mol dm^{-3} = 63.75 cm^3

To get *pH* of 7.40 we need:

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-}$$

Initial mmol	51.0	x	0
Final mmol	51.0 – x	0	x

$pH = pK_2 + \log [HPO_4^{2-}] / [H_2PO_4^-]$

7.40 = 7.20 + log {x / (51.0 – x)}; x = 31.27 mmol

The volume of NaOH needed to convert 31.27 mmol is:

31.27 mmol / 0.80 mol dm^{-3} = 39.09 cm^3

The total volume of NaOH = 63.75 + 39.09 = 102.84 cm^3 ≈ 103 cm^3

5.3 $pK = 3.52$

$pH = pK_a + \log ([A^-] / [HA])$

$[A^-] / [HA] = 10^{(pH-pKa)}$

In blood, *pH* = 7.40, $[A^-] / [HA] = 10^{(7.40-3.52)} = 7586$

Total ASA = 7586 + 1 = 7587

In stomach, *pH* = 2.00, $[A^-] / [HA] = 10^{(2.00 - 3.52)} = 3.02\times10^{-2}$

Total ASA = $1 + 3.02\times10^{-2} = 1.03$

Ratio of total aspirin in blood to that in stomach = 7587 / 1.03 = 7400

PROBLEM 6

Electrochemistry

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

6.1 Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic. Write a balanced half-reaction for the reduction of water.

6.2 Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write a balanced half-reaction for the oxidation of water.

6.3 When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis. Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

6.4 Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+ 0.340
Reduction of oxygen	– 2.710
Reduction of water	– 0.830
Reduction of sodium ion (Na^{+})	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $Cu(OH)_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25 °C. Note that $K_w = 1.00 \times 10^{-14}$ at 25 °C.

6.5 Precipitation of $Cu(OH)_2$ begins at pH = 4.84. Determine the solubility product of $Cu(OH)_2$.

6.6 Calculate the standard reduction potential for $Cu(OH)_2(s) + 2\ e^- \rightarrow Cu(s) + 2\ OH^-$.

6.7 Calculate the electrode potential at *pH* = 1.00.

Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge recharge cycles, the following reversible half-reactions occur.

$LiCoO_2 \rightleftarrows Li_{1-x}\,CoO_2 + x\ Li^+ + x\ e^-$

$C + x\ Li^+ + x\ e^- \rightleftarrows CLi_x$

The total amount of energy a battery can store, is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

6.8 Graphite has lithium intercalation sites between its layers. Assuming a maximum 6 : 1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.

SOLUTION

6.1 $4\ H_2O + 4\ e^- \rightarrow 2\ H_2(g) + 4\ OH^-$ (or $2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$)

6.2 $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ (or $H_2O \rightarrow 1/2\ O_2 + 2\ H^+ + 2\ e^-$)

6.3 $Cu \rightarrow Cu^{2+} + 2e^-$

6.4 Reduction of sodium ion seldom takes place.

It has a highly negative reduction potential of –2.710 V.

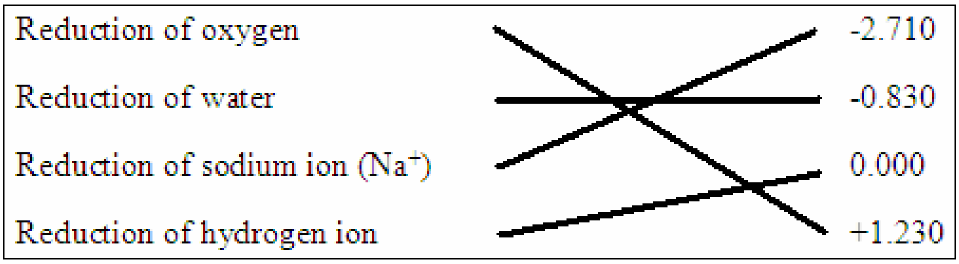
Reduction potential for water to hydrogen is negative (water is very stable).

But, it is not as negative as that for sodium ion. It is –0.830 V.

Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.

In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.

Reduction potential for hydrogen ion is defined as 0.000 V.



6.5 $pOH = 14.00 – 4.84 = 9.16$

$[OH^-] = 6.92\times10^{-10}$

$K_{sp} = [Cu^{2+}]\,[OH^-]^2 = 0.100 \times (6.92\times10^{-10}) = 4.79\times10^{-20}$

6.6 $E = E^o(Cu^{2+}/\,Cu) + (0.0592\,/\,2)\log[Cu^{2+}] = +0.340 + (0.0592/2)\log[Cu^{2+}] =$

$= +0.340 + (0.0592\,/\,2)\log(K_{sp}\,/\,[OH^-]^2)$

$= +0.340 + (0.0592\,/\,2)\log K_{sp} - (0.0592\,/\,2)\log[OH^-]^2$

$= +0.340 + (0.0592\,/\,2)\log K_{sp} - 0.0592\log[OH^-]$,

By definition, the standard potential for

$Cu(OH)_2(s) + 2\,e^- \rightarrow Cu(s) + 2\,OH^-$

is the potential where $[OH^-] = 1.00$.

$E = E^o\left(Cu(OH)_2\,/\,Cu\right) = +\,0.340 + (0.0592/2)\log K_{sp}$

$= +\,0.340 + (0.0592\,/\,2)\log(4.79\times10^{-20})$

$= +\,0.340 – 0.572$

$= –\,0.232$ V

One may solve this problem as follows.

Eqn 1: $Cu(OH)_2(s) + 2\ e^- \rightarrow Cu + 2\ OH^-$

$E_+^o = E^o\left(Cu(OH)_2 / Cu\right) = ?$

Eqn 2: $Cu(OH)_2(s) \rightarrow Cu^{2+} + 2\ OH^-$

$E^o = (0.05916 / n) \log K_{sp} = (0.05916 / 2) \log(4.79\times10^{-20}) = -0.5715$ V

Eqn 1 – Eqn 2 : $Cu^{2+} + 2\ e^- \rightarrow Cu$

$E_-^o = E_+^o - E^o = E^o\,(Cu^{2+} / Cu) = 0.34$ V

Therefore, $E_+^o = E_-^o + E^o = +0.34 + (-0.5715) = = -0.232$ V

6.7 Below $pH = 4.84$, there is no effect of $Cu(OH)_2$ because of no precipitation. Therefore,

$E = E\,(Cu^{2+} / Cu) = +0.340 + (0.0592 / 2) \log [Cu^{2+}] =$

$= +0.340 + (0.0592 / 2) \log 0.100 = +0.340 - 0.0296 = +0.310$ V

6.8 1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge 96487 × 0.0139 = 1340 coulombs.

1340 coulombs / g = 1340 A sec / g = 1340 × 1000 mA × (1 / 3600) h =

= 372 mAh / g

PROBLEM 7

Hydrogen Economy

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7.1 Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, estimate the density of hydrogen in the cylinder in kg m^{-3}.

7.2 Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. ΔH_f^o [H_2O(l)] = -286 kJ/mol, ΔH_f^o [CO_2(g)] = -394 kJ/mol.

7.3 Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by $[1 - T_{cold}/T_{hot}]$.

$S^o_{298}[H_2(g)] = 131\ \text{J mol}^{-1}\ \text{K}^{-1}$
$S^o_{298}[O_2(g)] = 205\ \text{J mol}^{-1}\ \text{K}^{-1}$
$S^o_{298}[H_2O(l)] = 70\ \text{J mol}^{-1}\ \text{K}^{-1}$

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

SOLUTION

7.1
$$\frac{n}{V} = \frac{p}{RT} = \frac{80\times 10^6\ \text{Pa}}{8,314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 298\ \text{K}} = 32\ \text{kmol m}^{-3}$$

$$\rho = \frac{m}{V} = \ 32\ \text{kmol m}^{-3}\times 2\ \text{kg kmol}^{-1} = 64\ \text{kg m}^{-3}$$

7-2. $Hg_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta H_{\text{rexn-1}} = \Delta H_f\,[H_2O(l)] = -286\text{ kJ mol}^{-1} = -143\text{ kJ g}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H_{\text{rexn-2}} = \Delta H_f\,[CO_2(g)] = -394\text{ kJ mol}^{-1} = -33\text{ kJ g}^{-1}$

$$\frac{(-\Delta H_{\text{rexn}-1})}{(-\Delta H_{\text{rexn}-2})} = 4.3 \quad \text{or} \quad \frac{(-\Delta H_{\text{rexn}-2})}{(-\Delta H_{\text{rexn}-1})} = 0.23$$

7.3 $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$\Delta H_c = -286\text{ kJ mol}^{-1} = -143\text{ kJ g}^{-1} = -143\times10^3\text{ kJ kg}^{-1}$

$\Delta G = \Delta H - T\Delta S$

$\Delta S_c = 70 - 131 - 205/2 = -163.5\text{ J mol}^{-1}\text{ K}^{-1}$

$\Delta G_c = -286\text{ kJ mol}^{-1} + 298\text{ K} \times 163.5\text{ J mol}^{-1}\text{ K}^{-1} = -237\text{ kJ mol}^{-1} = -1.2\times10^5\text{ kJ kg}^{-1}$

(a) electric motor: $W_{\max} = \Delta G_c \times 1\text{ kg} = -1.2\times10^5\text{ kJ}$

(b) heat engine: $W_{\max} = \text{efficiency} \times \Delta H_c$

$= (1 - 298 / 573) \times (-143\times10^3\text{ kJ}) = -6.9\times10^4\text{ kJ}$

$119\times10^3\text{ kJ} = 1\text{ W} \times \text{t(sec)}$

$t = 1.2\times10^8\text{ s} = 3.3\times10^4\text{ h} = 1.4\times10^3\text{ days} = 46\text{ month} = 3.8\text{ yr}$

$\Delta G = -n\,F\,E$ n = number of electrons involved in the reaction

$F = 96.5\text{ kC mol}^{-1}$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ n = 2

$$E = \frac{-\Delta G}{n\,F} = \frac{237\text{ kJ mol}^{-1}}{2\times96.5\text{ kC mol}^{-1}} = 123\text{ V}$$

$$I = \frac{W}{E} = 0.81\text{ A}$$

PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0 = -393.51$ kJ(/mol) (1)

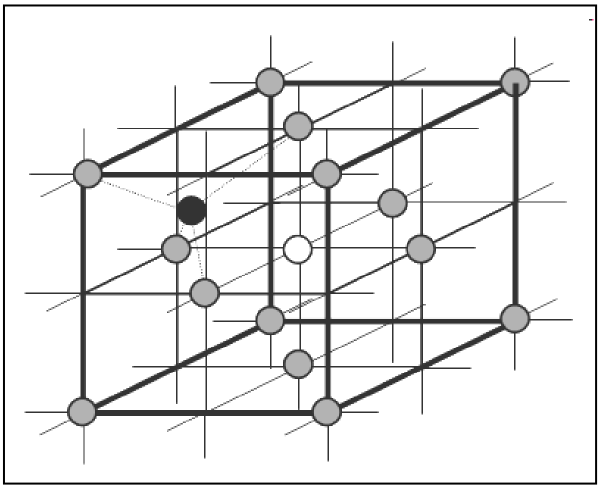
$CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0 = 172.46$ kJ(/mol) (2)

$Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$ $\Delta H^0 = ?$ (3)

8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(Fe_2O_3(s)) = -824.2$ kJ mol^{-1},
S°(J mol^{-1} K^{-1}): Fe(s) = 27.28, Fe_2O_3(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO_2(g) = 213.74

In the manufacture of celadon pottery, Fe_2O_3 is partially reduced in a charcoal kiln to mixed oxides of Fe_3O_4 and FeO. The amount of the different oxides seems to be related to the "mystic" color of celadon ceramics. Fe_3O_4 (magnetite) itself is a mixed oxide containing Fe^{2+} and Fe^{3+} ions and belongs to a group of compounds with a general formula of AB_2O_4. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.



8.3 How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

8.4 What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4?

8.5 Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

8.1 (1): C (2): C (3): CO

8.2 Balanced equation (3): $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0_{(1)} = -393.51\text{ kJ} = \Delta H_f^0\,(CO_2(g))$

(2) $CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0_{(2)} = 172.46\text{ kJ}$

From (1) and (2):

$\Delta H_f^0(CO(g)) = (1/2)\ \{172.46 + (-393.51)\} = -110.525\text{ kJ}$

$\Delta H_f^0(Fe_2O_3) = –824.2$ kJ

$\Delta H^0_{(3)} = 3 \times \Delta H_f^0(CO_2(g)) – \Delta H_f^0(Fe_2O_3) – 3 \times \Delta H_f^0(CO(g))$

$= [3 \times (–393.51)] – (–824.2) – [3 \times (–110.525)] = –24.8$ kJ

$\Delta S°_{(3)} = (2 \times 27.28) + (3 \times 213.74) – 87.4 – (3 \times 197.674) = 15.36$ J K^{-1}

$\Delta G^0_{(3)} = \Delta H^0 – T\Delta S^0 = –24.8$ kJ – (15.36 J K^{-1} $\times$ 1 kJ /1000 J x 1473.15 K) =

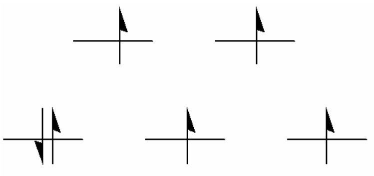
= – 47.43 kJ

$$K = e^{(-\Delta G°/RT)} = e^{(47430\text{ J } / \text{ } (8.314\text{ J K}^{-1} \times 1473.15\text{ K}))} = 48$$

8.3 One AB_2O_4 unit has available 4 (= 1 + (1/4 $\times$ 12) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) x 100 % = 12.5 % occupancy in available tetrahedral sites.

8.5

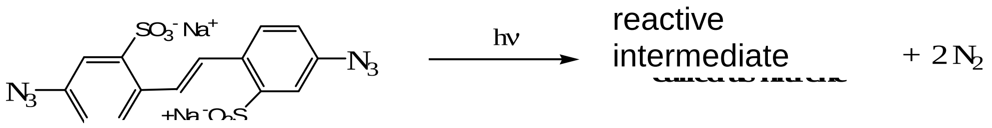


PROBLEM 9

Photolithographic process

Photolithography is a process used in semiconductor device fabrication to transfer a pattern from a photomask to the surface of a substrate. In a typical photolithography process, light is projected, through a mask that defines a particular circuitry, onto a silicon wafer coated with a thin layer of photoresist.

The earliest photoresists were based on the photochemistry that generates a reactive intermediates from bis(aryl azide). Patterning becomes possible through the cross-linking reaction of the nitrenes generated from the azides.



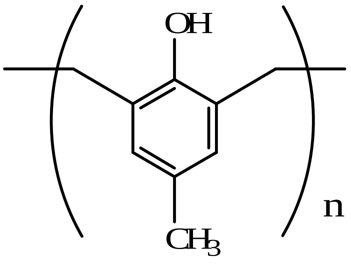
Bis(aryl azide)

9.1 Draw two possible Lewis structures of CH_3-N_3, the simplest compound having the same active functional group of bis(aryl azide). Assign formal charges.

9.2 Draw the Lewis structure of nitrene expected from CH_3-N.

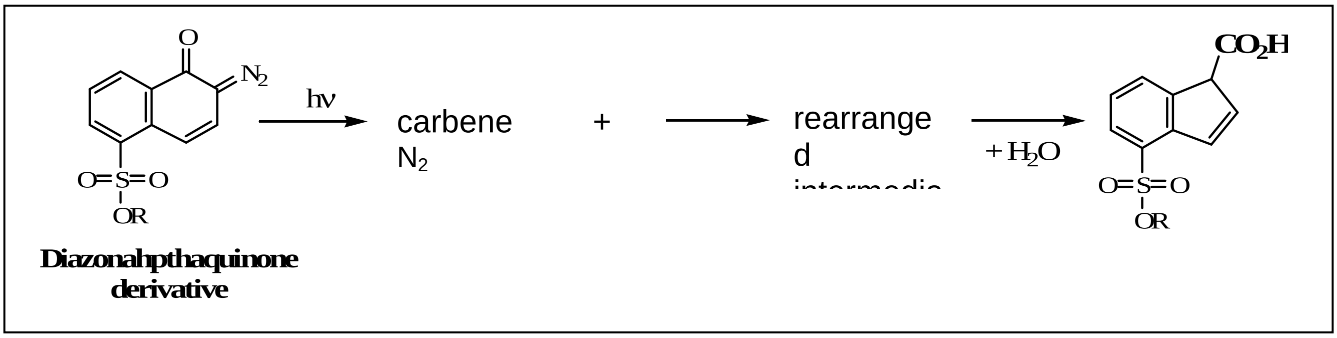
9.3 Draw the structures for two possible products, when this nitrene from CH_3-N_3 reacts with ethylene gas (CH_2CH_2).

Photoresists consisting of Novolak polymers, utilizes acid to change their solubility. The acid component can be produced photochemically from diazonaphthaquinone. In fact, “Novolaks” have been the representative “positive” photoresists of the modern microelectronic revolution.



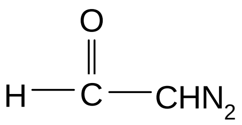
Novolak

When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.



9.4 Draw three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.

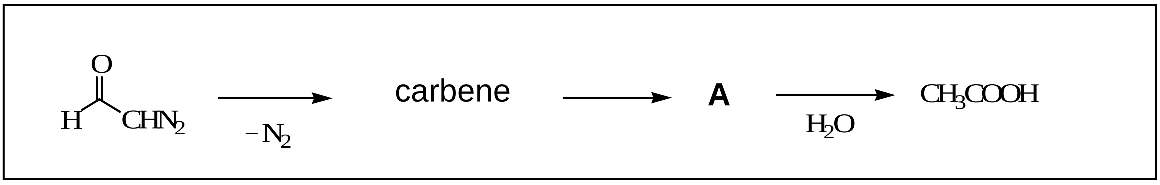
Diazonaphthaquinone
derivative



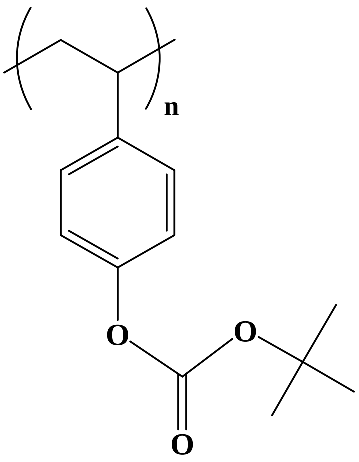
$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CHN_2$$

diazoacetaldehyde

9.5 Draw a Lewis structure of the rearranged intermediate, A (see below), generated from diazoacetaldehyde after losing N_2. A satisfies Lewis' octet rule and reacts with water to form acetic acid, CH_3COOH.

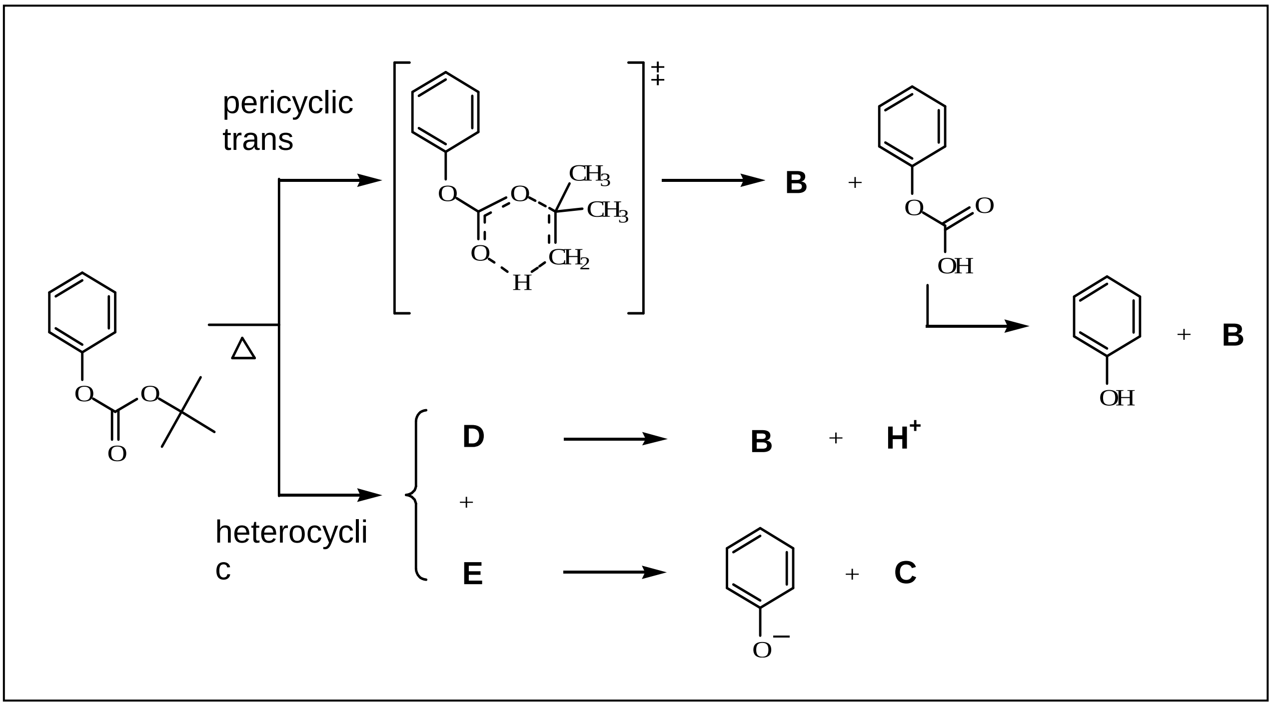


Advanced photoresists were invented in 1982 based on chemical amplification. The most popular chemical amplification for positive-tone involves the acid catalyzed deprotection of poly(*p*-hydroxystyrene) resin protected by various acid-sensitive protecting groups such as *t*-butyloxycarbonyl (*t*-BOC).

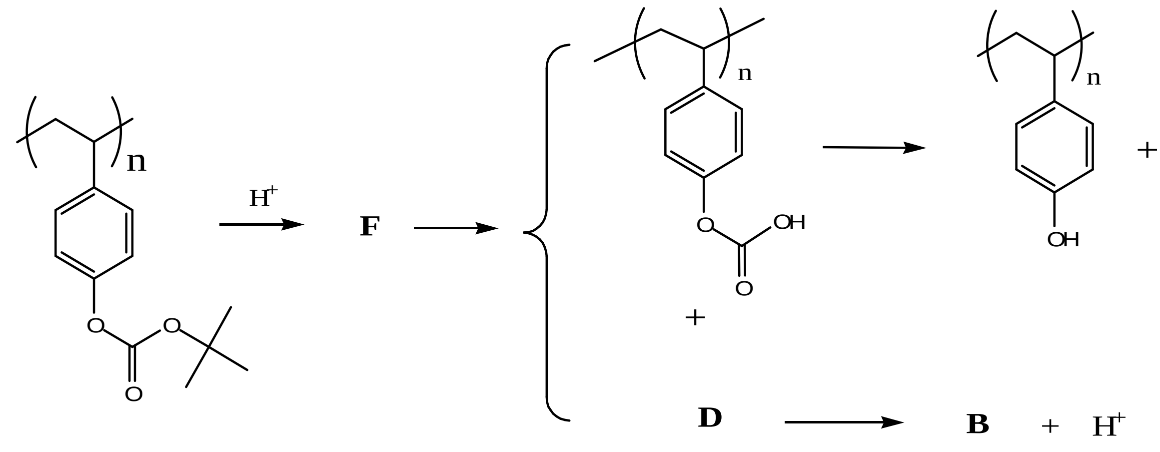


The thermal decomposition of carbonate ester itself normally occurs well above 150 ℃.

9.6 Two plausible mechanisms have been suggested for this decomposition reaction having relatively high activation energy. Draw expected intermediates and products from this reaction.

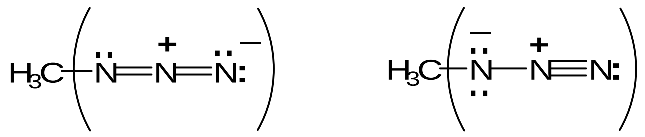


9.7 In the presence of a trace amount of acid, the reaction temperature can be reduced to below 100 ℃. Draw expected intermediate F from the following chemical amplification process based on using *t*-BOC.

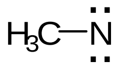


SOLUTION

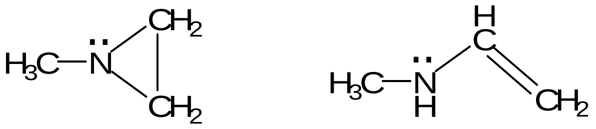
9.1



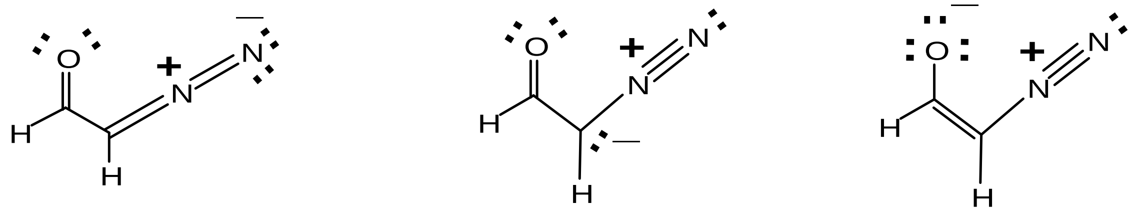
9.2



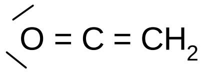
9.3



9.4

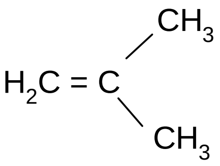


9.5



$O = C = CH_2$

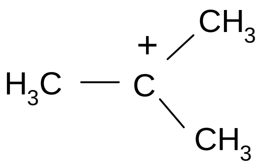
9.6


$H_2C=C(CH_3)_2$

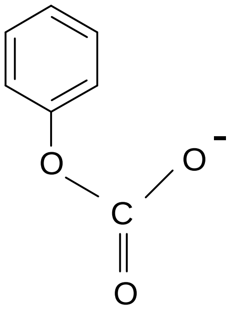
B

CO_2

C

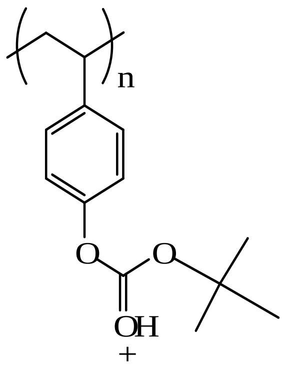

$H_3C-C^{+}(CH_3)_2$

D



E

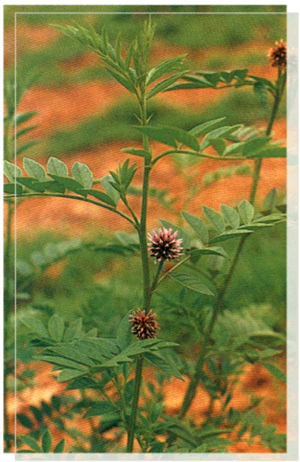
9.7



F

PROBLEM 10

Natural Products – Structural Analysis



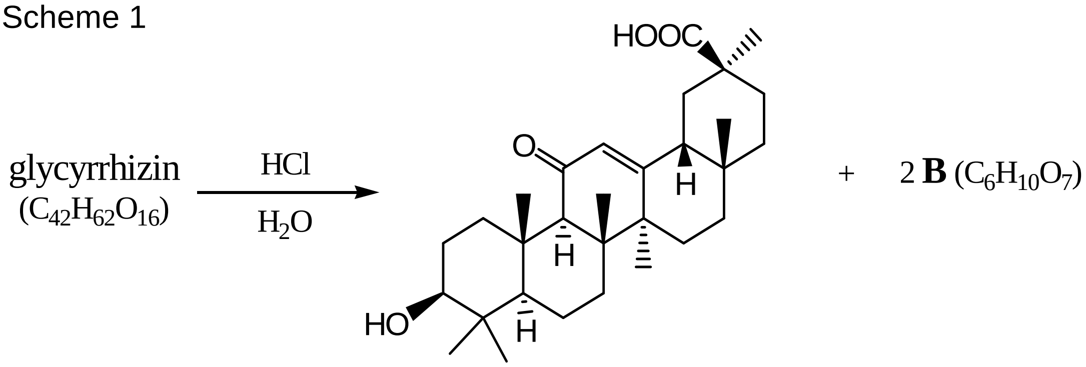
Licorice (Glycyrrhizia. Uralensis)

Licorice Root

The flavour extracted from the licorice root is 50 – 150 times sweeter than table sugar. The most important and abundant compound responsible for the sweetness and medicinal effects of licorice is *glycyrrhizin* ($C_{42}H_{62}O_{16}$).

Glycyrrhizin requires three equivalents of NaOH to effect neutralization. When *glycyrrhizin* was subjected to acid hydrolysis, *Glycyrrhizinic acid* (**A** ($C_{30}H_{46}O_{4}$)) and **B** ($C_6H_{10}O_7$) were obtainned in a 1:2 molar ratio (Scheme 1).

Scheme 1



A (Glycyrrhizinic acid)

When *glycyrrhizin* was methylated with methyl iodide (MeI) at every possible site before hydrolysis, hydrolysis produced **A'** (methyl glycyrrhizinate), **C** and **D** (Scheme 2). **B**, **C** and **D** exist as mixtures of anomers.

Scheme 2

$$\underset{(C_{42}H_{62}O_{16})}{\text{glycyrrhizin}} \xrightarrow[\text{ii) HCl / }H_2O]{\text{i) MeI, }Ag_2O} \mathbf{A'}\ (C_{31}H_{48}O_4) \quad + \quad \mathbf{C}\ (C_9H_{16}O_7) \quad + \quad \mathbf{D}\ (C_{10}H_{18}O_7)$$

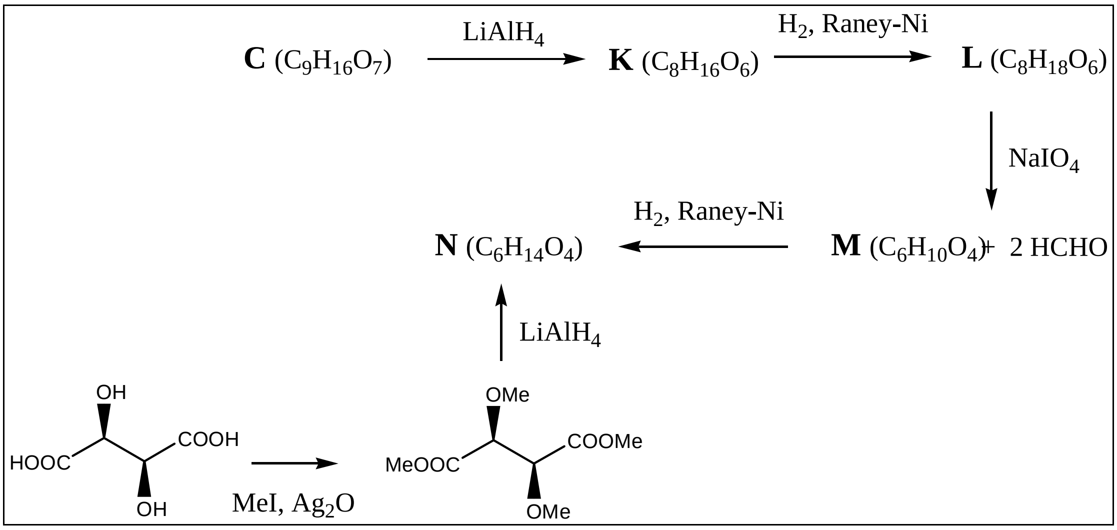
Methylation of **C** and **D** with MeI produced the same isomeric mixture of compounds, **J** (Scheme 3).

Scheme 3

$$\mathbf{C}\ (C_9H_{16}O_7) \xrightarrow{\text{MeI, }Ag_2O} \mathbf{J}\ (C_{11}H_{20}O_7) \xleftarrow{\text{MeI, }Ag_2O} \mathbf{D}\ (C_{10}H_{18}O_7)$$

C was reduced with $LiAlH_4$ to give **K**, and **L** was produced by the reduction of **K**. Oxidative cleavage of vicinal diol of **L** with $NaIO_4$ produced **M** and two equivalents of formaldehyde. Reduction of **M** produced **N**. The structure and stereochemistry of **N** was confirmed by the synthesis of **N** from D-(-)-tartaric acid through methylation followed by reduction (Scheme 4). A ^{1}H-NMR spectrum of **L** showed two distinct peaks for methyl groups. (There is no symmetry in L)

Scheme 4

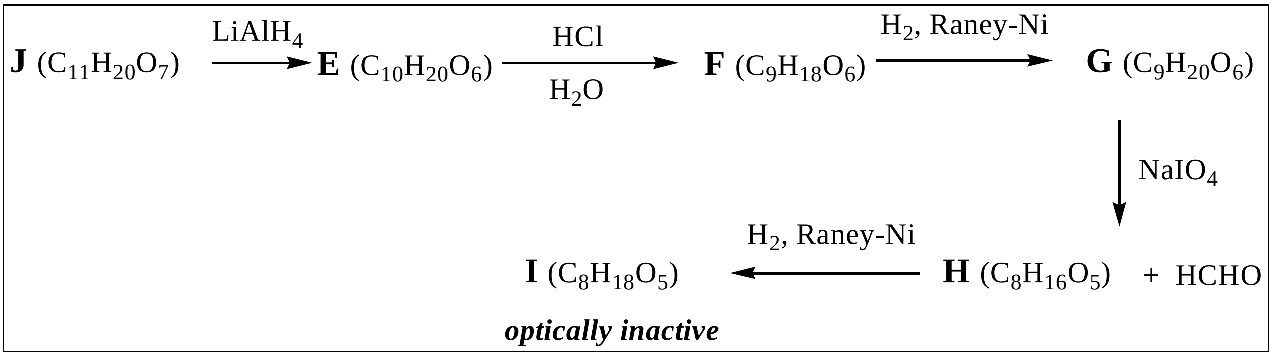


10.1 <u>Complete</u> structures for **L , M, and N** in the answer sheet.

10.2 How many structures for **C** are possible? <u>Complete</u> possible structures for **C**.

To determine the correct structure of **C**, following set of reactions were performed. **J** was reduced to **E,** and acid hydrolysis of **E** produced **F**. Reduction of **F** generated **G,** and **G** was oxidized with $NaIO_4$ to **H** with formation of one equivalent of formaldehyde. **I** was obtained from **H** through reduction. Among all compounds from **A** to **I**, only **I** was optically inactive (Scheme 5).

Scheme 5



10.3 Complete structures for **G** and **I**.

10.4 Which one is the correct structure for **C** among ones you have drawn in **10-2**?

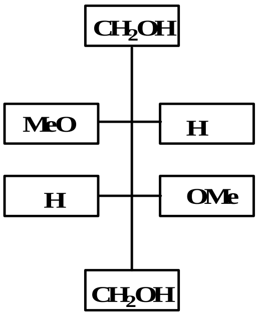
10.5 Complete structures for **B, D,** and **J**.

10.6 Complete the structure for Glycyrrhizin.

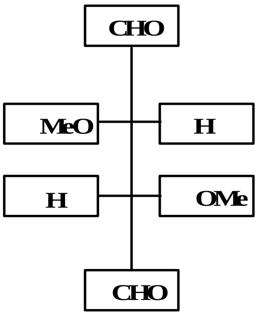
SOLUTION

10.1

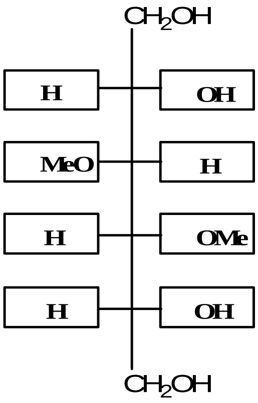
N



M

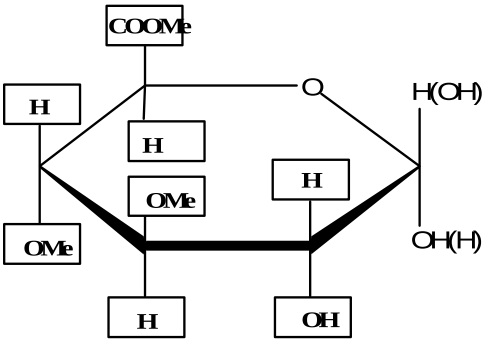


L

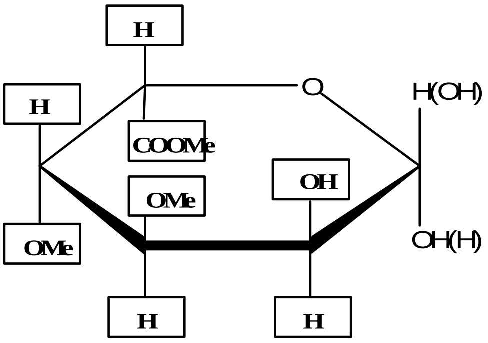


10.2 Number of possible structures **2**

1

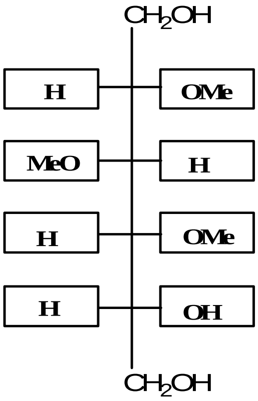


2

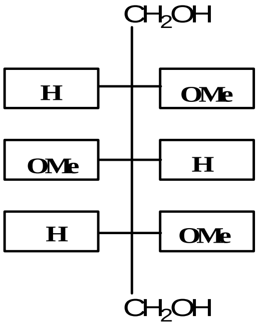


10.3

G



I

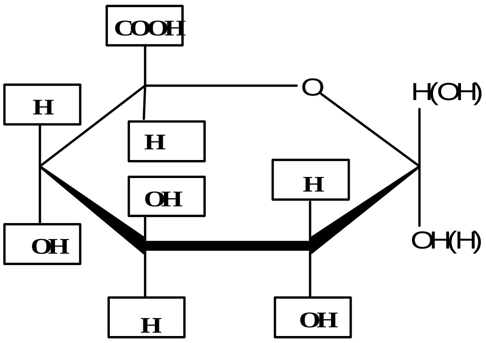


10.4

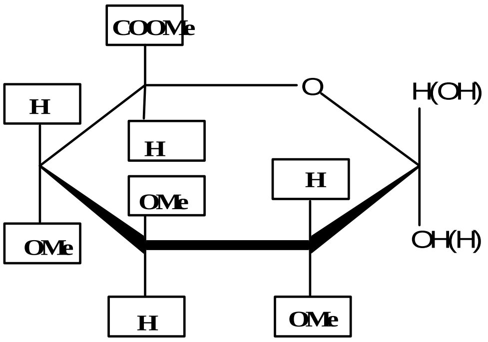
The correct structure for **C** from 10-2 is No. 1

10.5

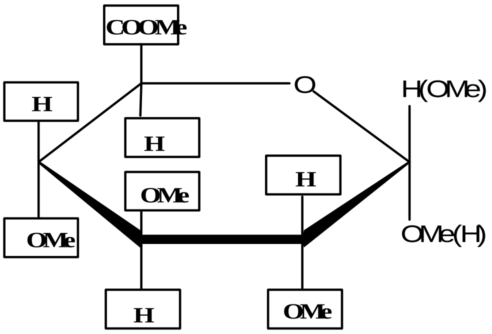
B



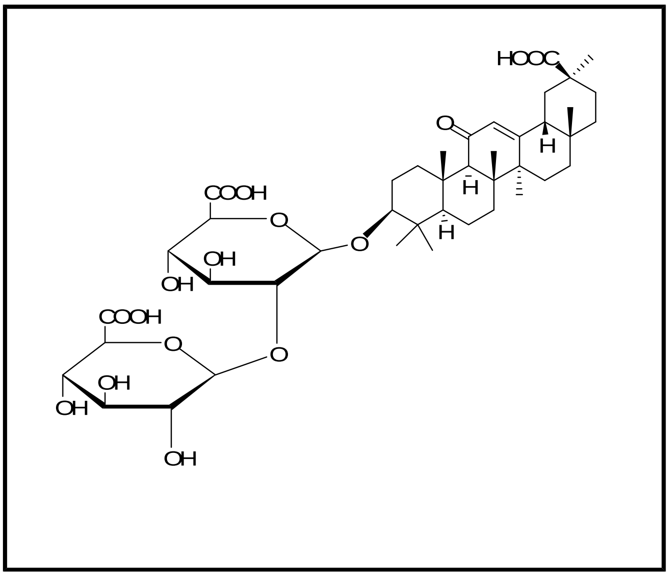
D


COOMe
O
H(OH)
H
H
H
OMe
OMe
OH(H)
H
OMe

J


COOMe
O
H(OMe)
H
H
H
OMe
OMe
OMe(H)
H
OMe

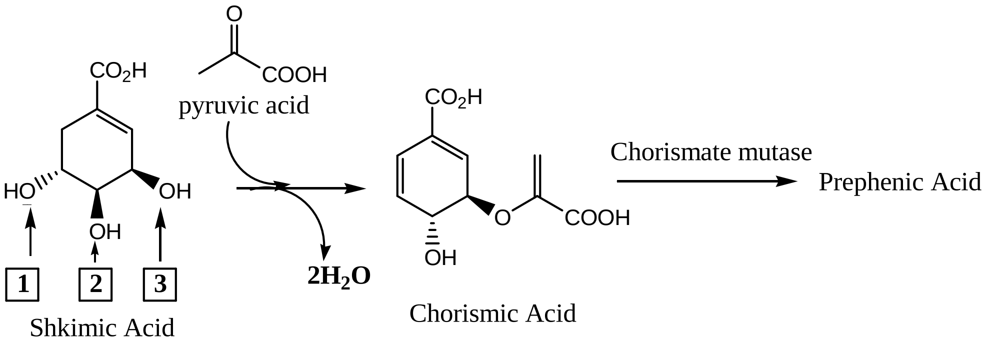
10.6


HOOC
O
H
COOH
O
H
O
OH
OH
H
COOH
O
O
OH
OH
OH

PROBLEM 11

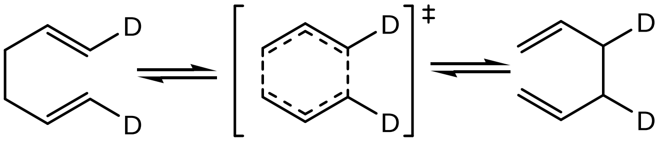
Enzyme Reaction

Shikimic acid biosynthesis is an important pathway for amino acids, alkaloids and heterocyclic natural product production. Nature converts shikimic acid to chorismic acid through a cascade of enzymatic reactions. Then chorismate mutase catalyzes the conversion of chorismic acid to prephenic acid at the branch point for the biosynthesis of aromatic amino acids such as tyrosine and phenylalanine.



11.1 During the transformation of shikimic acid to chorismic acid, dehydration is occurring. Choose the hydroxyl group in shikimic acid that is lost through above dehydration among all possible reactions.

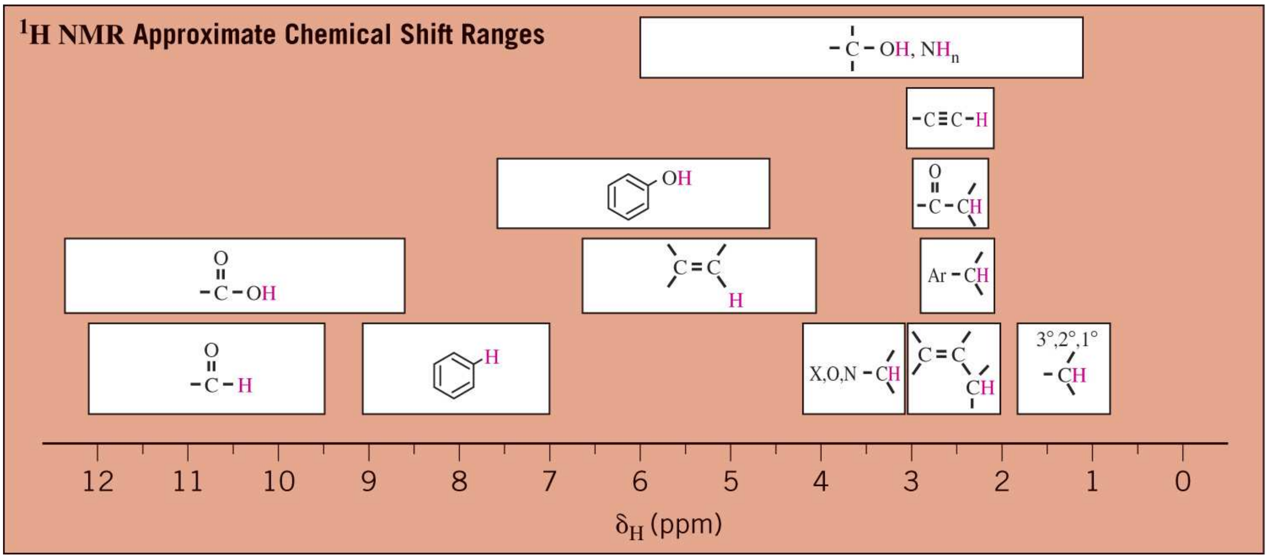
11.2 Chorismate mutase rearranges chorismic acid into prephenic acid without changing the molecular formula. Chorismic acid becomes prephenic acid through the Claisen rearrangement, a concerted pericyclic process like the Cope rearrangement as shown below:



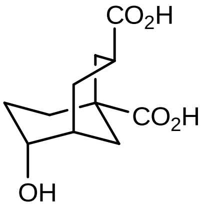
Based on the following spectral data, propose the structure of prephenic acid.

^{1}H-NMR (D_2O, 250 MHz): δ 6.01 (2H, d, J = 10.4 Hz), 5.92 (2H, dd J = 10.4, 3.1 Hz), 4.50 (1H, t, J = 3.1 Hz), 3.12 (2H, s). Note that there are three protons, which have been exchanged by D_2O very fast, and two protons at δ 3.12, which are exchanged slowly in prephenic acid. ^{13}C-NMR (D_2O, 75 MHz): δ 203, 178, 173, 132 (for two identical carbons), 127 (for two identical carbons), 65, 49, 48.

δ, chemical shift; H, integrals; d, doublet; dd, doublet of doublet; J, coupling constant; t, triplet; s, singlet

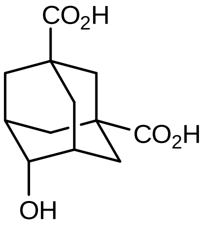


Chorismate mutase is believed to stabilize the transition state of Claisen rearrangement. Thus it is an interesting target for inhibitor design. Inhibitors, called transition state analog (TSA)s that resemble the transition state (TS, *e.g.*, the species in brackets “[ ]” above) of the reaction are designed to occupy the active site. Several inhibitors were designed and synthesized, and among them eight turned out to be potent inhibitors of the enzyme. The lower is the IC_{50} (inhibitor concentration of 50 % of the enzymatic activity) value, the better is the inhibitor.



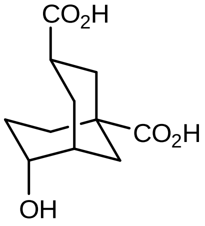
1

IC_{50} = 2.5 mM



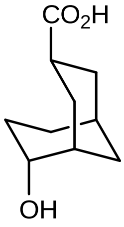
2

IC_{50} = 1.3 mM



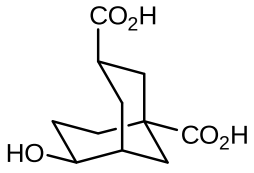
3

IC_{50} = 0.78 mM



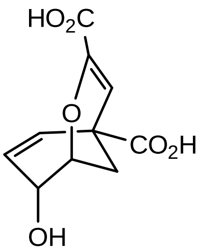
4

IC_{50} = 1.1 mM



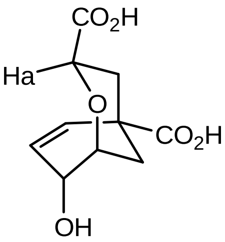
5

IC_{50} = 5.3 mM



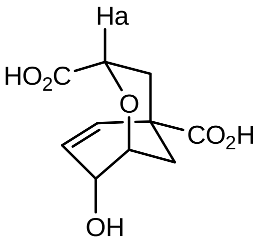
6

IC_{50} = 0.017 mM



7

IC_{50} =0.0059 mM



8

IC_{50} = 0.00015 mM

11.3 Choose all correct statements based on the structures and IC_{50} values of above inhibitors. Increase of factor 5 is considered to be important.

(a) Configuration of the hydroxyl group plays an important role in the TS and inhibitor design.

(b) The presence of both carboxylic groups is important in the TS and inhibitor design.

(c) Transition state of the reaction contains two six-membered rings with one chair and one twist-boat conformation.

(d) **7** and **8** can be distinguished on the basis of the ^{1}H-NMR of H_a.

11.4 Draw the transition state of the transformation of chorismic acid to prephenic acid based on the TSA structures and their IC_{50} values.

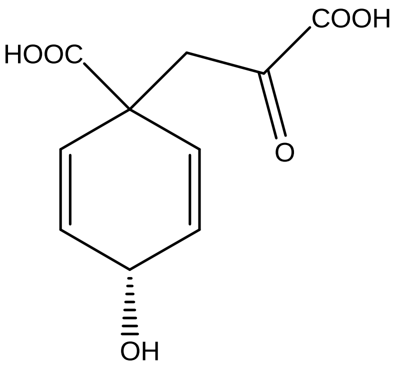
11.5 Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid 1.0×10^6 fold at 25 °C by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at 25 °C.

$\Delta H^{\neq}_{uncat}$ is 86,900 J mol^{-1} for the thermal conversion of chorismic acid to prephenic acid. At what temperature will the rate of the *uncatalyzed* thermal conversion be the same as that of the *enzyme-catalyzed* conversion at 25 °C, assuming that $E_a = \Delta H^{\neq}$.

SOLUTION

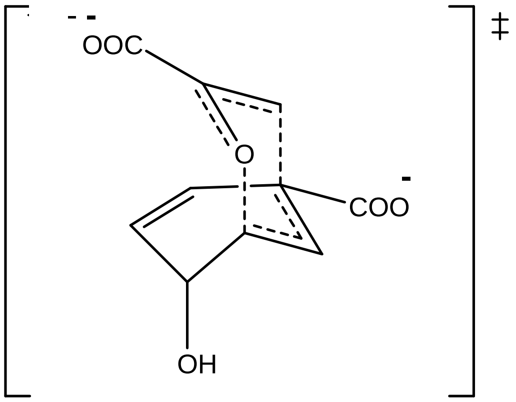
11.1 Hydroxyl group No. 3

11.2



11.3 Correct statements: (a), (c), (d).

11.4



Transition state

11.5 For the enzyme-catalyzed reaction, Arrhenius equation could be applied.

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A\ \exp\left(-E_{a,\ \text{cat}}/\text{RT}\right)}{A\ \exp\left(-E_{a,\ \text{uncat}}/\text{RT}\right)} = \exp\left[-\Delta E_{a,\ \text{cat-uncat}}/RT\right] =$$

$$= \frac{\exp\left(-\Delta E_{a,\ \text{cat}-\text{uncat}}\ (\text{J mol}^{-1})\right)}{2{,}480\ \text{J mol}^{-1}} = 1\times10^{6}$$

Therefore, $-\Delta E_{a,\ \text{cat-uncat}} = 34{,}300\ \text{J mol}^{-1}$

$$\frac{k_{\text{uncat, T}}}{k_{\text{uncat, 298}}} = \frac{A\ \exp\left(-\Delta H^{\neq}{}_{\text{uncat}}\ /RT\right)}{A\ \exp\left(-\Delta H^{\neq}{}_{\text{uncat}}\ /\ 298\ R\right)} = \exp\left[\left(\frac{-\Delta H^{\neq}{}_{\text{uncat}}}{R}\right)\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$\frac{k_{\text{uncat, T}}}{k_{\text{uncat, 298}}} = 13.8 = \exp\left[\left(\frac{-86900}{8.32}\right)\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

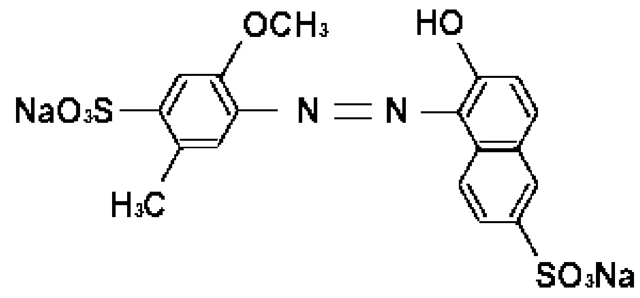
Therefore, T = 491 K, or 218 $^{\text{o}}$C

PRACTICAL PROBLEMS

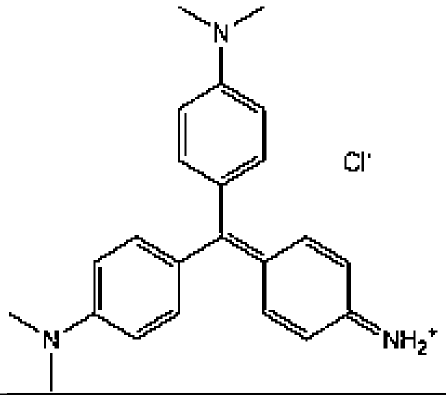
PROBLEM 1 (Practical)

Reverse-phase Chromatography: Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the non-polar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



Food Red No. 40



Methyl Violet 2B

1.1 Spectrophotometric Analysis of R and B in a Mixed Solution

a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1.1).

b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1.1.

c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1.2 Chromatographic Separation Followed by Spectrophotometric Analysis

a) Elute the cartridge with about 10 cm^3 of Solution E using 10 cm^3 syringe (Fig. C).

b) Load 1.00 cm^3 of solution MD onto the cartridge (Fig. D).

c) Using 1 cm^3 syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 cm^3 volumetric flask. Repeat until the red compound is completely eluted and collected.

d) Fill the flask to the 10 cm^3 mark with Solution E and mix. Call this Solution F.

e) Obtain the absorption spectrum of solution F as in Experiment 1.1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1.1 in red ink.

f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1.2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.

g) Report the concentration of R in the original Solution MD.

h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.

PROBLEM 2 (Practical)

Reverse-phase Chromatography:
Acid-Base Titration of Acetic Acid and Salicylic Acid

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

a) Titrate 10 cm^3 of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 cm^3 of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.

b) Standardize NaOH solution with 2.00 cm^3 of the standard KHP (potassium hydrogen phthalate) solution (1.00 x 10^{-2} M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.

c) Withdraw 1.00 cm^3 of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 cm^3 of Solution MA.

2-2. Reverse-phase Separation and Titration

a) Elute a new C-18 cartridge with about 10 cm^3 of distilled water using 10 cm^3 syringe.

b) Load 1.00 cm^3 of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).

c) Elute with 1 cm^3 of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 cm^3 liquid in each tube.

d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.

e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.

f) Calculate the mole percent of AA in solution MA.

PROBLEM 3 (Practical)

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

Procedure

Helpful Comments

a) The weight of a spatula tip-full of a solid is about 15~20 mg.
b) Wipe spatula cleanly with Kimwipe between uses.
c) After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.
d) To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 cm^3 of CH_3CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 cm^3 of 95 % EtOH. (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulphuric acid and 95% ethanol (labelled as 2,4-DNPH).

Test 3: CAN test

Mix 3 cm^3 of the cerium(IV) ammonium nitrate solution in dilute HNO_3 (labelled as CAN) with 3 cm^3 of CH_3CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 cm^3 of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water first, and then add 1 cm^3 of CAN.) If there is a colour change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Bayer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of CH_3CN. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) To the solution, slowly add five drops of the 0.5 % $KMnO_4$ solution, drop by drop while shaking.

Test 5: *pH* test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of 95 % EtOH. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water). Measure the pH of the solution with pH paper.

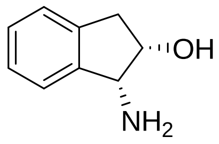
Test 6: Iron(III) chloride test

Take the solution from Test 5 and add five drops of a 2.5 % $FeCl_3$ solution.

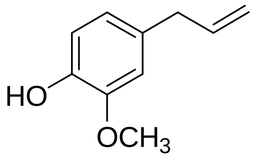
Results

1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.
2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

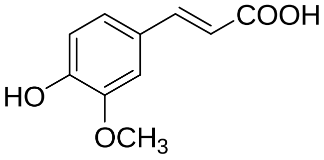
Possible Unknown Compounds (next page):



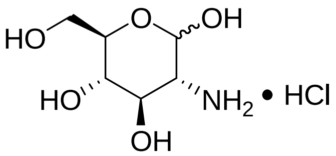
(A)



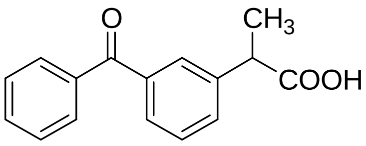
(E)



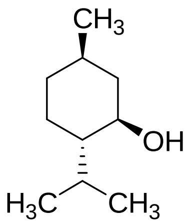
(F)



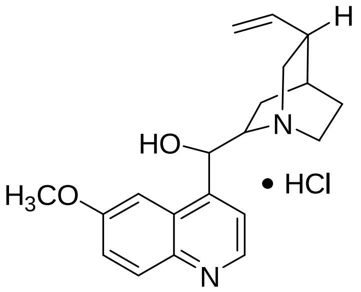
(G)



(K)



(M)



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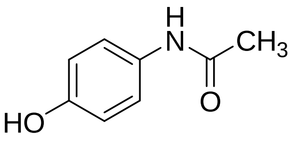

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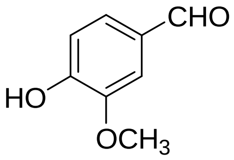
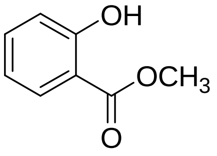


(V)



(W)

39th

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International Chemistry Olympiad

8 theoretical problems
2 practical problems

THE THIRTY-NINTH
INTERNATIONAL CHEMISTRY OLYMPIAD
15–24 JULY 2007, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

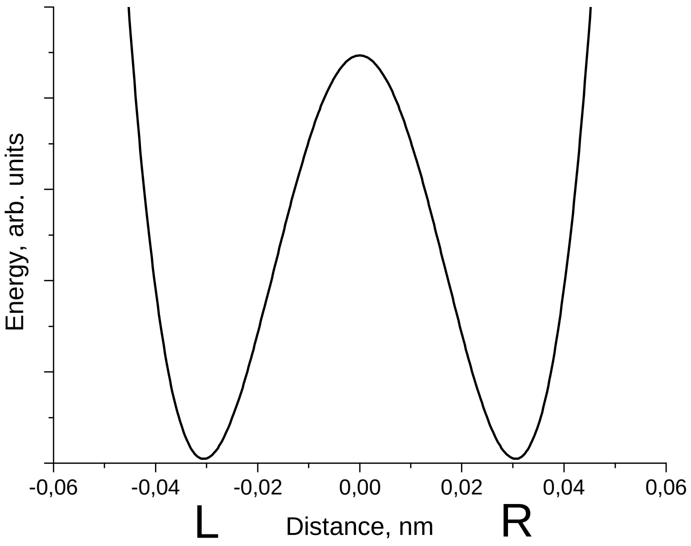
Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.

1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

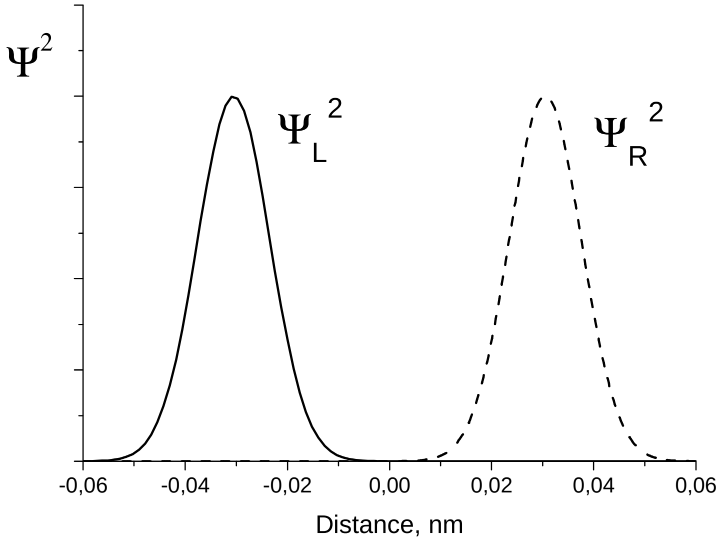


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48 \times 10^{11}$ s^{-1}. Probability density for a proton depends on time as follows:

$$\Psi^2(x,t) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x) + \left(\Psi_L^2(x) - \Psi_R^2(x)\right)\cos\left(\omega t\right)\right],$$

wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.

1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$

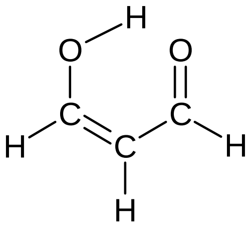
1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?

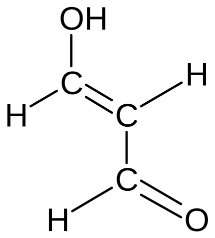
1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in **1.6** and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

SOLUTION

1.1 The structures of propanedial and two of its isomers:

$O{=}CH{-}CH_2{-}CH{=}O$





1.2 Acidic hydrogen atom is in CH_2 (in enol forms acidic hydrogen is in OH).

The stability of propanedial is caused by (one of the following answers had to be chosen):

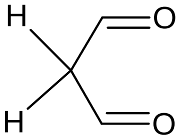
a) the stability of carbanion due to conjugation with two carbonyl groups,

b) weakness of C – H bond in a carbonyl group,

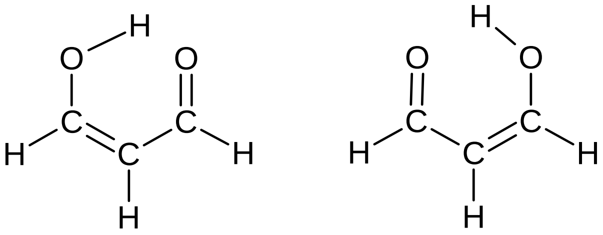
c) hydrogen bonds between two propanedial molecules.

The first answer is correct.

1.3 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



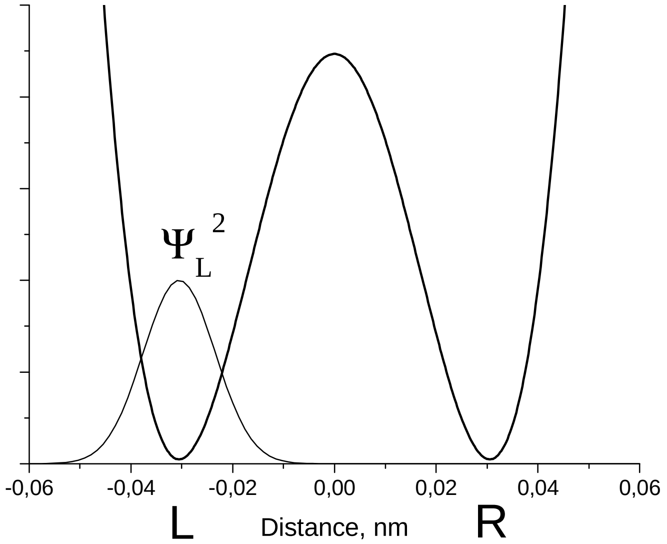
such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1.4 Expressions and plots of probability density

(a) $\Psi^2(x,0) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)+\Psi_L^2(x)-\Psi_R^2(x)\right] = \Psi_L^2(x)$

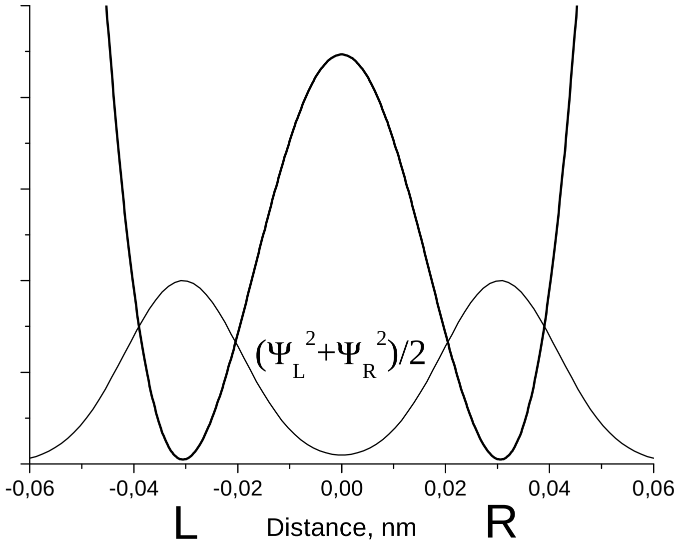
The probability density is concentrated in the left well:



(b) In the middle of the time interval

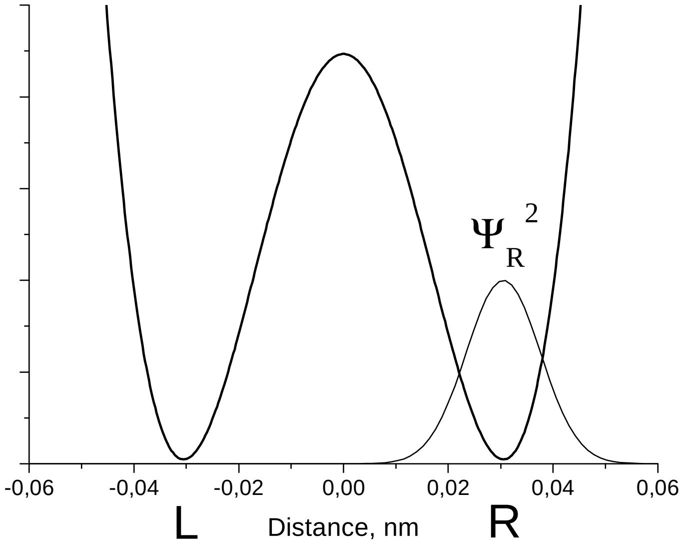
$$\Psi^2\left(x,\frac{\pi}{2\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)\right]$$

The probability density has a symmetric form, a proton is delocalized between two wells:



(c) $$\Psi^2\left(x,\frac{\pi}{\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)-\Psi_L^2(x)+\Psi_R^2(x)\right] = \Psi_R^2(x)$$

The probability density is concentrated in the right well:



1.5 The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.6 The time of transfer from one well to another is t = π / ω.

$$t = \frac{3.14}{6.48\times10^{11}} = 4.85\times10^{-12} \text{ s.}$$

The proton velocity:

$$v = \frac{0.06\times10^{-9}}{4.85\times10^{-12}} = 12\ \text{m s}^{-1}.$$

1.7 The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (<u>0.06 nm will be also accepted</u>).

The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta v = \frac{h}{2\,m\,\Delta x} = \frac{1.055\times10^{-34}}{2\times\dfrac{0.001}{6.02\times10^{23}}\times0.03\times10^{-9}} \approx 1000\ \text{m s}^{-1}.$$

Comparing this uncertainty with the velocity 12 m s^{-1} we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

PROBLEM 2

Nanochemistry

Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)

$$CO + 3\,H_2 \xrightarrow{\text{Fe,Co}} CH_4 + H_2O$$

Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:

$$Co(s) + H_2O(g) \rightleftarrows CoO(s) + H_2(g) \qquad (1)$$

Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

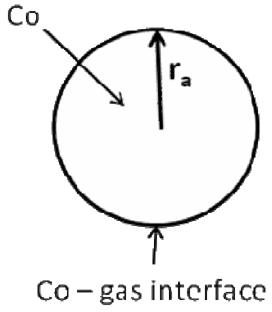


Fig. 1

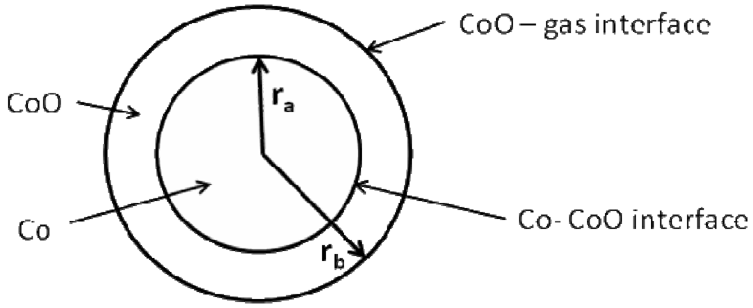


Fig. 2

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^0(r) = G^0(\text{bulk}) + \frac{2\sigma}{r}V$$

2.1 Calculate the standard Gibbs energy $\Delta_r G^0(1)$ and the equilibrium constant for the reaction (1) at T = 500 K.

2.2 Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

(a) 10^{-8} m,·

(b) 10^{-9} m.

The surface tension at the Co-gas interface is 0.16 J m^{-2}. CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO, CH_4, H_2, H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is p = 1 bar, temperature is T = 500 K. The mole fraction of hydrogen (%) in the mixture is 0.15 %.

2.3 At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of

(a) a bulk phase

(b) spherical nanoparticles with r_a = 1 nm (Fig. 1).

2.4 What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(H_2O)/p(H_2)$ and a constant temperature:

(a) to increase r_a;

(b) to decrease r_a;

(c) change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a, r_b, molar volumes as V(Co); V(CoO).

2.5 Write down the expression for the standard molar Gibbs function of CoO.

2.6 Write down the expression for the standard molar Gibbs function of Co.

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{in} - P_{ex} = \Delta P = \Delta P_1 + \Delta P_2 = 2\frac{\sigma_1}{r_1} + 2\frac{\sigma_2}{r_2}$$

r_i, σ_i are radius and surface tension at the spherical interface i, respectively.

2.7 Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1, r_a, r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a, r_b, V(Co); V(CoO) and $\Delta_r G^0(1)$.

2.8 When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, r_a = r_b = r_0, and $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. Assume that

$\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1,r_0)$ on r_0?

2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(H_2O)/p(H_2)$ and a constant temperature:

a) increase r_0

b) decrease r_0

c) change of r_0 has no effect.

.

Reference data:

Substance	ρ, g cm^{-3}	$\Delta_f G^o_{500}$, kJ mol^{-1}
Co (s)	8.90	
CoO (s)	5.68	–198.4
H_2O (gas)		–219.1

SOLUTION

2.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G^0_{500}(1) = \Delta G^0_{f,500}(\text{CoO,s}) - \Delta G^0_{f,500}(\text{H}_2\text{O,g}) = -198.4 + 219.1 = 20.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta_r G^0_{500}(1)}{RT}} = e^{-\frac{20700}{8.314 \times 500}} = 6.88 \times 10^{-3}$$

2.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\Delta_r G^o_{500}(1,r_a) = G^0_{\text{bulk},500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,g}) - G^0_{\text{sph}}(\text{Co}) =$$

$$= G^0_{500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,gas}) - \left(G^0_{500}(\text{Co,s}) + \frac{2\,\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} \right) =$$

$$= \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a};$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{1 \times 10^{-6} \times 59.0}{8.90} = 6.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$$\frac{2\,\sigma_{\text{Co-gas}}\,V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J mol}^{-1}$$

$\Delta_r G^o_{500}(1,r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ mol^{-1}, respectively.

The equilibrium constant is calculated from the equation

$$K(1,r_a) = \exp\left(-\frac{\Delta_r G^o_{500}(1,r_a)}{RT} \right)$$

$K(1,\text{r}_a) = 7.22\times10^{-3}$; $r_a = 10^{-8}$ m $\qquad K(1,r_a) = 11.4\times10^{-3}$; $r_a = 10^{-9}$ m

2.3 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G^o_{500}(1,r_a) = \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co})$$

$\Delta_r G^o_{500}(1)$ is 20.7 kJ mol^{-1}. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^o_{500}(1,r_a)$ is 18.6 kJ mol^{-1}.

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G^o_{500}(1) + RT\ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G^o_{500}(1) - \text{RT}\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and for spherical cobalt nanoparticles with r_a = 1 nm:

$$\Delta_r G(1,r_a) = \Delta_r G^o_{500}(1,r_a) + \text{RT}\ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) =$$

$$= \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - \text{RT}\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

$\Delta_r G^o_{500}(1)$ is equal to 20.7 kJ mol^{-1}. For spherical cobalt particles with r_a = 1 nm equals to 18.6 kJ mol^{-1}

2.4 For the spontaneous oxidation

$$\Delta_r G(1,r_a) = \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and

$$\Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \le RT\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right)$$

The left hand side of the last inequality becomes more positive with the increase of r_a. At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a. The answer (a) is correct.

2.5 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G^0_{\text{sph}}(\text{CoO},r_b) = G_{\text{bulk}}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}V(\text{CoO}) = G^o(\text{CoO,s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}V(\text{CoO})$$

2.6 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$G^0_{\text{sph}}(\text{Co},r_a,r_b) = G_{\text{bulk}}(\text{Co}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= G^o(\text{Co,s}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right)$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

2.7 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\Delta_r G^0(1,r_a,r_b) = G^0_{\text{sph}}(\text{CoO},\text{r}_b) + G^o(\text{H}_2,\text{gas}) - G^o(\text{H}_2\text{O},\text{gas}) - G^0_{\text{sph}}(\text{Co},r_a,r_b) =$$

$$= G^o(\text{CoO,s}) + G^o(\text{H}_2,\text{gas}) - G^o(\text{H}_2\text{O},\text{gas}) - G^o(\text{Co,s}) +$$

$$+ \frac{2\sigma_{\text{CoO-gas}}}{r_b}V(\text{CoO}) - 2V(\text{Co})\left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= \Delta_r G^o(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a}V(\text{Co})$$

2.8 Under the assumptions made

$$\Delta_r G^{o}(1,r_a,r_b) = \Delta_r G^{0}(1,r_0) =$$

$$= \Delta_r G^{o}(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a}\text{V(Co)} =$$

$$= \Delta_r G^{o}(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right)$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) = 6.56\times10^{-6}\ \text{m}^3$$

$\Delta_r G^0(1,r_0)$ is directly proportional to $\left(\frac{1}{r_0}\right)$. The plot (a) is correct.

2.9 The spontaneous forward reaction (1) is possible, when $\Delta_r G(1,r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) \leq RT\ln\frac{p_{H_2O}}{p_{H_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0. At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0.

The answer (b) is correct.

PROBLEM 3

Unstable chemical reactions

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:

$$B + 2\,X \xrightarrow{k_1} 3\,X$$

$$X + D \xrightarrow{k_2} P$$

(B and D are reagents, X is an intermediate and P is a product).

3.1 Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.

3.2 Deduce a rate equation using steady-state approximation. Find the orders:

(i) a partial reaction order with respect to B;

(ii) a partial reaction order with respect to D;

(iii) the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: [B] = [D] = const.

3.3 Without solving the kinetic equation draw the kinetic curve [X](t) for the cases:

1) $[X]_0 > \dfrac{k_2}{k_1}$; 2) $[X]_0 < \dfrac{k_2}{k_1}$.

3.4 Without solving the kinetic equation draw the kinetic curve [X](t) for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[B]_0 = [D]_0$, $[X]_0 > \dfrac{k_2}{k_1}$.

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:

$$C_2H_6 + X + ... \xrightarrow{k_1} 2\,X$$

$$X + Y \xrightarrow{k_2} 2\,Y + ...$$

$$C_2H_6 + Y + ... \xrightarrow{k_3} 2\,P$$

Under specific conditions this reaction displays oscillatory behavior: Intermediates are peroxide $C_2H_6O_2$ and aldehyde C_2H_4O, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, $cm^3\ mol^{-1}s^{-1}$	E_A, $kJ\ mol^{-1}$
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

SOLUTION

3.1 The overall reaction equation

B + D → P

The kinetic equation for X

$$\frac{d[X]}{dt} = k_1[B][X]^2 - k_2[D][X]$$

3.2 Under the steady-state conditions

$$\frac{d[P]}{dt} = k_2[D][X] = k_1[B][X]^2,$$

whence

$$[\mathrm{X}] = \frac{k_2[\mathrm{D}]}{k_1[\mathrm{B}]}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = \frac{k_2^2[\mathrm{D}]^2}{k_1[\mathrm{B}]}$$

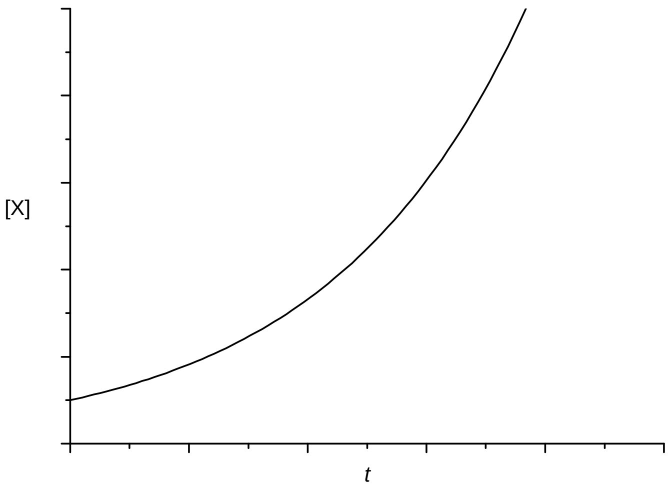
The reaction order is 2 with respect to D, and –1 with respect to B.

The overall order is 1.

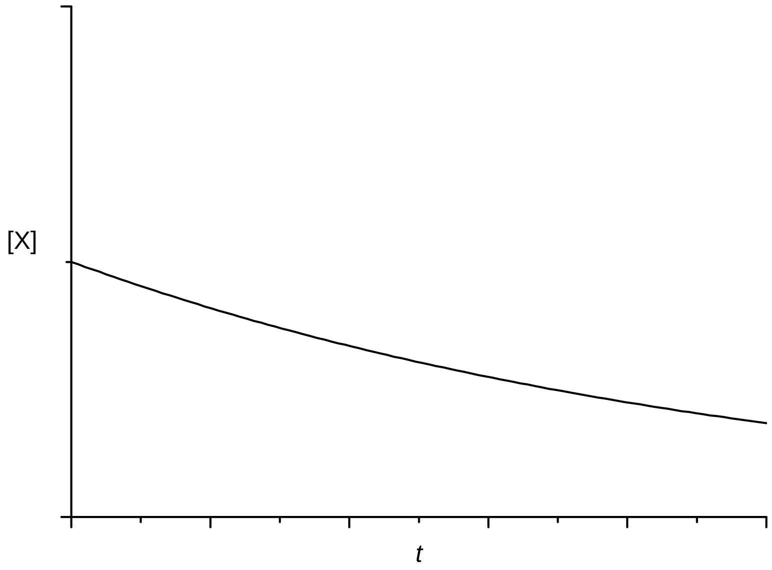
3.3 In an open system the initial reaction rate is:

$$\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = [\mathrm{B}][\mathrm{X}]\left(k_1[\mathrm{X}] - k_2\right)$$

1) If $[\mathrm{X}]_0 > k_2/k_1$, then d[X]/dt > 0 at any time, and the concentration of X monotonically increases:



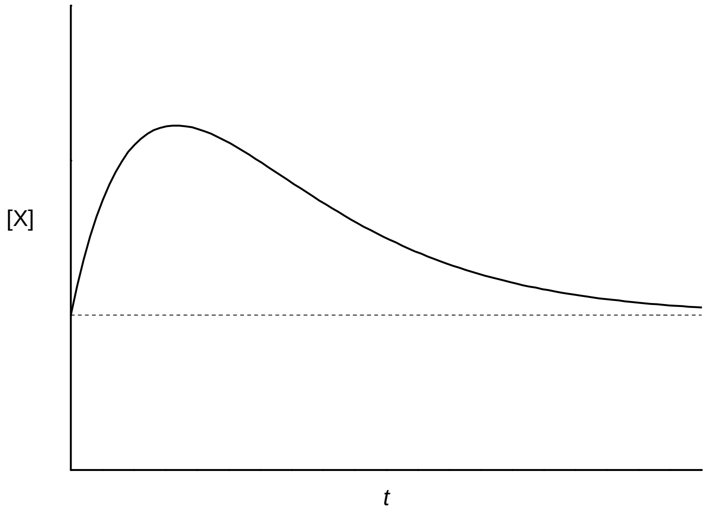
2) If $[\mathrm{X}]_0 < \frac{k_2}{k_1}$1, then $\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} < 0$ at any time, and the concentration of X monotonically decreases:



3.4 In a closed system the initial reaction rate is:

$$\left.\frac{d[X]}{dt}\right|_{t=0} = k_1[B]_0[X]_0^2 - k_2[D]_0[X]_0 = [B]_0[X]_0\left(k_1[X]_0 - k_2\right) > 0$$

Hence, at the beginning of the reaction [X] increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.5 X – $C_2H_6O_2$, Y – C_2H_4O, P – C_2H_6O. Dots denote O_2 and H_2O.

$$C_2H_6 + C_2H_6O_2 + O_2 \rightarrow 2\,C_2H_6O_2$$

$$C_2H_6O_2 + C_2H_4O \rightarrow 2\,C_2H_4O + H_2O$$

$$C_2H_6 + C_2H_4O + H_2O \rightarrow 2\,C_2H_6O$$

3.6 At the highest possible temperature the rate constants are equal:

$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R\ln\dfrac{A_2}{A_1}} = 354\ \text{K}$$

PROBLEM 4

Determination of water by Fischer titraton

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO_2 and pyridine (C_5H_5N, Py) – Fischer reagent. The following reactions occur during the titration:

$SO_2 + CH_3OH + H_2O + I_2 \rightarrow 2\ HI + CH_3OSO_3H$

$Py + HI \rightarrow PyH^+I^-$

$Py + CH_3OSO_3H \rightarrow PyH^+CH_3OSO_3^-$

Iodine content is usually expressed in mg of water reacting with 1 cm^3 of the titrant solution (hereunder T, mg cm^{-3}), which equals the mass of water (mg) reacting with 1.00 cm^3 of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I_2 with SO_2 and H_2O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

4.2 12.20 cm^3 of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2\ H_2O$.

4.3 A known amount of water (21.537 g) was placed into a 1.000 dm^3 volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm^3 of the obtained solution, 22.70 cm^3 of Fischer reagent solution were needed, whereas 2.20 cm^3 of iodine were used for titration of 25.00 cm^3 of methanol.

4.4 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm^3 (solution **A**); 22.45 cm^3 of this solution were used for titration of 15.00 cm^3 of a Fischer reagent (solution **B**).

Then 25.00 cm^3 of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm^3 of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm^3 of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound $Fe_2(SO_4)_3 \cdot x\ H_2O$, 10.59 cm^3 of iodine solution (T = 15.46 mg/ cm^3) were consumed.

4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

4.7 Write down an equation of the overall reaction of $Fe_2(SO_4)_3 \cdot x\ H_2O$ with the Fischer reagent.

4.8 Calculate the composition of the hydrate $Fe_2(SO_4)_3 \cdot x\ H_2O$ (x = integer).

SOLUTION

4.1 Equation:

$$I_2 + SO_2 + 2\ H_2O + 4\ Py \rightarrow 2\ PyHI + (PyH)_2SO_4$$

4.2 T is equal to:

$M(Na_2C_4H_4O_6 \cdot 2\ H_2O) = 230.05\ g\ mol^{-1}$ $\quad 2 \times M(H_2O) = 36.04\ g\ mol^{-1}$

$$m(H_2O) = \frac{13520 \times 36.04}{230.05} = 0.2118\ g = 211.8\ mg$$

$$T = \frac{2118}{12.20} = 17.36\ mg\ cm^{-3}$$

T = 17.36 mg cm^{-3}

4.3 T is equal to:

Volume of iodine consumed for 10 cm^3 of pure CH_3OH = $\dfrac{2.20 \times 10.00}{25.00}$ = 0.88 cm^3

$$T = \frac{21537 \times 0.01 \times 10^3}{22.70 - 0.88} = 9.87\ mg\ cm^{-3}$$

More exactly

10.00 cm^3 of the solution contains $\frac{(1000 - 21.5) \times 10.00}{1000}$ = 9.785 cm^3 of methanol.

Volume of iodine consumed for 9,785 cm^3 of pure CH_3OH = $\frac{2.20 \times 9,785}{25.00}$ =

= 0.86 cm^3

$$T = \frac{21537 \times 0.01 \times 10^3}{22.70 - 0.86} = 9.86 \text{ mg cm}^{-3}$$

T = 9.87 mg cm^{-3}

4.4 T is equal to:

Approach 1

Let 1 cm^3 of CH_3OH contains x mg H_2O, then 1 cm^3 of **A** contains

[(1.000 – 0.006) x + 5.624] mg H_2O.

$15.00\ T = 22.45\ (0.994\ x + 5.624)$ – 1st titration,

$10.00\ T = 25.00\ x + 10.79\ (0.994\ x + 5.624)$ – 2nd titration.

Hence, x = 1.13 mg cm^{-3}, T = 10.09 mg cm^{-3} (10.10 without taking into account 0.994 factor)

Approach 2

Let y cm^3 of **B** be consumed for the titration of water, contained in 1 cm^3 of CH_3OH.

Then $T = \frac{22.45 \times 5.624}{15.00 - 22.45 \times 0.994 \times y}$ (1st titration) = $\frac{10.79 \times 5.624}{10.00 - 25.00\,y - 10.79\,y}$

(2nd titration).

Hence, y = 0.1116 and T = 10.10 mg cm^{-3}

T = 10.09 mg cm^{-3} (10.10 without taking into account 0.994 factor)

4.5 Equation(s):

$CaO + SO_2 \rightarrow CaSO_3$

$2\ CaO + 2\ I_2 \rightarrow CaI_2 + Ca(OI)_2$

$6\ CaO + 6\ I_2 \rightarrow 5\ CaI_2 + Ca(IO_3)_2$

(Instead of CaO, $Ca(OH)_2$ may be written.)

4.6 Equation(s):

$Fe_2(SO_4)_3 + 2\ HI \rightarrow 2\ FeSO_4 + \mathbf{I_2} + H_2SO_4$

$Fe_2(SO_4)_3$ + $\mathbf{H_2O}$ + SO_2 + CH_3OH → 2 $FeSO_4$ + CH_3OHSO_3 + H_2SO_4

(or in ionic form)

4.7 Equation:

$$Fe_2(SO_4)_3 \cdot x\ H_2O + (x - 1)\ I_2 + x\ SO_2 + x\ CH_3OH \rightarrow 2\ FeSO_4 + x\ CH_3OHSO_3 + H_2SO_4 + 2(x - 1)\ HI$$

4.8 The composition of the crystallohydrate is:

$M(Fe_2(SO_4)_3 \cdot x\ H_2O) = 399.9 + 18.02\ x$

$$m(\ H_2O) = \frac{0.6387 \times 18.02\ x}{(399.9 + 18.02\ x)}$$

$$m(\ H_2O) = 10.59\ cm^3 \times 15.46\ mg\ cm^{-3} \times 0.001\ g\ mg^{-1} \times \frac{x}{x - 1}$$

$0.1637 \times (399.9 + 18.02\ x) = 11.51\ x - 11.51$

$x = 8.994 \approx 9$

Formula: $Fe_2(SO_4)_3 \cdot 9\ H_2O$

PROBLEM 5

A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three coluorless organic liquids **A**, **B**, **C** was treated by water containing a drop of hydrochloric acid at heating to give (after separation from water) a 1 : 2 (molar ratio) mixture of acetic acid and ethanol without any other components. A catalytic amount (one-two drops) of concentrated sulfuric acid was added o the mixture after hydrolysis and after a long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical with any of **A**, **B**, **C**.

5.1 Draw the structure of compound **D**?

5.2 Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.

5.3 Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1 : 1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85 %); b) higher than 85 %; c) lower than 85 %.

^{1}H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1 : 3 : 2.

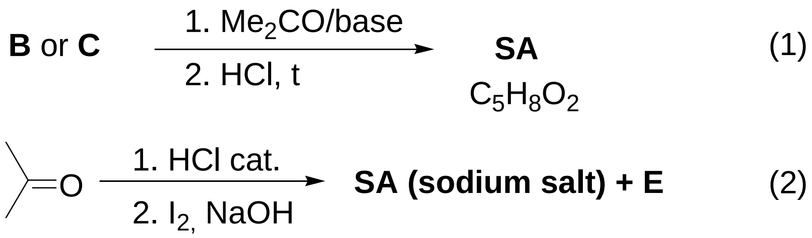
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. After acidification and short boiling the remaining solution gave 2 : 3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 dm^3 (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds, except diethyl ether, could be identified after hydrogenation.

5.4 Determine and draw the structures of **A**, **B**, and **C**.

5.5 Which intermediate compounds are formed during the acidic hydrolysis of **C** and the basic hydrolysis of **B**.

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).

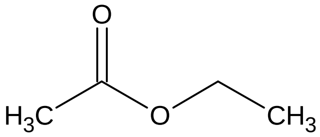


5.6 Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.

5.7 Give structure of **E**

SOLUTION

5.1 Structure of product **D**



Ethyl acetate, ethyl ethanoate

5.2 Which class of organic compounds does **D** belong to? Check the appropriate box.

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
☐	☐	☐	☑	☐	☐	☐

5.3 The expected yield of **D**

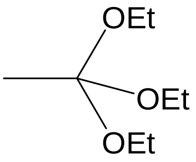
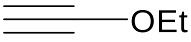
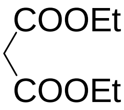
The reaction is an equilibrium without any further actions. Qualitative estimation: The yield is lower than 85 %.

Assuming that the reaction is at equilibrium and that the equilibrium constant is supposed not to vary with temperature and composition of the reaction mixture, we can calculate:

$$K = \frac{[\text{AcOEt}][\text{H}_2\text{O}]}{[\text{AcOH}][\text{EtOH}]} = \frac{(0.85)^2}{0.15 \times 1.15} = 4.2$$

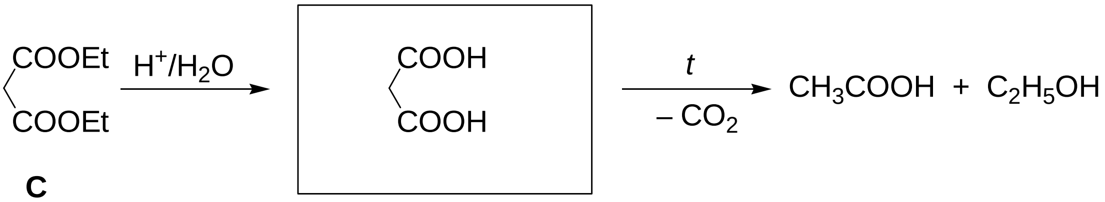
Using this constant calculation of yield in 1 : 1 mixture gives 67 %.

5.4 The structures of **A**, **B**, and **C**.

 $CH_3C(OEt)_3$ triethyl orthoacetate, 1,1,1-triethoxyethane	 HC≡COEt ethoxyacetylene, ethynylethyl ether	 $CH_2(COOEt)_2$ diethyl malonate
A	**B**	**C**

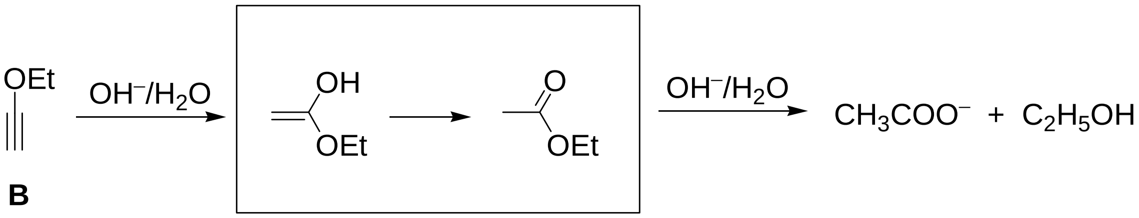
5.5 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of **C**, and basic hydrolysis of **B**.

a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate:



C

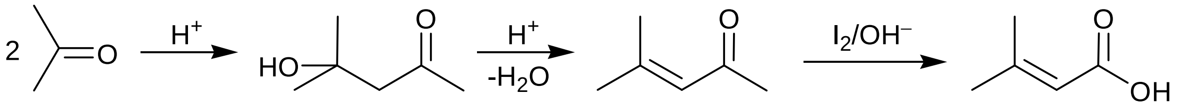
b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed



B

5.6 The structure of senecioic acid:

From acetone alone the synthesis includes aldol condensation and dehydration with subsequent iodoform reaction:



5.7 The structure of **E**.

Iodoform, triiodomethane, CHI_3

PROBLEM 6

Silicates as the base of the Earth crust

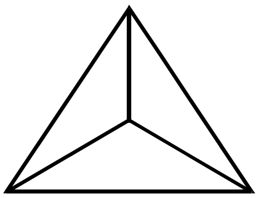
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of "liquid glass" (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the "Yes" box if it leads to changes of pH. Otherwise check the "No" box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-}, **1**):



(**1**)

For $[Si_3O_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.

Charged monolayers with the composition $[Si_4O_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3 - 6.5**, depict a fragment of the layered structure joining 16 tetrahedra **(1)**. Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

Being placed into the LGL solution, salts of transition metals give rise to fancy "trees" tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $CuSO_4 \cdot 5\ H_2O$ produce "trees" of blue colour, whereas those of $NiSO_4 \cdot 7\ H_2O$ form green "trees".

6.7 Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[Cu(H_2O)_4]^{2+}$ $K_a^{I} = 1\times10^{-7}$.

6.8 Write down equation of a reaction between aqueous solutions of $CuSO_4$ and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

SOLUTION

6.1 $SiO_3^{2-} + 2\ CO_2 + 2\ H_2O \rightarrow$ "H_2SiO_3"↓ (Silica acid gel) + 2 HCO_3^- or

$SiO_2(OH)_2^{2-} + 2\ CO_2 + H_2O \rightarrow$ "H_2SiO_3"↓+ 2 HCO_3^- or

$SiO_3^{2-} + CO_2 + H_2O \rightarrow$ "H_2SiO_3"↓ + CO_3^{2-}

6.2 a) protonation of ortho-silicate ions leading to the formation of Si-OH groups:

$SiO_4^{4-} + H_2O \rightarrow [SiO_3(OH)]^{3-} + OH^-$ or

$SiO_4^{4-} + H^+ \rightarrow [SiO_3(OH)]^{3-}$ or YES ☑

$[SiO_2(OH)_2]^{2-} + H^+ \rightarrow [SiO(OH)_3]^-$

b) formation of hydrated $[SiO_4(H_2O)_2]^{4-}$ anions NO ☑

$SiO_4^{4-} + 2\ H_2O \rightarrow [SiO_4(H_2O)_2]^{4-}$

c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds

$2\ SiO_4^{4-} + H_2O = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + 2\ OH^-$ or

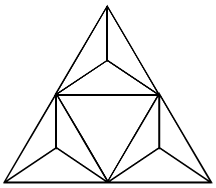
$2\ SiO_4^{4-} + 2\ H^+ = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + H_2O$ or YES ☑

$2\ SiO_2(OH)_2^{2-} + H_2O = [O\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}O]^{2-} + 2\ OH^-$

6.3 n = 6 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

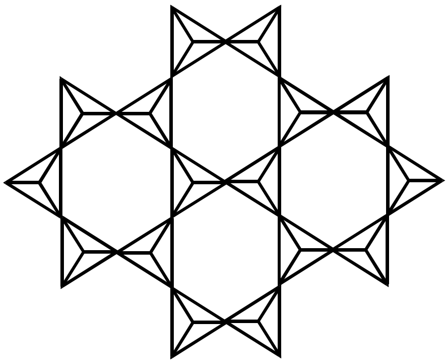
6.4 $Si_3O_9 \equiv 3\ [SiO_4] - 3\ O$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

6.5



6.6 m = 4 (assuming oxidation numbers of silicon (IV) and oxygen (-II), or taking into account its structure and the charge of orthosilicate ion (-4))

$Si_4O_{10} \equiv 4[SiO_4] - 6\ O$, i. e. the formula of the tetrahedron is now $SiO_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution = 3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.7 $Cu(H_2O)_4^{2+} + H_2O \rightleftharpoons Cu(OH)(H_2O)_3^{+} + H_3O^{+}$,

$[H^{+}] \approx (c\ K_a^{I})^{1/2} = 1\times10^{-4}$, $pH = -\log[H^{+}] = 4$

$pH = 4$

6.8 $CuSO_4 + Na_2SiO_3 + 2\ H_2O \rightarrow Cu(OH)_2\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

or

$2\ CuSO_4 + Na_2SiO_3 + 2\ H_2O \rightarrow Cu_2(OH)_2SO_4\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.7**).

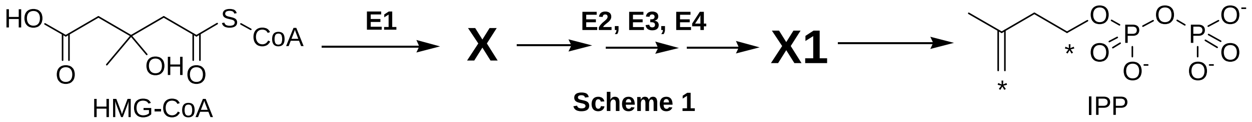
PROBLEM 7

Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

X is an optically active monocarbonic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:

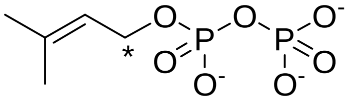


Scheme 1

7.1 In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.

7.2 Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.

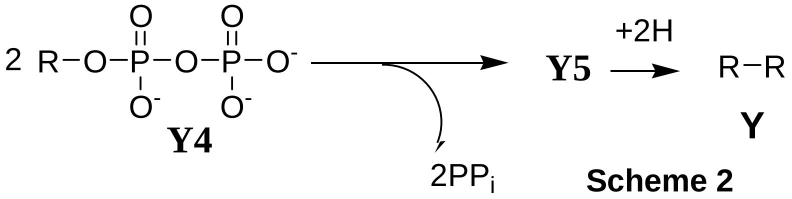
Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



DAP

7.3 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



Scheme 2

At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1 : 1 to the coupling product.

7.4 Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.

7.5 Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.

7.6 Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.

The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in trans configuration.

7.7 Draw structures of **Y** and **Y4** with stereochemical details.

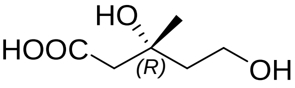
SOLUTION

7.1 **E2** - **E4** catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β-oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

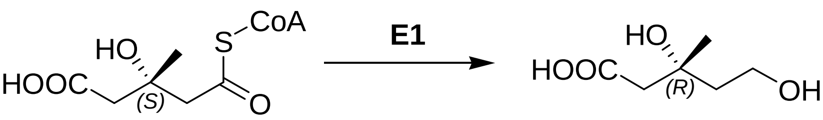
E1 4, 5
E3 6

7.2 Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:

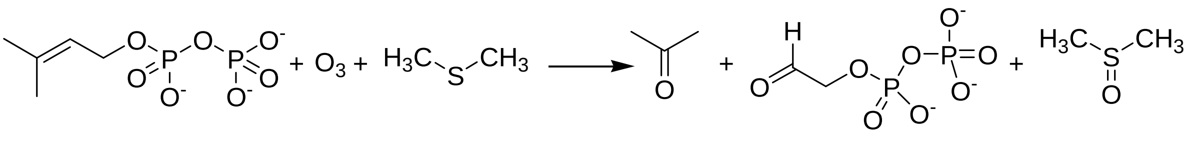


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



7.3 Reaction equation for reductive ozonolysis:



7.4 DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in **7.2.1**). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(C) = 2*n_{Y1}(C) + 4* n_{Y2}(C) + n_{Y3}(C) = 2*3 + 4*5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$$n(H) = 2*n_Y(C)+2 – 2*n_{c=c} = 30*2 + 2 – 6*2 = 50$$

Y (squalene) formula – $C_{30}H_{50}$.

Number of carbon atoms: 30	Work: $n_Y(C) = 2*n_{Y1}(C)+4*n_{Y2}(C)+ n_{Y3}(C) = 2*3 + 4*5 + 4 = 30$
Number of hydrogen atoms: 50	Work: $n(H) = 2*n_Y(C)+2–2*n_{c=c} = 30*2 + 2 - 6*2 = 50$

Gross formula of **Y** $\underline{C_{30}H_{50}}$

7.5 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

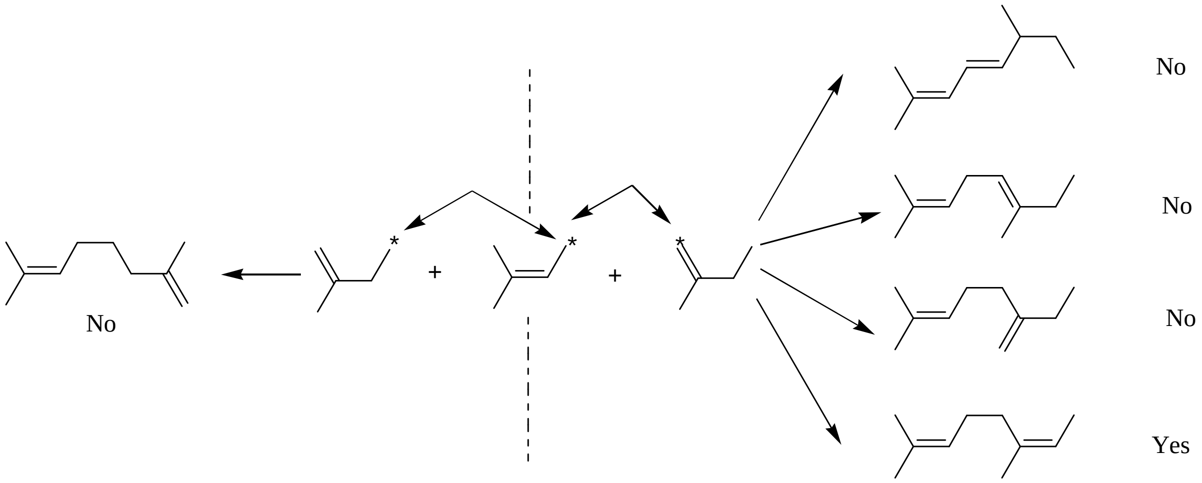
$$n(IPP\&DAP) = n_Y(C)/5 = 30/5 = 6$$

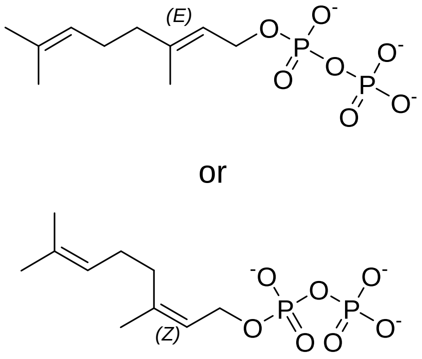
The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

n(IPP&DAP) = n_Y(C)/5 = 30/5 = 6

Number of DAP molecules: 2 Number of IPP molecules: 4

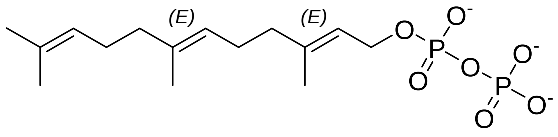
7.6 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details





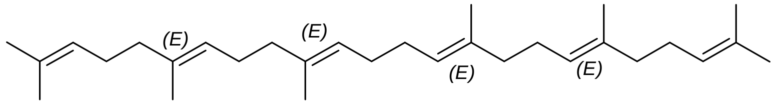
The upper isomer is geranyl pyrophosphate

7.7 It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4,** since **Y3** is formed as a result of ozonolysis in a molar ratio of 1 : 1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in trans configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



Y4, farnesyl pyrophosphate

Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:

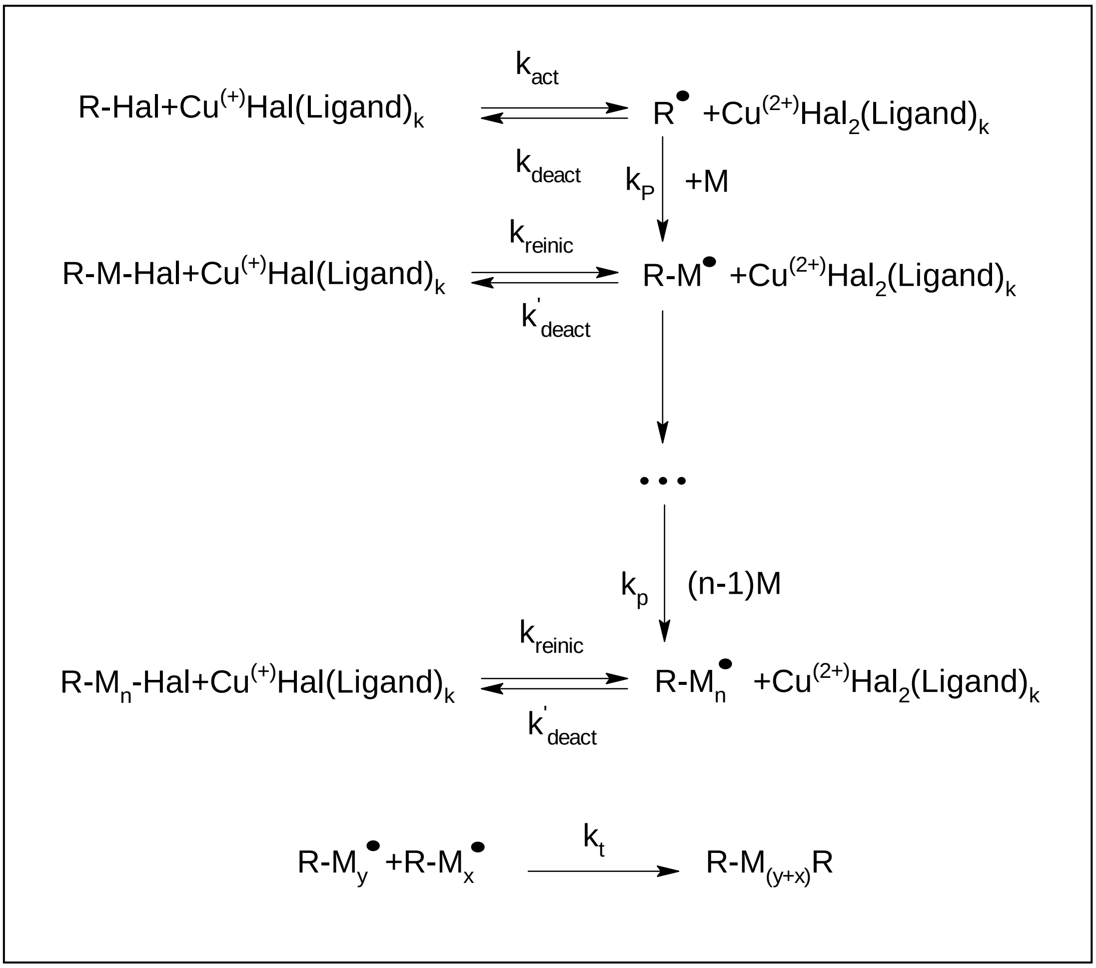


Y, squalene

PROBLEM 8

ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

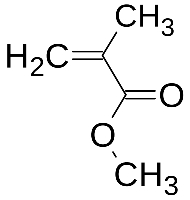
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration ([M]) on reaction time (t) for ATRP is:

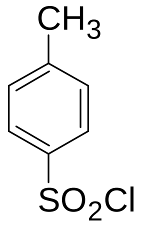
$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -k_p\,[\mathrm{R}\bullet]\,t\,,$$

$[M]_0$ - initial monomer concentration, k_p – rate constant of propagation, [R•] – concentration of active radicals.

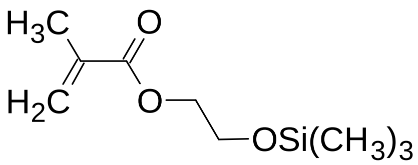
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is 1616 L mol^{-1}s^{-1}, and the steady state concentration of radicals is 1.76×10^{-7} mol dm^{-3}.



MMA



TsCl



HEMA-TMS

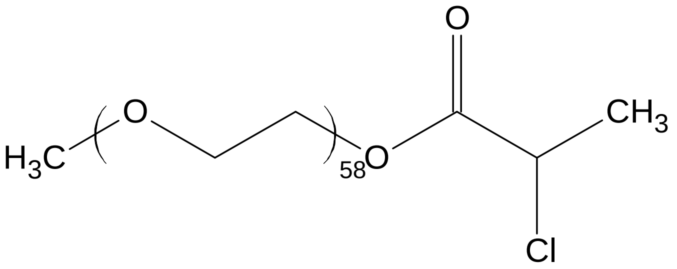
8.3 Calculate mass (*m*) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, (A_{65}-graft-C_{100})-stat-B_{34} means that chains of polymer C are grafted on units A in the statistic copolymer of A and B.

ATRP was applied to synthesize two block copolymers, P_1 and P_2. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P_1 consisted of styrene (C), and in P_2 of p-chloromethylstyrene (D) units.

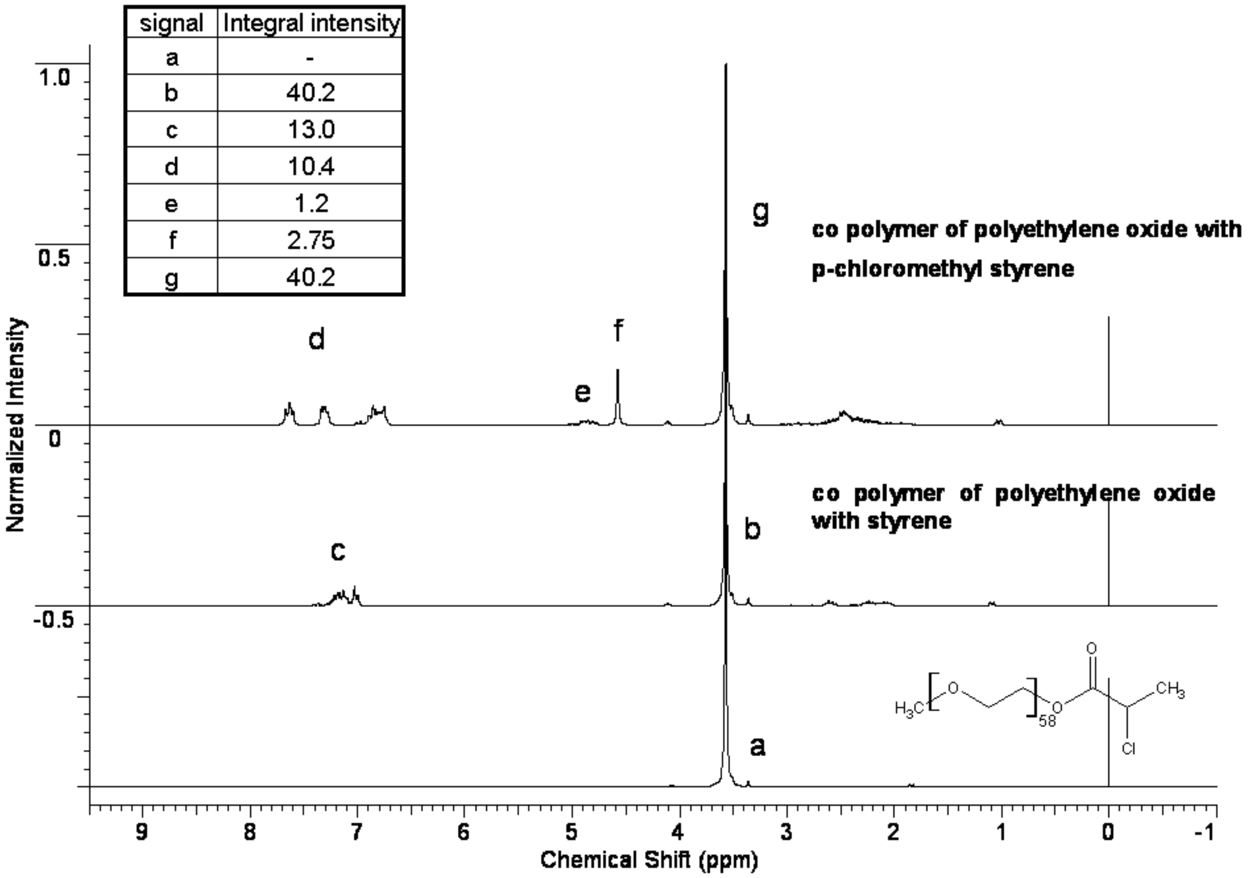
^{1}H NMR spectra of the macroinitiator, P_1 and P_2 are given below. Integral intensities of characteristic signals can be found in the table.

8.6 Assign ^{1}H NMR signals to substructures given in the Answer Sheet.

8.7 Determine molar fractions of units C and D and molecular weights of P_1 and P_2.

8.8 Write down all possible reactions of activation occurring during the synthesis of P_1 and P_2. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.

8.9 Draw the structure of P_1 and one of possible structures of P_2 representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.



signal	Integral intensity
a	-
b	40.2
c	13.0
d	10.4
e	1.2
f	2.75
g	40.2

SOLUTION

8.1 Expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t)

$v_{act} = k_{act}$ [R-Hal] [CuHal(Ligand)$_k$]

$v_{deact} = k_{deact}$ [R•] [CuHal$_2$(Ligand)$_k$]

$v_p = k_p$ [R•] [M]

$v_t = 2\ k_t\ [R\bullet]^2$

8.2 Comparison of rates of ATRP elementary stages

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination.

Thus:

$$v_{\text{deact}} >> v_{\text{act}}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$v_{\text{deact}} >> v_{\text{p}}$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$v_{\text{deact}} >> v_{\text{t}}$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$$v_{\text{deact}} >> v_{\text{act}}$$

$$v_{\text{deact}} >> v_{\text{p}}$$

$$v_{\text{deact}} >> v_{\text{t}}$$

8.3 Calculation of mass (m) of the obtained polymer.

1st variant

$[\text{M}] = [\text{M}]_0 \exp(-k_\text{P}[\text{R}\bullet]\,t)$ or $n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_\text{P}[\text{R}\bullet]\,t)$

Quantity of MMA monomer remaining after polymerization during 1400 s is

$31.0 \times \exp(-1616 \times 1.76 \times 10^{-7} \times 1400) = 20.8$ mmol.

Quantity of monomer consumed during polymerization: 31 – 20.8 = 10.2 mmol

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = \frac{10.2}{1000} \times 100.1 = 1.03 \text{ g}$$

2nd variant

$[\text{M}] = [\text{M}]_0 \exp(-\,k_P[\text{R}\bullet]\,t)$ or $n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_P[\text{R}\bullet]\,t)$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$$\Delta n(\text{MMA}) = n_0(\text{MMA})\,(1\text{-}\exp(-k_p \times [\text{R}\bullet] \times t)) = 31.0 \times (1\text{-}1616 \times 1.76 \times 10^{-7} \times 1400) =$$

$$= 10.2 \text{ mmol}$$

Mass of the obtained polymer is:

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2\,/\,1000) \times 100.1 = 1.03\,\text{g}$$

3rd variant

$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_P[R\bullet]\,t = -1616\times1.76\times10^{-7}\times1400 = -0.398$$

$$\frac{[M]}{[M]_0} = e^{-0.398} = 0.672$$

$$\frac{[M]}{[M]_0} = \frac{n(\text{MMA})}{n_0(\text{MMA})}$$

$$n(\text{MMA}) = 0.672\times n_0(\text{MMA}) = 20.8\ \text{mmol}$$

Quantity of monomer consumed during polymerization is 31 – 20.8 = 10.2 mmol.

Mass of the obtained polymer is

$$m\ = \Delta n(\text{MMA})\times M(\text{MMA}) = (10.2/1000)\times100.1 = 1.03\ \text{g}$$

8.4 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73 / 100.1).

The total quantity of monomers at the beginning of the 2nd stage is 23.7 + 23.7 = 47.4 mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$\Delta n = n_0(1-\exp(-k_P[R\cdot]\,t)) = 47.4\ (1-\exp(-1616\times1.76\times10^{-7}\times1295)) = 14.6\,\text{mmol.}$$

Totally 7.3 + 14.6 = 21.9 mmol of monomers was polymerized during two stages.

DP = 21.9 / 0.12 = 182.5

DP = 182 – 183 (all answers within this range are credited)

8.5 Structure of the obtained polymer.

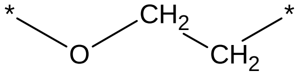
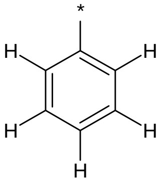
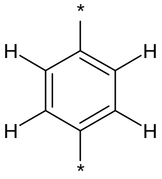
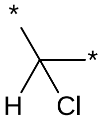
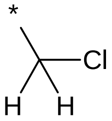
The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is 7.3 / 0.12 = 60.8 ≈ 61 monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning of the 2nd stage were equal. The DP of the 2nd block is 183 – 61 = 122 monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A_{61}-block-(A-stat-B)$_{61}$-Cl or Ts-A_{61}-block-(A_{61}-stat-B_{61})-Cl

8.6 Assignment of NMR signals to substructures given in the Answer Sheet.

	a, b, g
	c
	d
	e
	f

8.7 Determination of molar fractions of units C and D and molecular weights of P_1 and P_2.

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is 40.2 / 4 / 58 = 0.173 for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to 13.0 / 0.173 = 75 protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is 75 / 5 = 15.

Molar fraction of styrene units in P1 is 15 / (15 + 58) = 20.5 %

Intensity of multiplet d is 10.4, which is equivalent to 10.4 / 0.173 = 60 protons. Since each monomer unit of p-chloromethylstyrene has 4 protons, DP of PCS is 60 / 4 =15.

Molar fraction of D is 15 / (15 + 58) = 20.5%

$M(P_1) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 104.15 + 35.45 = \mathbf{4240}$

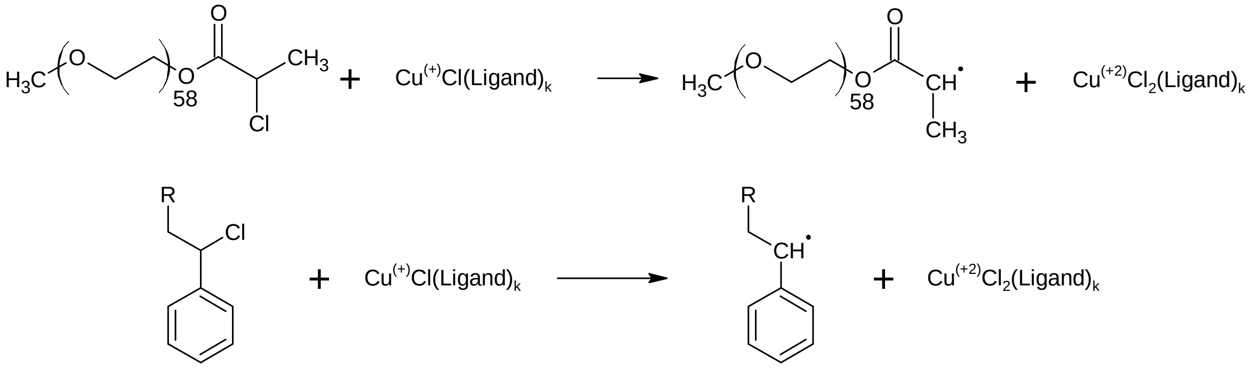
$M(P_2) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 152.62 + 35.45 = \mathbf{4967}$

$M(P_1) = 4240$; $M(P_2) = 4967$

$n(C) = 20.5\ \%$; $n(D) = 20.5\ \%$

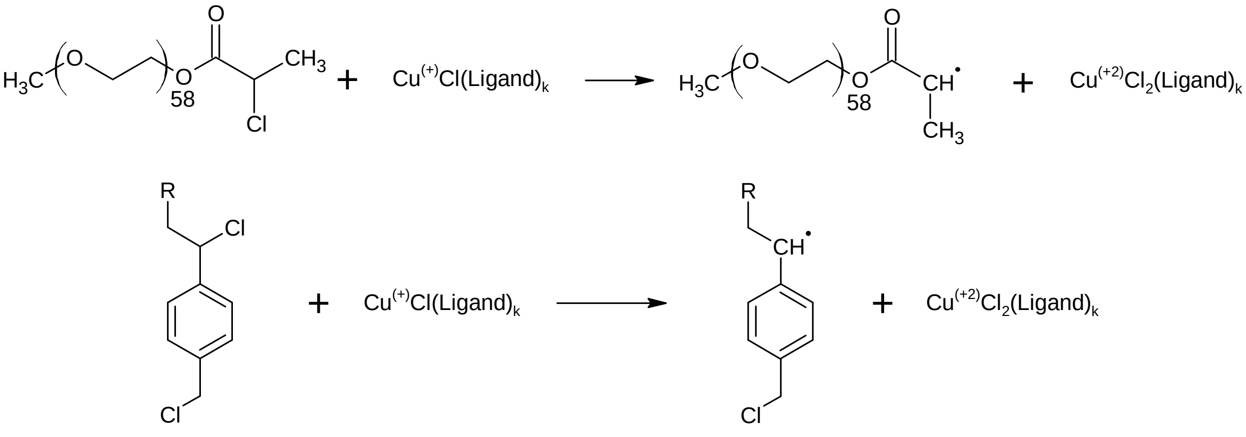
8.8 All possible reactions of activation occurring during the synthesis of P_1 and P_2.

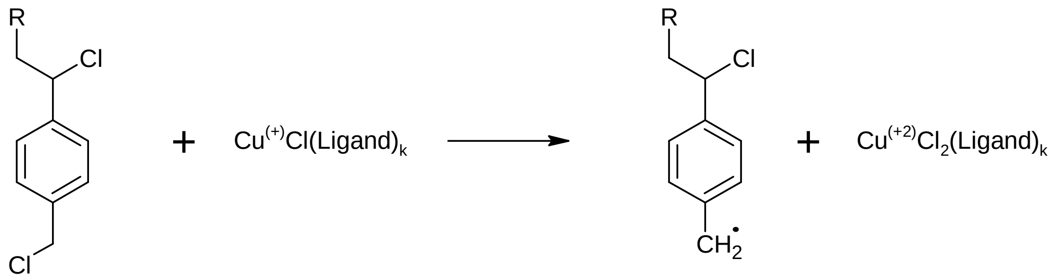
P1:



Here R is used for the macroinitiator fragment with one or several styrene units attached.

P_2:





Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

8.9 The structure of P_1 and one of possible structures of P_2

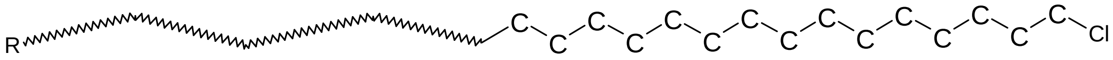
P_1 is a block copolymer of PEO and PS. The PS block contains 15 units.

P_2 is a block copolymer composed of PEO block and branched styrene block.

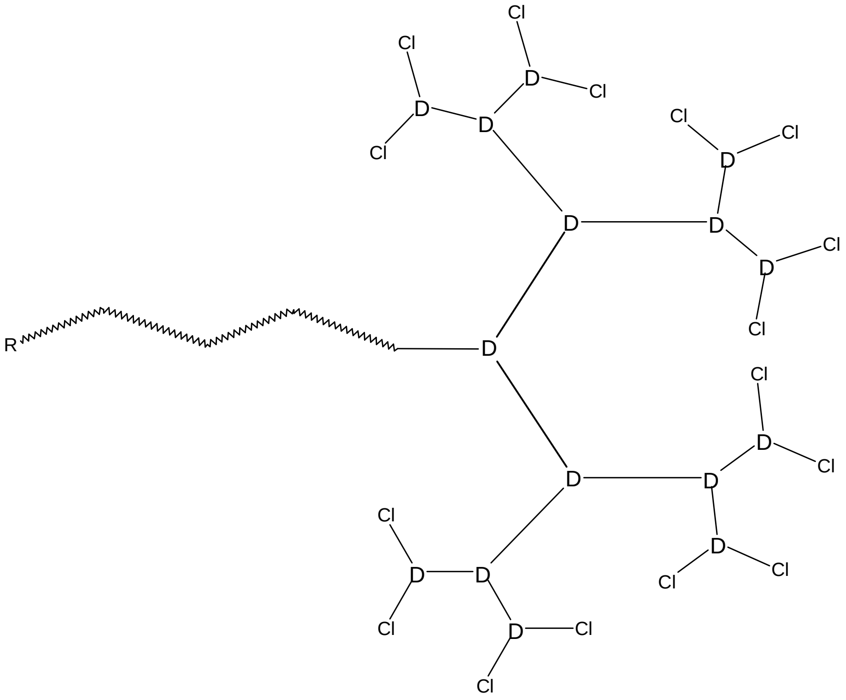
The integral intensity of multiplet f is 2.75, so 2.75/0.173=15.9, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P_2, it would contain 15 choromethyl groups. Each branching reduces the number of such groups by 1. Thus P_2 has 15 – 8 = 7 branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units

P_1



P_2

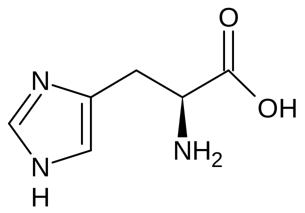


PRACTICAL PROBLEMS

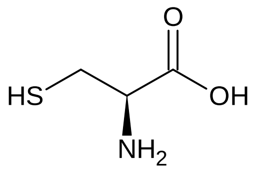
PROBLEM 1 (Practical)

Ion-exchange chromatography of amino acids

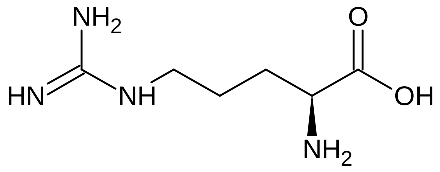
Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.



His



Cys



Arg

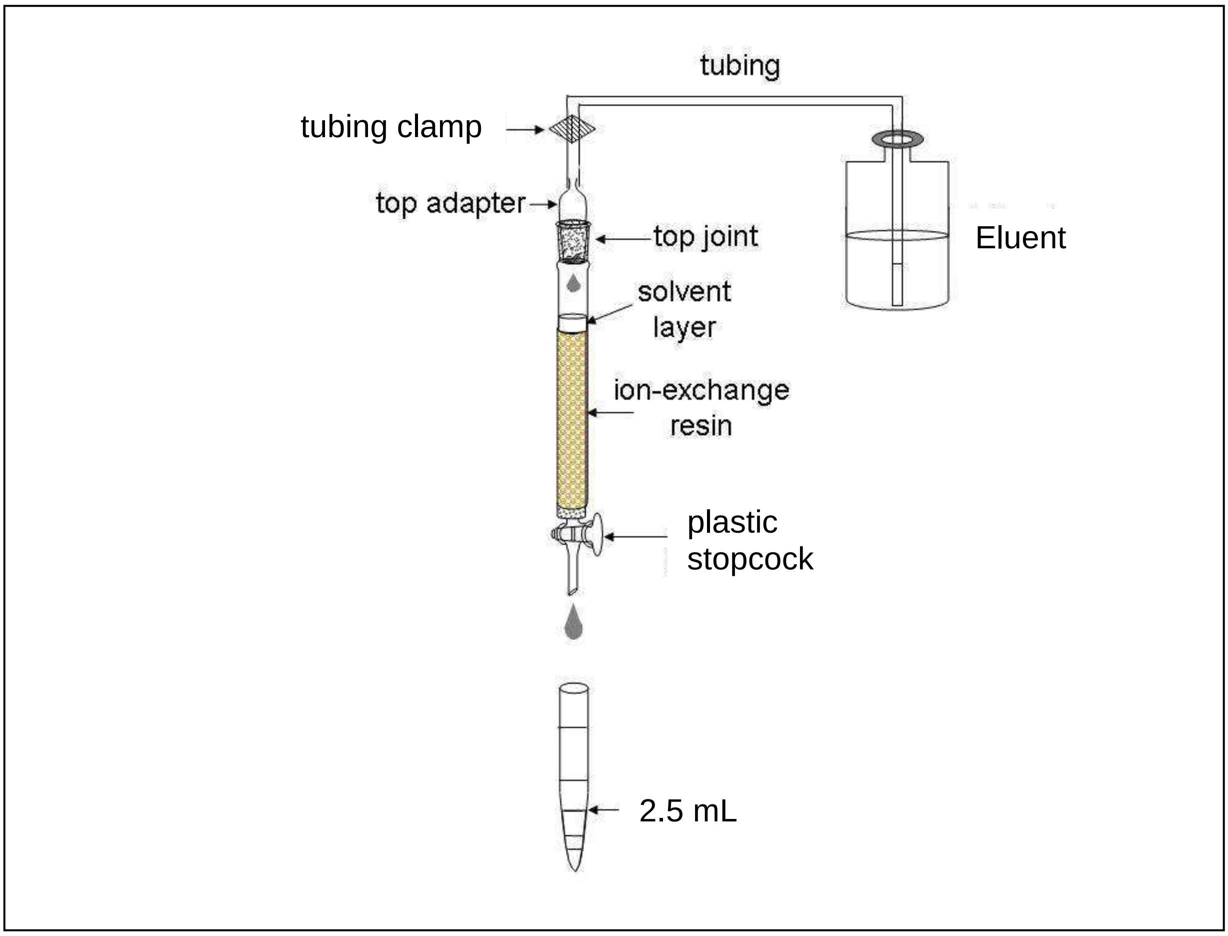
Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (*pH* 4.9).

Procedure

<u>Chromatography. Step 1</u>

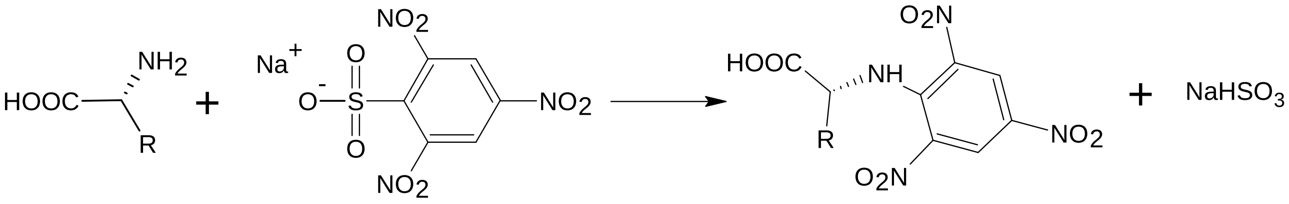
Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labelled “Waste” so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the “Waste” flask). Close the stopcock and add about 1 cm^3 of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always pen the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 cm^3 (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α-amino groups with sodium 2,4,6–trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 cm^3 of TNBS solution with 10 cm^3 of carbonate buffer solution and place 0.1 cm^3 of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 cm^3 of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 cm^3 should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1 a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1 b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.

1.1 Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.

1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labelled “Peak 1”, “Peak 2”, “Peak 3”. Prepare samples for quantitative spectrophotometric analysis as described below.

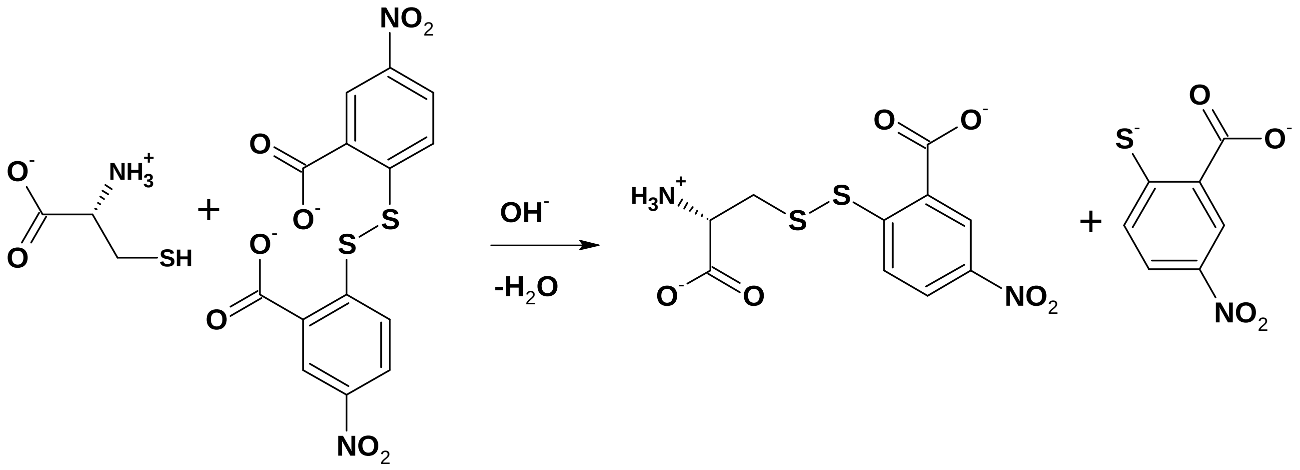
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cells to the operator. Prepare the probes as follows.

Important! When storing, always put cell in the cell holder! All cells have 2 ribbed and 2 working vertical surfaces. While operating with cells, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A_1 (Reference).

Place 0.1 cm^3 of Eluent 1 from plastic microtube into a test tube and add 2.9 cm^3 of Ellmann reagent (DTNB).

Test tube B_1 (Sample).

Place 0.1 cm^3 of the analyzed solution into a test tube and add 2.9 cm^3 of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A_1 (for reference) and B_1 (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A_2 (Reference).

Place 2.8 cm^3 of Tris-HCl buffer solution into a test tube, add 0.1 cm^3 of Eluent 2 from plastic microtube and 0.1 cm^3 of Pauli reagent.

Test tube B_2 (Sample).

Place 2.8 cm^3 of Tris-HCl buffer solution into a test tube, add 0.1 cm^3 of the analyzed solution and 0.1 cm^3 of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A_2 (for reference) and B_2 (for sample).

Assay 3 (peak 3). Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions

(Sakaguchi reaction).

Test tube A_3 (Reference).

Place 0.1 cm^3 of Eluent 3 into a test tube and add 1.5 cm^3 of 10 % NaOH solution, 1 cm^3 of 8-hydroxyquinoline solution and 0.5 cm^3 of sodium hypobromite solution.

Test tube B_3 (Sample).

Place 0.1 cm^3 of the analyzed solution into a test tube and add 1.5 cm^3 of 10 % NaOH solution, 1 cm^3 8-hydroxyquinoline solution and 0.5 cm^3 of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange colour. Add 0.2 cm^3 of 8 M urea solution to each test tube, mix the contents and transfer about 3 cm^3 of each mixture to the corresponding cells labelled A_3 (for reference) and B_3 (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cells to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:

The values of extinction coefficients: Product of Ellmann reaction: 13600 M^{-1}cm^{-1} at 410 nm Product of Pauli reaction: 6400 M^{-1}cm^{-1} at 470 nm Product of Sakaguchi reaction: 7700 M^{-1}cm^{-1} at 500 nm	Molar masses of the amino acids. Cysteine: 121 g mol^{-1} Histidine: 155 g mol^{-1} Arginine: 174 g mol^{-1}

1.4 Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

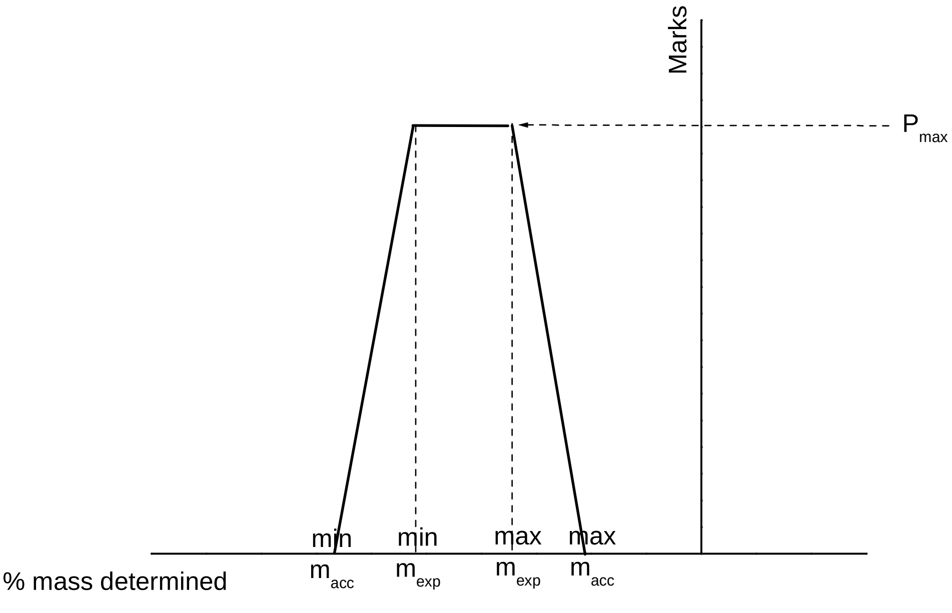
SOLUTION

1.2 – 1.3

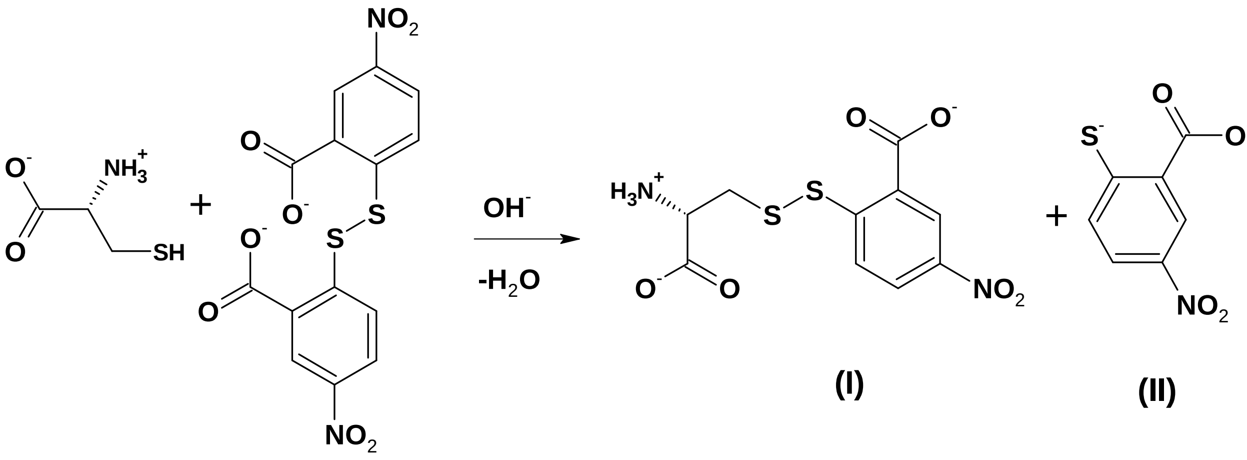
Content of an amino acid = $\dfrac{A_\lambda n\, V\, M}{\varepsilon\, l}$,

A_λ is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 cm^3) and the final volume of the sample in the cells, V is the volume of the combined fraction from the corresponding peak, and M is the molar mass of the amino acid.

Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer).

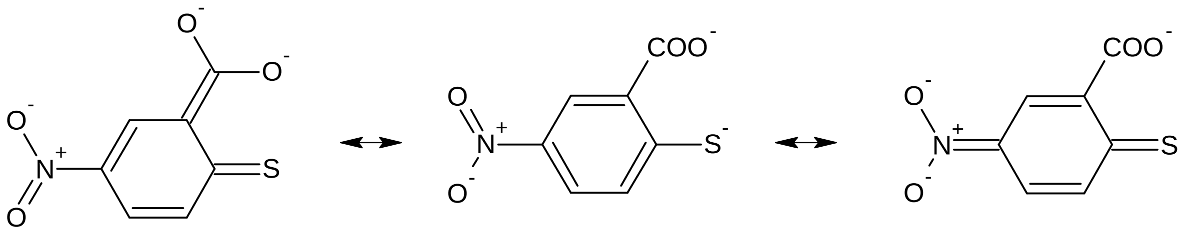


1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.



(I) **(II)**

Under slightly alkaline conditions, thiol group of (**II**) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:



The electronic structure of asymmetrical disulfide (**I**) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing C=S bond).

PROBLEM 2 (Practical)

Determination of Carbonate and Hydrogen Phosphate in an Abrasive Sample

Na_2CO_3, $CaCO_3$ and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4, whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to $H_2PO_4^-$ ion, the endpoint lying in slightly acidic medium (*pH* of ~4.5). It corresponds to the colour change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colourless to blue (moderately alkaline medium, *pH* of ~10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

a) the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
b) the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. <u>Dissolution of the sample and removal of CO_2</u>

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 cm^3 (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. 1 mol dm^{-3} HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2 – 3 min.

Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1 – 2 cm^3 of 15 % $K_2C_2O_4$ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 cm^3 of HCl solution into a 100 cm^3 volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 cm^3 of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1 – 2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5 – 10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 cm^3. Report all the final volume values with 0.01 cm^3 accuracy.

2.1 a Complete the table in the Answer Sheet.

2.1 b Calculate the concentration of NaOH solution (in mol dm^{-3}).

Step 4. Filtering off calcium oxalate

After the most part of CaC_2O_4 precipitates filter the precipitate off collecting the filtrate into a 100 cm^3 volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15 – 20 cm^3 of distilled water. Titrate the sample solution with NaOH solution until the colour coincides with that of the reference solution.

2.2 Complete the table in the Answer Sheet.

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5 – 10 s appears.

2.3 Complete the table in the Answer Sheet.

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+}.

2.6b A list of mistakes possible at different steps is given in the table in the answer sheet. Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+”or “–“ if the result is higher (positive error) or lower (negative error) than the true one.

SOLUTION

2.1 a, 2.2, 2.3

The values of the final volumes $V_{1,f}$, $V_{2,f}$, and $V_{3,f}$, (as reported in the Answer Sheet) were graded according to a scheme approved by the International Jury.

The values of $\Delta V_{\text{expected}}$ and $\Delta V_{\text{acceptable}}$ (in cm^3) are listed in the table below.

	ΔV, cm^3	
	expected	acceptable
$V_{1,\text{f}}$	**0.10**	**0.25**
$V_{2,\text{f}}$	**0.15**	**0.40**
$V_{3,\text{f}}$	**0.15**	**0.40**

2.1 b Calculation of NaOH concentration

$$c(\text{NaOH}) = \frac{c(\text{HCl})\times V(\text{HCl})\times V(\text{aliquot})}{V(\text{flask})\times V(\text{NaOH})} = \frac{1.214\ \text{mol dm}^{-3}\times 10.00\ \text{cm}^3\times 10.00\ \text{cm}^3}{100.0\ \text{cm}^3\times V_{1,\text{f}}\text{cm}^3}$$

2.4 Calculation of the mass of CO_3^{2-}

$$\text{m}(\text{CO}_3^{2-}) = M(\text{CO}_3^{2-})\times 1/2\times\frac{c(\text{NaOH})\times(V_{1,f}-V_{3,f})\times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 60.01\ \text{g mol}^{-1}\times 1/2\times\frac{c(\text{NaOH})\ \text{mol dm}^{-3}\times(V_{1,f}-V_{3,f})\ \text{cm}^3\times 100.0\ \text{cm}^3}{10.00\ \text{cm}^3}\times 0.001\ \text{dm}^3/\text{cm}^3 =$$

2.5 Calculation of the mass of HPO_4^{2-}

$$m(\text{HPO}_4^{2-}) = M(\text{HPO}_4^{2-})\times\frac{c(\text{NaOH})\times(V_{3,f}-V_{2,f})\times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 95.98\ \text{g mol}^{-1}\times\frac{c(\text{NaOH})\ \text{mol dm}^{-3}\times(V_{3,\text{f}}\text{-}V_{2,\text{f}})\ \text{cm}^3\times 100.0\ \text{cm}^3}{10.00\ \text{cm}^3}\times 0.001\ \text{dm}^3/\text{cm}^3 =$$

2.6 a

$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{CaHPO}_4 + \text{H}^+$

or

$3\ \text{Ca}^{2+} + 2\ \text{HPO}_4^{2-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2\ \text{H}^+$

40th

International Chemistry Olympiad

9 theoretical problems
3 practical problems

THE FORTIETH
INTERNATIONAL CHEMISTRY OLYMPIAD
12–21 JULY 2008, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A *pH* meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

1.1 Give the formulae of four acids that could have been in the solution if the *pH* changed one unit after a tenfold dilution.

1.2 Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $\text{p}K_{a2} = 1.99$

☐ Yes ☐ No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.3 Could it be possible that the solution contained acetic acid?

Acetic acid: $\text{p}K_a = 4.76$

☐ Yes ☐ No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.4 Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $\text{p}K_{a1} = 1.70$, $\text{p}K_{a2} = 2.60$, $\text{p}K_{a3} = 6.30$, $\text{p}K_{a4} = 10.60$

☐ Yes ☐ No

If yes, calculate the concentration.

SOLUTION

1.1 Any univalent, strong acid (HCl, HBr, HI, HNO_3, $HClO_4$) is acceptable. HF is not!

1.2 ☐ Yes ☑ No

No, the first dissociation step can be regarded as complete in aqueous solutions, thus $[H^+] > c_{acid.}$

No text or calculations are needed.

1.3 ☑ Yes ☐ No

Yes, but it can happen only in quite dilute solutions.

$c = [HA] + [A^–] = [H^+]$

$[H^+] = [A^–] + [OH^–]$

This means that $[HA] = [OH^–]$

$$K = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]([H^+] - [OH^-])}{[OH^-]} = \frac{[H^+]^3}{K_w} - [H^+]$$

The *pH* of the solution must be acidic, but close to 7.

6.5 is a good guess.

A good approximation is: $[H^+] = \sqrt[3]{(K\,K_w)}$

The full equation can be solved through iteration: $[H^+] = \sqrt[3]{(K + [H^+])K_w}$

Starting with a neutral solution two cycles of iteration give identical results:

$5.64 \times 10^{–7}$ mol dm^{-3} as the required concentration. Exact *pH* is 6.25.

1.4 ☑ Yes ☐ No

We can suppose that this solution would be quite acidic, so the 3rd and 4th dissociation steps can be disregarded. The following equations are thus true:

$c = [H_4A] + [H_3A^–] + [H_2A^{2–}] = [H^+]$

$[H^+] = [H_3A^–] + 2\,[H_2A^{2–}]$

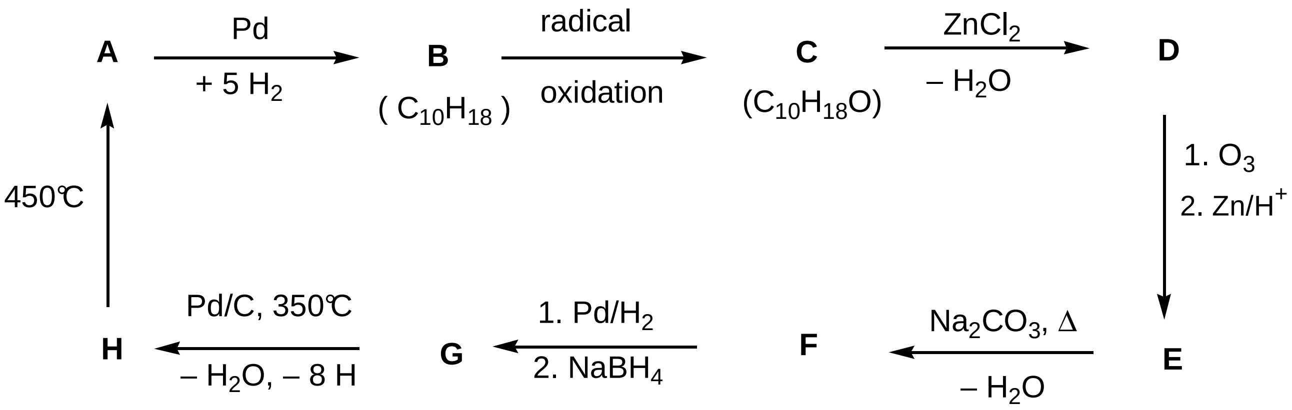
This means that $[H_4A] = [H_2A^{2–}]$

$$K_1\,K_2 = \frac{[H^+]^2[H_2A^{2-}]}{[H_4A]} = [H^+]^2$$ (or $pH = (pK_1 + pK_2)\,/\,2 = 2.15$)

$c = 0.0071$ mol dm^{-3}

PROBLEM 2

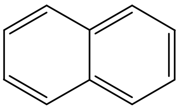
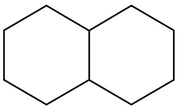
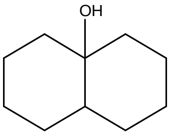
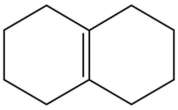
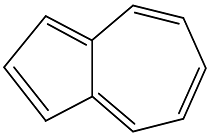
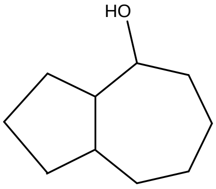
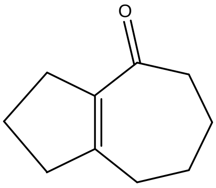
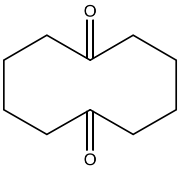
Determine the structure of the compounds **A** - **H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

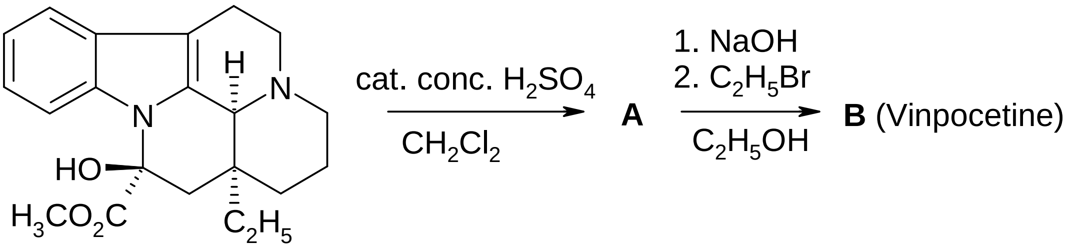
- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ^{13}C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH_2 groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

SOLUTION

A 	**B** 	**C** 	**D** 
H 	**G** 	**F** 	**E** 

PROBLEM 3

Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine ($C_{21}H_{26}$ N_2O_3), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in two steps depicted below.



Vincamine

All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

3.1 Propose structures for the intermediate **A** and vinpocetine (**B**).

A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Hints:

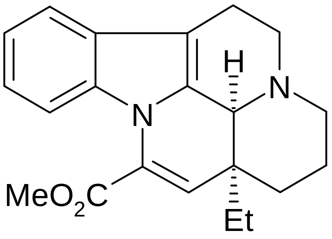
- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**: C 72.11 %, H 7.15 %, N 7.64 %, O 13.10 %.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

3.2 Propose one <u>possible</u> structure for each of the metabolites **C**, **D**, **E** and **F**!

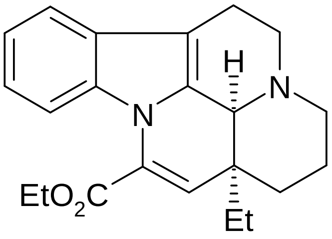
3.3 Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.

SOLUTION

3.1



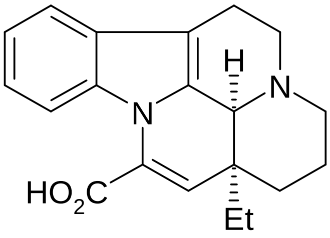
A



B

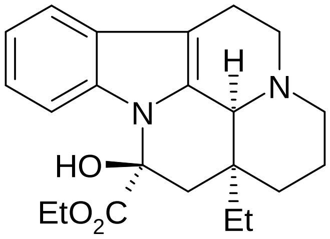
3.2

C



apovincaminic acid

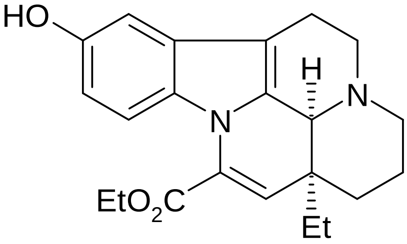
D



ethyl vincaminate

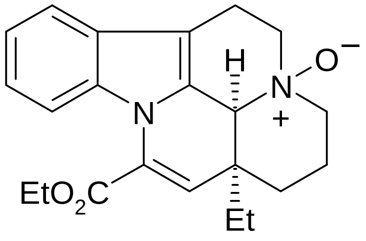
Both stereoisomers around the new chiral center are acceptable.

E



10-hydroxyvinpocetine

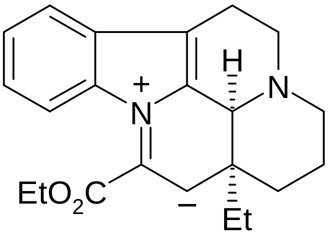
F



vinpocetine N-oxide

All aromatic positions for the OH are acceptable in **E**.

3.3



All aromatic positions for the OH are acceptable in **E**.

PROBLEM 4

A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

On base catalysis the sterically less hindered C–O bond is cleaved predominantly. Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the ◀ ⁞⁞⁞ — bond symbols and nothing else where necessary.

4.1 Draw the structure of the reactant and the predominant products when 2,2-dimethyl-oxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by

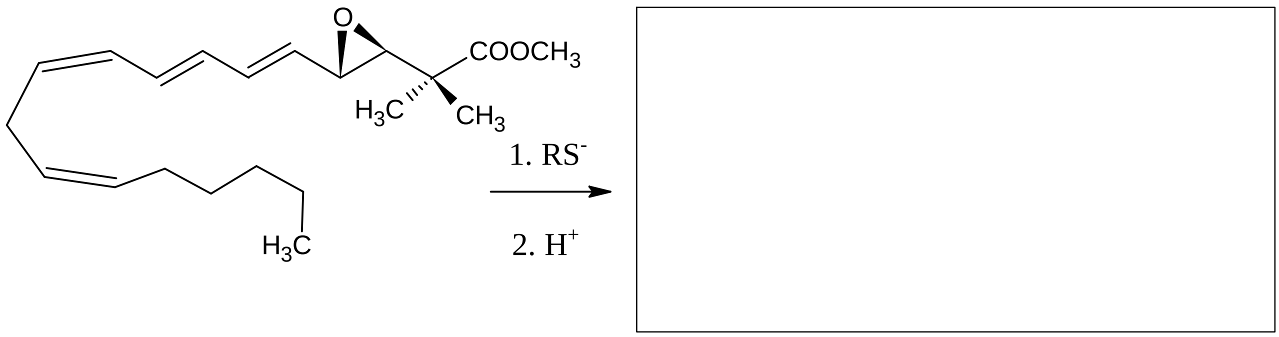
(i) sulphuric acid

(ii) $NaOCH_3$.

2,2-dimethyloxirane

$$\xleftarrow[CH_3OH]{H^+} \qquad\qquad \xrightarrow[CH_3OH]{NaOCH_3}$$

4.2 Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS^-).



Different porous acidic aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

4.3 Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (*S*)-2-methyloxirane ((*S*)-1,2-epoxypropane). Give the structure of the reactant as well.

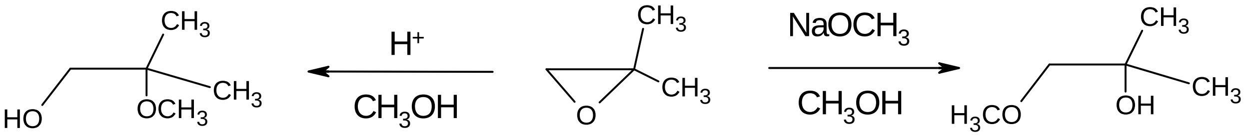
4.4 Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (*R*)-1,2-epoxy-2-methylbutane ((*R*)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.

4.5 Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).

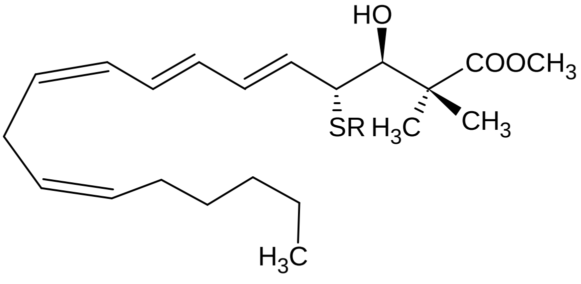
SOLUTION

4.1

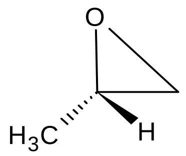
2,2-dimethyloxirane



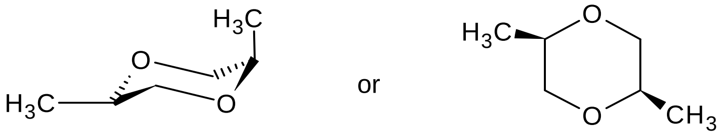
4.2



4.3

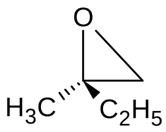


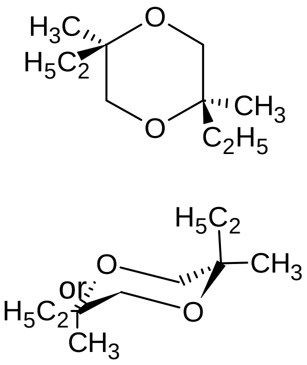
(*S*)-2-methyloxirane



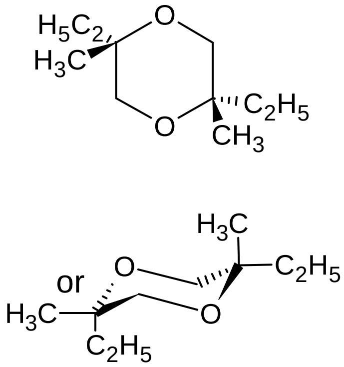
product

4.4 (*R*)-1,2-epoxy-2-methylbutane:

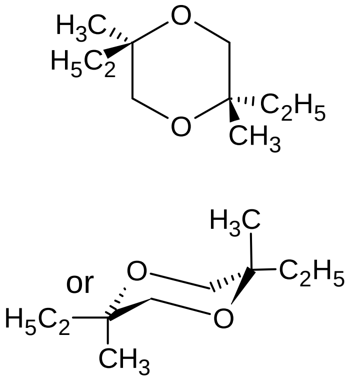




R,R

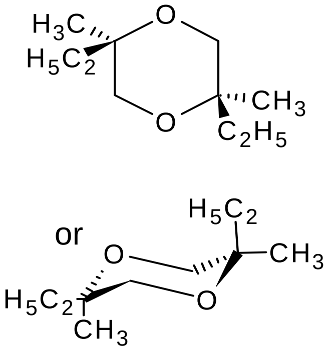


S,S

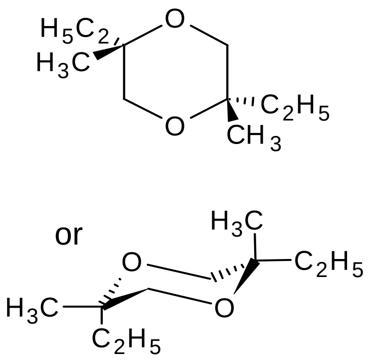


R,S

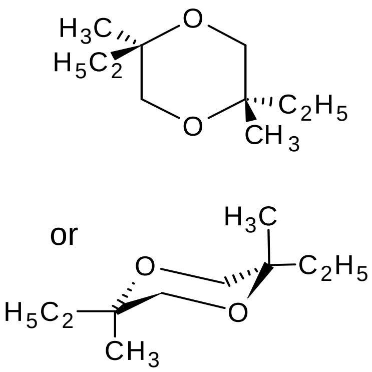
4.5



R,R



S,S



R,S

PROBLEM 5

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 ℃) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, *pH* ≈ 8.5-9) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, *pH* ≈ 4.5-5) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 ℃ produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 ℃ is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

5.1 Give the formulae of the substances **A** - **F**

5.2 Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

SOLUTION

5.1 The formulae of the substances **A** – **F:**

A $Ba(NO_2)_2$	**B** $(NH_4)_2SO_4$	**C** $BaSO_4$
D BaO	**E** $BaCO_3$	**F** BaO_2

5.2 Equations:

$Ba(NO_2)_2 = BaO + NO + NO_2$

$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$

$Ba^{2+} + SO_4^{2-} = BaSO_4$

$2\ NO_2^- + 2\ I^- + 4\ H^+ = 2\ NO + I_2 + 2\ H_2O$

$NH_4^+ + NO_2^- = N_2 + 2\ H_2O$

$BaO + H_2O = Ba^{2+} + 2\ OH^-$

$Ba^{2+} + 2\ OH^- + CO_2 = BaCO_3 + H_2O$

$BaO + CO_2 = BaCO_3$

$2\ BaO + O_2 = 2\ BaO_2$

$BaO_2 + 2\ I^- + 4\ H^+ = Ba^{2+} + I_2 + 2\ H_2O$

$BaCO_3 = BaO + CO_2$

$NH_4^+ + OH^- = NH_3 + H_2O$

Detailed solution:

The problem contains quite a number of clues to the identification of the compounds. It is clear that **A**, **D**, **E**, and **F** all contain the same element; with a water-soluble solid compound stable at 1400 °C, probably a metal. The aqueous solution of a metal compound giving a precipitate and pure water upon standing in the air strongly hints at the formation of a carbonate, possibly from a soluble hydroxide. A likely conclusion is that **D** is an oxide, limiting the choice of the metal to Sr or Ba. (One might also consider Li, Ca, or Tl which are less satisfactory because $Ca(OH)_2$ is poorly soluble while the solubilities of Li_2CO_3 and Tl_2CO_3 are quite significant.) If **E** is an alkaline earth metal carbonate, then the molar mass of **F** could be either M_{Ca} + 45.8, or M_{Sr} + 39.05, or M_{Ba} + 32. Since **F** is formed by heating the oxide in air, the former two do not make any sense while the latter is consistent with BaO_2. This is confirmed by the oxidative capability of **F**.

The odour appearing in the reaction of **B** with $Ba(OH)_2$ indicates that the former might be an ammonium salt. Assuming that the reaction of **A** and **B** is a simple precipitation between a barium salt and an ammonium salt, we get an equivalent mass of 48 for the anion of the precipitate. This might be either SO_4^{2-} or HPO_4^{2-} but the acidity of **B** is consistent with the former and, in addition, $(NH_4)_2HPO_4$ would not give the same $BaHPO_4$ precipitate with $Ba(OH)_2$ as with $Ba(NO_2)_2$. If we accept that **B** is $(NH_4)_2SO_4$, we obtain an equivalent mass of 46 for the anion of **A**. This and the surrounding chemistry are consistent with the nitrite ion.

PROBLEM 6

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates. The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm.

There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

6.1 How many type **A** cavities can be found in a unit cell?

6.2 How many water molecules are there in a unit cell?

6.3 If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?

6.4 Methane hydrate is formed with the structure in **c)** at temperatures between 0-10 °C. What is the density of the clathrate?

6.5 The density of chlorine hydrate is 1.26 g/cm^3. What is the ratio of the number of water and guest molecules in the crystal?

Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

☐ Some **A** ☐ Some **B** ☐ All **A** ☐ All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Non-bonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modelled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

6.6 Based on the covalent and non-bonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes

$H_2O(l) \rightarrow H_2O(s)$ (1)

$x\ CH_4(g) + H_2O\ (l) \rightarrow\ x\ CH_4.1H_2O(clathrate)$ (2)

6.7 What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a –, 0 or +.

	sign
$\Delta G_m(1)$	
$\Delta G_m(2)$	
$\Delta H_m(1)$	
$\Delta H_m(2)$	
$\Delta S_m(1)$	
$\Delta S_m(2)$	
$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta H_m(2) - \Delta H_m(1)$	

SOLUTION

6.1 The number of **A** cavities in a unit cell: $\boxed{2}$

6.2 The number of water molecules in a unit cell?

46 = 20 x 2 (dodecahedra) + 6 x 2 /2 (faces)

6.3 The number of water to the number of guest molecules?

46 : 8 = 5.75

6.4 A unit cell has a volume of 1.182^3 nm^3 = 1.651 nm^3.

It contains 8 methane and 46 water molecules with a mass of 957 g mol^{-1}/ N_A = 1.589×10^{-21} g.

The density is 1.589 / 1.651 = 0.962 g/cm^3.

6.5 The mass of a unit cell with this density is: 1.651 $nm^3 \times$ 1.26 g cm^{-3} = 2.081×10^{-21} g, meaning 1253 g/mol for the contents.

Substracting the waters, this means 424.3 g mol^{-1} for the chlorine atoms, giving 11.97 chlorine atoms in a unit cell.

The ratio is then 6 (5.98) chlorine molecules for the 46 waters, or a ratio of 7.68.

It is expected that only the 6 larger B type cavities contain chlorine. Thus:

☐ Some **A** ☐ Some **B** ☐ All **A** ☑ All **B**

6.6 Methane fits in both cavities, its radius is approximately 37 + 77 + 120 pm = 234 pm.

The chlorine molecule, with a radius of 180 + 99 pm = 279 pm, fits only in **B**.

Thus 234 pm < *r*(**A**) < 279 pm and 279 pm < *r*(**B**)

6.7

	sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	–
$\Delta H_m(1)$	–
$\Delta H_m(2)$	–
$\Delta S_m(1)$	–
$\Delta S_m(2)$	–
$\Delta S_m(2) - \Delta S_m(1)$	–
$\Delta H_m(2) - \Delta H_m(1)$	–

Under these conditions, methane clathrate forms, while ice melts to water, so the Gibbs energy changes are of opposite signs.

Freezing is an exothermic process with an entropy decrease in both cases.

The entropy decrease of the clathrate formation is larger in magnitude, as it involves a gas-solid transition.

The relation of the reaction enthalpies can be inferred from these facts:

$\Delta G_\text{m}(1) > \Delta G_\text{m}(2)$

$\Delta H_\text{m}(1) - T\,\Delta S_\text{m}(1) > \Delta H_\text{m}(2) - T\,\Delta S_\text{m}(2)$

$T\,(\Delta S_\text{m}(2) - \Delta S_\text{m}(1)) > \Delta H_\text{m}(2) - \Delta H_\text{m}(1)$

a negative quantity $> \Delta H_\text{m}(2) - \Delta H_\text{m}(1)$

PROBLEM 7

The dithionate ion ($S_2O_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

7.1 Write the balanced chemical equations for the two reactions.

After the reaction is complete, $Ba(OH)_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3.

7.2 Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3.

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with $BaCl_2$ solution. When the solid is heated and maintained at 130 ℃, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with $BaCl_2$ solution. When another sample of the original crystals is kept at 300 ℃ for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with $BaCl_2$ solution.

7.3 Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At 75 ℃, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

7.4 Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at 75 ℃.

$[Br_2]_0$ (mmol dm^{-3})	$[Na_2S_2O_6]_0$ (mol dm^{-3})	$[H^+]_0$ (mol dm^{-3})	v_0 (nmol dm^{-3}s^{-1})
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

7.5 Determine the order of the reaction with respect to Br_2, H^+ and $S_2O_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are 2.53×10^{-5} (Cl_2), 2.60×10^{-5} (BrO_3^-), 2.56×10^{-5} (H_2O_2), and 2.54×10^{-5} ($Cr_2O_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

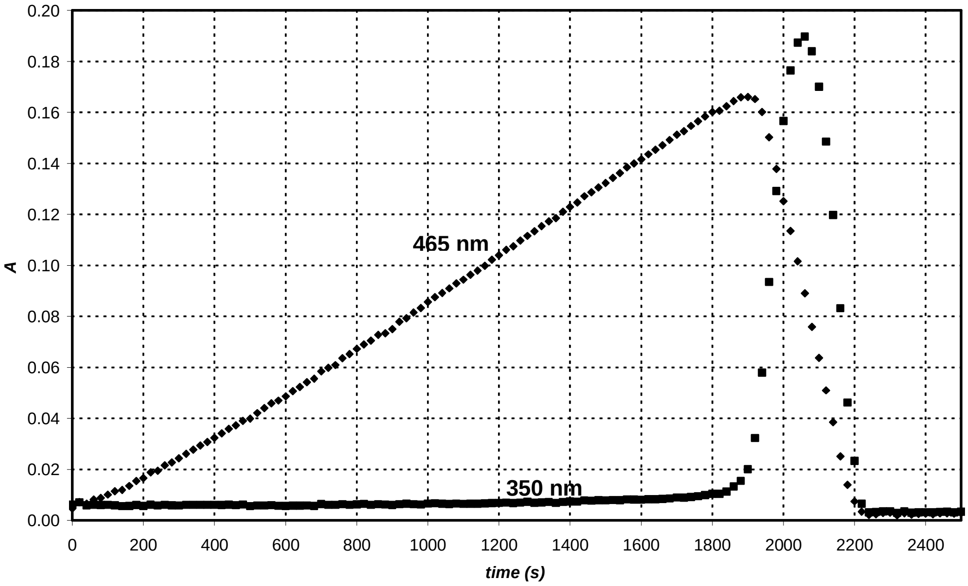
7.6 Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: [$Na_2S_2O_6$] = 0.0022 mol dm^{-3}, [$HClO_4$] = 0.70 mol dm^{-3}, and the temperature was 75 ℃. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

7.7 Calculate the rate constant of the reaction.

Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as $H_4IO_6^-$ in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 ℃ in the same experiment at two different wavelengths. The initial concentrations were [$H_4IO_6^-$] = $5.3\cdot10^{-4}$ mol dm^{-3}, [$Na_2S_2O_6$] = 0.0519 mol dm^{-3}, [$HClO_4$] = 0.728 mol dm^{-3}. At 465 nm, only I_2 absorbs and its molar absorption coefficient is 715 dm^3 mol^{-1} cm^{-1}. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is 11000 dm^3 mol^{-1} cm^{-1}. The optical path length was 0.874 cm.



7.8 Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm.

SOLUTION

7.1 $MnO_2 + 2\ SO_2 \rightarrow Mn^{2+} + S_2O_6^{2-}$

$MnO_2 + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$

7.2 $MnS_2O_6 + Na_2CO_3 \rightarrow Na_2S_2O_6 + \underline{MnCO_3}$

7.3 Formula: $Na_2S_2O_6 \cdot 2\ H_2O$

Equation (130 ℃): $Na_2S_2O_6 \cdot 2\ H_2O \rightarrow Na_2S_2O_6 + 2\ H_2O$

Equation (300 ℃): $Na_2S_2O_6 \rightarrow Na_2SO_4 + SO_2$ or with H_2O

7.4 $S_2O_6^{2-} + Br_2 + 2\ H_2O \rightarrow 2\ SO_4^{2-} + 2\ Br^- + 4\ H^+$

7.5 Reaction order for Br_2: 0 for H^+: 1 for $S_2O_6^{2-}$: 1

Experimental rate equation: $v = k\,[HSO_4^-]\,[H^+]$

$k = 2.56 \cdot 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

7.6 Species: SO_2 (or H_2SO_3)

Reaction: $S_2O_6^{2-} + H^+ \rightarrow HSO_4^- + SO_2$

7.7 $t_{½} = 10$ h 45 min $= 3.87 \cdot 10^4$ s

$k_{obs} = \ln 2 / t_{½} = 1.79 \times 10^{-5}\ s^{-1}$

$k = k_{obs} / [H^+] = 2.56 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

Rate determining step: $S_2O_6^{2-} + H^+ \rightarrow HSO_4^- + SO_2$

7.8 Increase: $2\ H_4IO_6^- + 7\ S_2O_6^{2-} + 2\ H_2O + 2\ H^+ \rightarrow 14\ HSO_4^- + I_2$

Decrease: $I_2 + S_2O_6^{2-} + 2\,H_2O \rightarrow 2\,HSO_4^- + 2\,I^- + 2\,H^+$

The expected time for the maximum absorbance of the kinetic curve measured at 465 nm:

$$t_{max} = \frac{7}{2}\frac{[H_4IO_6^-]_0}{k[S_2O_6^{2-}]_0[H^+]_0} = \frac{7\times 5.3\times 10^{-4}\ \text{M}}{2\times 2.56\times 10^{-5}\ \text{M}^{-1}\text{s}^{-1}\times 0.0519\ \text{M}\times 0.728\ \text{M}} = 1900\ \text{s}$$

The expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm: 1; –7 (it reflects the stoichiometry).

PROBLEM 8

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-VIS absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified $CeCl_3$ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c_{NaCl} (mol/dm^3)	E (mV)
0.1000	26.9
1.000	–32.2

8.1 Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

Ms. Z also determined the molar absorption coefficient for Ce^{3+} (ε = 35.2 dm^3 mol^{-1}cm^{-1}) at 295 nm, and, as a precaution, also for Ce^{4+} (ε = 3967 dm^{3}mol^{-1}cm^{-1}).

8.2 Give a formula to calculate the Ce^{3+} concentration from an absorbance reading at 295 nm (A) measured in a solution containing $CeCl_3$ (cuvette path length: 1.000 cm).

Ms. Z prepared a solution which contained 0.0100 mol/dm^3 $CeCl_3$ and 0.1050 mol/dm^3 HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

8.3 What were the expected initial absorbance (A_{295nm}) and voltage (E) readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

8.4 Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectophotometric measurements is ±0.002 and the accuracy of the voltage measurements is ±0.3 mV.

time (min)	0	120	240	360	480
$A_{295\ \mathrm{nm}}$	0.3496	0.3488	0.3504	0.3489	0.3499
E (mV)	19.0	18.8	18.8	19.1	19.2

8.5 Estimate the average rate of change in the concentrations of Ce^{3+}, Cl^-, and H^+.
$d[Ce^{3+}]/dt = d[Cl^-]/dt = d[H^+]/dt = ?$

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic $CeCl_3$ solution she had used before. She measured the molar absorption coefficient for Ce^{3+} (ε = 2400 $dm^3\ mol^{-1}\ cm^{-1}$) at 254 nm.

8.6 What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3. The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was 22.0 ℃.

8.7 Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

8.8 Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.

8.9 What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?

8.10 Estimate the quantum yield of product formation in the Ce(III) solution.

SOLUTION

8.1 $[\mathrm{Cl^-}] = 10^{-(E+32.2\,mV)/59.1\,mV}$

8.2 $[\mathrm{Ce^{3+}}] = \dfrac{A_{295nm}}{35.2\,\mathrm{dm^3 mol^{-1}}}$

8.3 $[\mathrm{Ce^{3+}}]$ = 0.0100 mol/dm^3 $\Rightarrow$ $A_{295\mathrm{nm}}$= 0.352

$[\mathrm{Cl^-}]$ = 3·0.0100 mol/dm^3 + 0.1050 mol/dm^3 = 0.1350 mol/dm^3 $\Rightarrow$ E = 19.2 mV

8.4 HCl, Cl_2, (O_3, ClO_2) (no oxidation of indicator)

8.5 d$[\mathrm{Ce^{3+}}]$/dt = ? d$[\mathrm{Cl^-}]$/dt = ? d$[\mathrm{H^+}]$/dt = ?

No significant change in either $\mathrm{Cl^-}$ or $\mathrm{Ce^{3+}}$ concentrations.

$[\mathrm{H^+}] = [\mathrm{Cl^-}] - 3\,[\mathrm{Ce^{3+}}]$, no significant change.

All three values are zero.

8.6 What percentage of the light is absorbed in this experimental setup?

A = 2400 dm^3 mol^{-1} cm^{-1} × 5 cm × 0.0100 M = 120 $\Rightarrow$ (100 – 10^{-118}) % ≈ 100 %

8.7 $p_{\mathrm{partial}} = p_{\mathrm{final}} - p_{\mathrm{initial}}$ = 114075 Pa – 102165 Pa = 11910 Pa

$n = p_{\mathrm{partial}}V/(RT)$ = 11910 Pa·0.000068 m^3 / (8.314 J mol^{-1} K × 295.15 K) =

= 3.3×10^{-4} mol

identity of gases: H_2, O_2

8.8 reaction: $2\ H_2O \xrightarrow{h\nu} 2\ H_2 + O_2$

8.9 Final pressure: 104740 Pa (saturated water vapour)

8.10 Quantum yield:

3.3×10^{-4} mol gas formed altogether: 2.2×10^{-4} mol H_2 and 1.1×10^{-4} mol O_2.

Light beam intensity 0.0500 J s^{-1} $\Rightarrow \dfrac{0.0500\ \text{J}\,\text{s}^{-1}\lambda}{h\,c\,N_A} = 1.06\times10^{-7}\text{mol s}^{-1}\text{photon}$

Total time 18.00 h = 64800 s

Total number of absorbed photons: 64800 s × 1.06×10^{-7} mol s^{-1} = 6.87×10^{-3} mol

Quantum yield for H_2 production: $\Phi = 2.2\times10^{-4}$ mol / 6.87×10^{-3} mol = 0.032

Quantum yield for O_2 production: $\Phi = 1.1\times10^{-4}$ mol / 6.87×10^{-3} mol = 0.016

Either value or the quantum yield of the gas production (0.048) is acceptable when demonstrated in a calculation.

PROBLEM 9

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+}. Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

The standard redox potentials for some relevant reactions are:

$Tl^+(aq) + e^- \rightarrow Tl(s)$ $E^o_1 = -0.336$ V

$Tl^{3+}(aq) + 3e^- \rightarrow Tl(s)$ $E^o_2 = +0.728$ V

$I_2(s) + 2e^- \rightleftharpoons 2\,I^-(aq)$ $E^o_3 = +0.540$ V

The equilibrium constant for the reaction $I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$: $K_1 = 0.459$.

Use T=25 ℃ throughout this problem.

9.1 Calculate the redox potentials E^o_4 and E^o_5 for the following reactions:

$Tl^{3+}(aq) + 2\,e^- \rightarrow Tl^+(aq)$ E^o_4

$I_3^-(aq) + 2\,e^- \rightarrow 3\,I^-(aq)$ E^o_5

9.2 Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one? Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $Tl^{3+} + 4I^- \rightarrow TlI_4^-$ is $\beta_4 = 10^{35.7}$

9.3 Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant K_2 for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

9.4 What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

SOLUTION

9.1 $E_4^0 = \dfrac{3\,E_2^0 - E_1^0}{2} = 1.26\ \text{V}$

$E_5^0 = E_3^0 + 0.059 / 2 \log(1 / K_1) = 0.550\ \text{V}$

9.2 Tl I, Tl I_3, Tl I_5, Tl I_7, Tl I_9

Tl I_3 can be either $\text{Tl}^{3+}(\text{I}^-)_3$ or $\text{Tl}^+(\text{I}_3^-)$

More stable: $\text{Tl}^+(\text{I}_3^-)$

as $E_4^0 > E_5^0$ or E_3^0,

Isomerisation: $\text{Tl}^{3+} + 3\ \text{I}^- = \text{Tl}^+ + \text{I}_3^-$

9.3 Reaction: $\text{Tl}^+ + \text{I}_3^- + \text{I}^- \rightarrow \text{Tl I}_4^-$

This reaction could be regarded as sum of three reactions:

$\text{Tl}^+(\text{aq}) \rightarrow \text{Tl}^{3+}(\text{aq}) + 2\text{e}^-$ $E_4^0 = -1.26$ V, thus $\Delta_r G_4^o = n\,F\,E_4^0 = 243.1\ \text{kJ mol}^{-1}$

$\text{I}_3^-(\text{aq}) + 2\ \text{e}^- \rightarrow 3\ \text{I}^-(\text{aq})$ $E^o_5 = 0.550$ V, thus $\Delta_r G_5^o = -n\,F\,E_5^o = -106.1\ \text{kJ mol}^{-1}$

$\text{Tl}^{3+} + 4\text{I}^- \rightarrow \text{Tl I}_4^-$ $\beta_4 = 10^{35.7}$ thus $\Delta_r G_6^o = -R\,T \ln\beta_4 = -203.8\ \text{kJ mol}^{-1}$

The net free enthalpy change is $\Delta_r G_7^o = \Delta_r G_4^o + \Delta_r G_5^o + \Delta_r G_6^o = -66.8\ \text{kJ mol}^{-1}$

Thus $K_2 = \exp\left(-\dfrac{\Delta_r G_7}{RT}\right) = 4.96 \cdot 10^{11}$

9.4 Supposing that the substance contains Tl and an anion, the formula of the compound is Tl_aX_b and the following equation holds:

$$\frac{a \cdot 204.4}{a \cdot 204.4 + bM_X} = 0.895$$

From the values b = 1, 3 and a = 1, 2, 3 only b = 3, a = 2 gives a realistic:

$M_X = 16.0\ \text{g mol}^{-1}$.

X is oxygen.

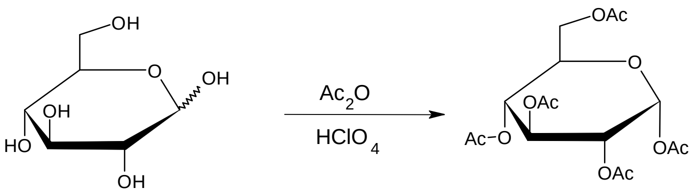
Formula: Tl_2O_3.

Equation: $2\ \text{Tl I}_3 + 6\ \text{OH}^- \rightarrow \text{Tl}_2\text{O}_3 + 6\ \text{I}^- + 3\ \text{H}_2\text{O}$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of α-D-glucopyranose pentaacetate

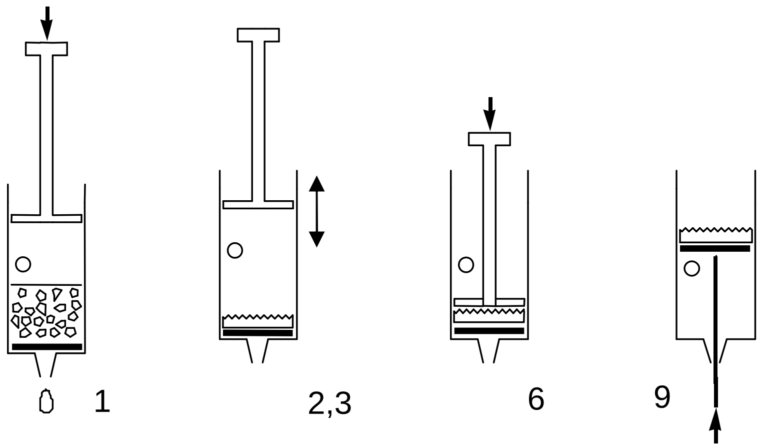


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm^3 of pure acetic acid to 12 cm^3 of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is in excess). Add with a Pasteur-pipette 5 drops of 30% $HClO_4$ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm^3 of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm^3 of water using the syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe



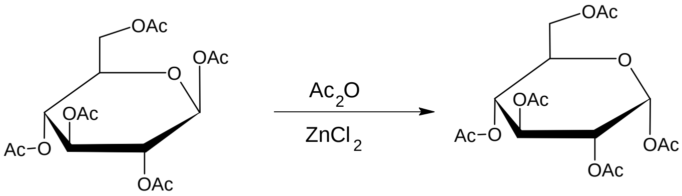
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid.
7. Wash the product twice with 10 cm^3 of water repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)

1.1 Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.

1.2 Calculate the theoretical yield (mass) of your product in g. (M(C) = 12 g mol^{-1}, M(O) = 16 g mol^{-1}, M(H) = 1.0 g mol^{-1}

Synthesis of α-D-glucopyranose pentaacetate from β-D-glucopyranose pentaacetate

An alternative synthesis of α-D-glucopyranose pentaacetate starts from readily available β-D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm^3 acetic anhydride to 50 mg of anhydrous $ZnCl_2$ (preweighed in a test tube). Add 100 mg of pure β-D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm^3 methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70ºC. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm^3 of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun (under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

1.3 Copy your plate on the answer sheet and place your plate in the labelled zip lock bag.

1.4 Interpret your experiment and choose the correct answer.

The acetylation reaction of glucose is exothermic.

☐ a) Yes
☐ b) No
☐ c) Cannot be decided based on these experiments

The isomerisation reaction of β-D-glucopyranose pentaacetate can be used for the preparation of pure α-D-glucopyranose pentaacetate.

☐ a) Yes
☐ b) No
☐ c) Cannot be decided based on these experiments

SOLUTION

1.1 Yield of the product in g, measured by the organizer.

The samples are dried by the organisers. The typical yield is 70 %.

Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.

1.1 Calculation of the theoretical yield of the product in g:

$C_6H_{12}O_6 \rightarrow C_{16}H_{22}O_{11}$

$$m = \frac{3.00\ \text{g} \times 390\ \text{g mol}^{-1}}{180\ \text{g mol}^{-1}} = 6.50\ \text{g}$$

1.3 The developed TLC plate was expected to be sketched on the answer sheet.

Full points were given if both standards and all samples are present.

1.4 Solutions: a), a).

PROBLEM 2 (Practical)

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6].3H_2O$ (M = 422.41 g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm^3 volumetric flask. Take 10.00 cm^3 portions of the hexacyanoferrate(II) solution. Add 20 cm^3 1 mol/dm^3 sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the 0.05136 mol/dm^3 Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming Ce(III).

2.1 Report the Ce^{4+} solution volumes consumed.

2.2 Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6].3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm^3 of the hexacyanoferrate(II) solution and add 20 cm^3 1 mol/dm^3 sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

2.3 Report the zinc solution volumes consumed.

2.4 Interpret the titration answering the questions on the answer sheet.

Mark the correct answer:

The diphenyl amine indicator changes in colour at the end point

☐ a) because the concentration of the Zn^{2+} ions increases.
☐ b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.
☐ c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.
☐ d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

☐ a) Oxidized

☐ b) Reduced

☐ c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

☐ a) True

☐ b) False

2.5 Determine the formula of the precipitate.

SOLUTION

2.1 Ce^{4+} consumptions:

Full marks if V_1 is within 0.15 cm^3 of the expected value recalculated from the $K_4[Fe(CN)_6]$ mass. Zero marks if deviation is more than 0.50 cm^3. Linear scale is applied in between.

2.2 The titration reaction:

$Ce^{4+} + [Fe(CN)_6]^{4-} = Ce^{3+} + [Fe(CN)_6]^{3-}$

$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$

2.3 Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $K_4[Fe(CN)_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3. Linear scale is applied in between.

2.4 Solutions: b), b), a)

2.5 Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc : hexacyanoferrate(II) in the precipitate can be evaluated as:

$$\frac{n(\text{Zn})}{n(\text{Fe(CN)}_6)} = \frac{10\, c(\text{Zn})\, V_2\, M}{m}$$

Values for c(Zn) are distributed according to a certain plan.

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio:

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $K_2Zn_3[Fe(CN)_6]_2$.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($H_2Zn_3[Fe(CN)_6]_2$ or $KHZn_3[Fe(CN)_6]_2$) is also acceptable.

PROBLEM 3 (Practical)

Caution:

> Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.
>
> The heat gun heats the expelled air up to 500 °C. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.
>
> Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+, NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Ba^{2+}, Pb^{2+}, Bi^{3+}

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, S^{2-}, HS^-, Cl^-, ClO_4^-, MnO_4^-, Br^-, I^-

You have test tubes and heating at your disposal but no additional reagents apart from distilled water and *pH* paper.

Identify the compounds in the solutions **1-8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks: The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

SOLUTION

The solutions received by the students contain the following compounds in eight test-tubes: $AgNO_3$, BaI_2, $KHCO_3$, $MgSO_4$, NaHS, NaOH, NH_4ClO_4, $Pb(CH_3COO^-{}_2$ ($Pb(OAc)_2$). There were eight sets of samples differing in order of the compounds in particular test tubes.

The problem can be approached in many ways. A systematic solution is given here for one of the sets of test tubes with the following order of the compounds:

Test tube No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Compound	$AgNO_3$	$KHCO_3$	NH_4ClO_4	NaOH	NaHS	$Pb(OAc)_2$	BaI_2	$MgSO_4$

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (*pH* paper reading about 5-6). Solution **2** is basic (*pH* = 9) while solutions **4** and **5** are very strongly basic (*pH* > 11).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and MnO_4^-. (In principle we should also exclude Mn^{2+} but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Bi^{3+}, and HSO_4^- with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Mn^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Ba^{2+}, Pb^{2+}.

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, S^{2-}, HS^-, Cl^-, ClO_4^-, Br^-, I^-.

The unknown solutions react with each other as follows (↓ = precipitate; ↑ = volatile product; “no change” means even when boiled, unless indicated otherwise):

	1 $AgNO_3$	**2** $KHCO_3$	**3** NH_4ClO_4	**4** NaOH	**5** NaHS	**6** $Pb(OAc)_2$	**7** BaI_2	**8** $MgSO_4$
1 $AgNO_3$	—	—	—	—	—	—	—	—
2 $KHCO_3$	↓ light yellow ↑ neutral, odourles	—	—	—	—	—	—	—
3 NH_4ClO_4	no change	↓ white crystals (*)	—	—	—	—	—	—
4 NaOH	↓ brown-black	no change	boiling: ↑ basic, odour of ammonia	—	—	—	—	—
5 NaHS	↓ black solution turns acidic	no change	boiling: ↑ basic, odour of NH_3, H_2S	no change	—	—	—	—
6 $Pb(OAc)_2$	↓ white crystals	↓ white ↑ neutral, odourles	no change	↓ white	↓ black	—	—	—
7 BaI_2	↓ yellow	↓ white ↑ (**)	no change	no change	no change	↓ yellow	—	—
8 $MgSO_4$	↓ white crystals	no change (***)	no change	↓ white	no change (****)	↓ white	↓ white	—

(*): upon boiling, the formation of NH_3 is detectable by its odour and by *pH* paper.

(**): gas bubbles are usually not observed when **2** is in excess.

(***): upon boiling, an odourless gas evolves and a white precipitate forms.

(****): upon boiling, a white precipitate forms and the odour of H_2S appears.

$2\ Ag^+ + 2\ HCO_3^- = Ag_2CO_3 + CO_2 + H_2O$

$Pb^{2+} + 2\ HCO_3^- = PbCO_3 + CO_2 + H_2O$

$Ba^{2+} + 2\ HCO_3^- = BaCO_3 + CO_2 + H_2O$

$Mg^{2+} + 2\ HCO_3^- = MgCO_3 + CO_2 + H_2O$ (more accurately, basic carbonates of variable composition are formed)

$Ag^+ + I^- = AgI$; $2\ Ag^+ + SO_4^{2-} = Ag_2SO_4$; $Ag^+ + CH_3COO^- = CH_3COOAg$

$Pb^{2+} + 2\ OH^- = Pb(OH)_2$; $Pb^{2+} + 2\ I^- = PbI_2$; $Pb^{2+} + SO_4^{2-} = PbSO_4$

$K^+ + ClO_4^- = KClO_4$; $Ba^{2+} + SO_4^{2-} = BaSO_4$; $Mg^{2+} + 2\ OH^- = Mg(OH)_2$

$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$

$2\ Ag^+ + HS^- = Ag_2S + H^+$; $Pb^{2+} + HS^- = PbS + H^+$; $CH_3COO^- + H^+ = CH_3COOH$

$NH_4^+ + OH^- = NH_3 + H_2O$

$NH_4^+ + HCO_3^- = NH_3 + CO_2 + H_2O$

Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2. Thus **2** contains CO_3^{2-} or HCO_3^-.

Second, there are only 3 dark precipitates that can be formed from the given ions: Ag_2O, Ag_2S, and PbS. This fact, together with the *pH* of the solutions, instantly identifies the cation of **1** as $\mathbf{Ag^+}$, the cation of **6** as $\mathbf{Pb^{2+}}$, the anion of **4** as $\mathbf{OH^-}$, and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the *pH* of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is $\mathbf{HS^-}$.

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as $\mathbf{HCO_3^-}$. (in accord with the moderately basic *pH*)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is $\mathbf{NH_4^+}$.

2+**4** form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+.

2+**5** do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+. Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+. Thus the anion of **3** is $\mathbf{ClO_4^-}$ and the cation of **2** is $\mathbf{K^+}$. **4** does not give a precipitate with NH_4ClO_4. The cation of **4** is $\mathbf{Na^+}$.

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of $KHCO_3$ and NaOH (Li^+). The cation of **5** is $\mathbf{Na^+}$.

7 forms no precipitate or ammonia with NaOH but gives a precipitate with $KHCO_3$. **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is $\mathbf{Ba^{2+}}$ and the anion of **7** is $\mathbf{I^-}$.

At room temperature **8** gives a precipitate with OH^- but not with HS^- which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one between Ba^{2+} and the anion of **8**. The latter is very likely SO_4^{2-} but HCO_3^- and $H_2PO_4^-$ are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+. This excludes both HCO_3^- and $H_2PO_4^-$. Thus the anion of **8** is $\mathbf{SO_4^{2-}}$. This instantly identifies the cation of **8** as $\mathbf{Mg^{2+}}$.

6 is a soluble compound of lead. The anion could be CH_3COO^-, NO_2^-, NO_3^-, or ClO_4^-. The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with HS^- does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+. It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with HS^- would also be noticeable). The absence of these reactions indicates that the anion of **6** is $\mathbf{CH_3COO^-}$.

Soluble salts of silver are even less numerous, the only choices are NO_3^-, F^-, and ClO_4^-. The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH. The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out F^-. The solubility of $KClO_4$ is quite significant;
therefore the absence of a precipitate with $KHCO_3$ is inconclusive. The anion of **1** is therefore either $\mathbf{NO_3^-}$ or $\mathbf{ClO_4^-}$.

QUANTITIES AND THEIR UNITS USED IN THIS PUBLICATION

SI Basic Units

Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol

Special names and symbols for certain derived SI Units

Force	F	Newton	N
Pressure	p	pascal	Pa
Energy	E	joule	J
Power	P	watt	W
Electric charge	Q	coulomb	C
Electric potential difference	U	volt	V
Electric resistance	R	ohm	Ω

Other derived SI Units used in chemistry

Area	S	square metre	m^2
Volume	V	cubic metre	m^3
Density	ρ	kilogram per cubic metre	kg m^{-3}
Concentration	c	mole per cubic metre	mol m^{-3} (mol dm^{-3})
Molar mass	M	kilogram per mole	kg mol^{-1} (g mol^{-1})

Some other quantities and constants

Relative atomic mass of an element	A_r
Relative molecular mass of a compound	M_r
Molar fraction	x
Mass fraction	w
Volume fraction	φ
Enthalpy	H
Entropy	S
Gibbs energy	G
Temperature in Celsius scale	℃

Elementary charge, e	$1.6021892 \times 10^{-19}$ C
Planck constant, h	6.626176×10^{-34} J s
Avogadro constant, A	6.022045×10^{23} mol^{-1}
Faraday constant, F	9.648456×10^{4} C mol^{-1}
Gas constant, R	8.31441 J mol^{-1} K^{-1}
Zero of Celsius scale, T_0	273.15 K (exactly)
Normal pressure, p_0	1.01325×10^{5} (exactly)
Standard molar volume of ideal gas, V_0	2.241383×10^{-2} m^3 mol^{-1}

Abbreviations and Mathematical symbols

IChO	International Chemistry Olympiad
STP	Standard temperature and pressure (T_0, p_0)
M	molar, mol dm^{-3}
N	normal
$\hat{=}$	corresponds to
$\approx$	approximately equal to
$\sim$	proportional to
$\Rightarrow$	implies