

21st



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

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

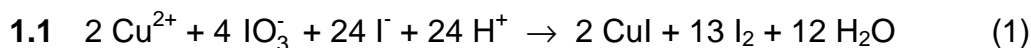
THEORETICAL PROBLEMS

PROBLEM 1

To determine the solubility product of copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, by iodometric titration in an acidic solution (25 °C) 30.00 cm³ of a 0.100 molar sodium thiosulphate solution are needed to titrate 20.00 cm³ of a saturated aqueous solution $\text{Cu}(\text{IO}_3)_2$.

- 1.1 Write the sequence of balanced equations for the above described reactions.
- 1.2 Calculate the initial concentration of Cu^{2+} and the solubility product of copper(II) iodate. Activity coefficients can be neglected.

SOLUTION



- 1.2 From (2):

$$n(\text{S}_2\text{O}_3^{2-}) = c V = 0,100 \text{ mol dm}^{-3} \times 0,03000 \text{ dm}^3 = 3,00 \times 10^{-3} \text{ mol}$$

From (2) and (1):

$$n(\text{I}_2) = 1,50 \times 10^{-3} \text{ mol}$$

$$n(\text{Cu}^{2+}) = \frac{1,50 \times 10^{-3} \text{ mol}}{13} \times 2 = 2,31 \times 10^{-4} \text{ mol}$$

$$c(\text{Cu}^{2+}) = \frac{2,31 \times 10^{-4} \text{ mol}}{0,02000 \text{ dm}^3} = 1,15 \times 10^{-2} \text{ mol}$$

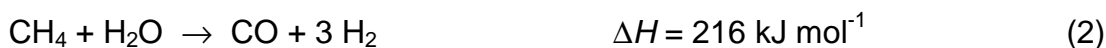
$$[\text{Cu}^{2+}] = 1,15 \times 10^{-2}$$

$$[\text{IO}_3^-] = 2 [\text{Cu}^{2+}]$$

$$K_{sp} = [\text{Cu}^{2+}] [\text{IO}_3^-]^2 = 4 [\text{Cu}^{2+}]^3 = 4 \times (1.15 \times 10^{-2})^3 = 6.08 \times 10^{-6}$$

PROBLEM 2

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



2.1 Using equations (1) and (2) write down an overall reaction (3) so that the net enthalpy change is zero.

2.2 The synthesis of methanol from carbon monoxide and hydrogen is carried out either

a) in two steps, where the starting mixture corresponding to equation (3) is compressed from 0.1×10^6 Pa to 3×10^6 Pa, and the mixture of products thereof compressed again from 3×10^6 Pa to 6×10^6 Pa

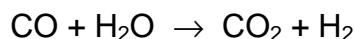
or

b) in one step, where the mixture of products corresponding to equation (3) is compressed from 0.1×10^6 Pa to 6×10^6 Pa.

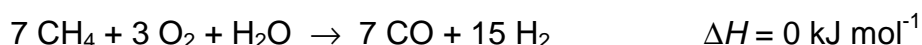
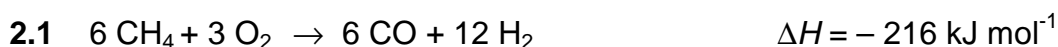
Calculate the work of compression, W_a , according to the two step reaction for 100 cm^3 of starting mixture and calculate the difference in the work of compression between the reactions 1 and 2.

Assume for calculations a complete reaction at constant pressure. Temperature remains constant at 500 K, ideal gas behaviour is assumed.

To produce hydrogen for the synthesis of ammonia, a mixture of 40.0 mol CO and 40.0 mol of hydrogen, 18.0 mol of carbon dioxide and 2.0 mol of nitrogen are in contact with 200.0 mol of steam in a reactor where the conversion equilibrium is established.



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

SOLUTION

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

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

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

- b) For a pressure increase in one step the work of compression only depends on n_2 , p_2 and p_0 :

$$W_1 = n_2 RT \ln \frac{p_2}{p_0} = 100 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K} \times \ln \frac{6.0 \text{ MPa}}{0.1 \text{ MPa}} = 3.40 \text{ MJ}$$

It means

$$\Delta W = W_1 - W_2 = \underline{1.41 \text{ MJ}}$$

2.3 With $K = 3.3$, the following equilibrium is valid:

$$K = \frac{n_{\text{CO}_2} \times n_{\text{H}_2}}{n_{\text{CO}} \times n_{\text{H}_2\text{O}}} = \frac{(18 + x)(40 + x)}{(40 - x)(200 - x)}$$

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

The composition of the leaving gas is:

6.8 mol CO, 51.2 mol CO₂, 2.0 mol CH₄ and N₂, 73.2 mol H₂ and 166.8 mol H₂O.

PROBLEM 3

Sulphur dioxide is removed from waste gases of coal power stations by washing with aqueous suspensions of calcium carbonate or calcium hydroxide. The residue formed is recovered.

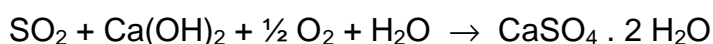
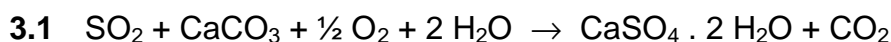
- 3.1** Write all reactions as balanced equations.
- 3.2** How many kilograms of calcium carbonate are daily consumed to remove 95 % of the sulphur dioxide if 10000 m³/h of waste gas (corrected to 0 °C and standard pressure) containing 0.15 % sulphur dioxide by volume are processed? How many kilograms of gypsum are recovered thereby?
- 3.3** Assuming that the sulphur dioxide is not being removed and equally spread in an atmospheric liquid water pool of 5000 m³ and fully returned on earth as rain, what is the expected pH of the condensed water?
- 3.4** If a sodium sulphite solution is used for absorption, sulphur dioxide and the sulphite solution can be recovered. Write down the balanced equations and point out possible pathways to increase the recovery of sulphur dioxide from an aqueous solution.

Note:

Protolysis of sulphur dioxide in aqueous solutions can be described by the first step dissociation of sulphurous acid. The dissociation constant $K_{a,1}(\text{H}_2\text{SO}_3) = 10^{-2.25}$.

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

$M(\text{CaCO}_3) = 100 \text{ g mol}^{-1}$; $M(\text{CaSO}_4) = 172 \text{ g mol}^{-1}$.

SOLUTION

3.2 Under given conditions:

$$n(\text{SO}_2)/\text{h} = v(\text{SO}_2/\text{h}) / V = 669.34 \text{ mol h}^{-1}$$

$$m(\text{CaCO}_3/\text{d}) = n(\text{SO}_2/\text{h}) \times M(\text{CaCO}_3) \times 24 \text{ h} \cdot \text{d}^{-1} \times 0.95 = 1.53 \times 10^3 \text{ kg/d}$$

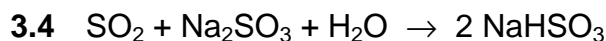
$$m(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}) = \frac{M(\text{CaSO}_4 \cdot 2 \text{H}_2\text{O})}{M(\text{CaCO}_3)} \times m(\text{CaCO}_3) / d = 2.63 \times 10^3 \text{ kg/d}$$

$$3.3 \quad pH = -\log[\text{H}_3\text{O}^+]; \quad K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{SO}_2] - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+]_{1/2} = -\frac{K_a}{2} \pm \sqrt{\frac{K_a^2}{4} + K_a [\text{SO}_2]}$$

Solving for $[\text{H}_3\text{O}^+]$:

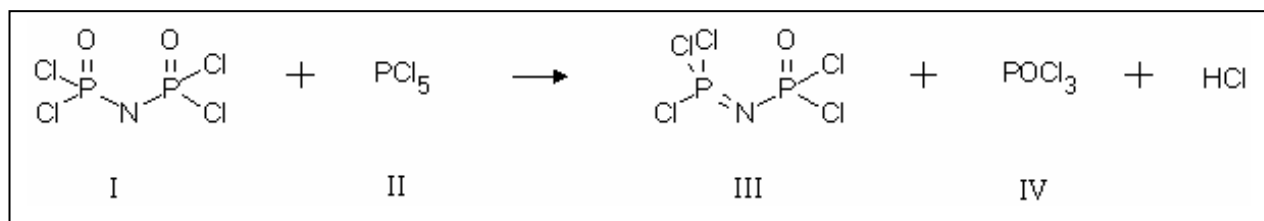
If $[\text{SO}_2] = n(\text{SO}_2) / V = 1.34 \times 10^{-4}$ and $K_a = 1 \times 10^{-2.25}$, then $[\text{H}_3\text{O}^+] = 1.32 \times 10^{-4}$ and $pH = 3.88$



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

PROBLEM 4

³²P labelled phosphorus pentachloride (half-life $t_{1/2} = 14.3$ days) is used to study the electrophilic attack of a PCl_4^+ cation on nitrogen or on oxygen.



The reaction is carried out in CCl_4 and the solvent and product **IV** distilled off. Samples of **III** (remaining in the distillation flask), of **IV** (in the distillate) and samples of the starting material **II** are hydrolyzed by heating with a strong sodium hydroxide solution. The phosphate ions formed are precipitated as ammonium magnesium phosphate. Purified samples of the three precipitates are then dissolved by known volumes of water and the radioactivity measured.

- 4.1 Write the balanced equations for the reaction of red phosphorus forming PCl_5
- 4.2 Write the reaction equations for complete hydrolysis of the compounds **II** and **III** using sodium hydroxide.
- 4.3 How long does it take in order to lower the initial radioactivity to 10^{-3} of the initial value?
- 4.4 Write two alternative mechanisms for the reaction of labelled PCl_4^- with the anion of **I**.
- 4.5 After hydrolysis the precipitated ammonium magnesium phosphates show the following values for radioactivity:
 - II. 2380 Bq for 128 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - III. 28 Bq for 153 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$
 - IV. 2627 Bq for 142 mg of $\text{Mg}(\text{NH}_4)\text{PO}_4$

Using these data, what can you say about the nucleophilic centre attacked by PCl_4^- ?

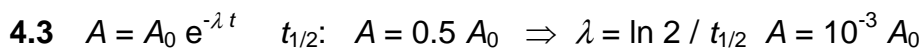
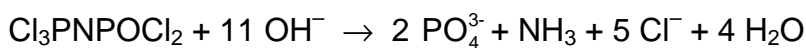
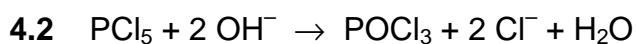
Data: For H_3PO_4 : $pK_1 = 2.2$; $pK_2 = 7.2$; $pK_3 = 12.4$

Solubility product of $\text{Mg}(\text{NH}_4)\text{PO}_4$: $pK_s = 12.6$

Equilibrium concentration of $\text{NH}_4^+ = 0.1 \text{ mol dm}^{-3}$

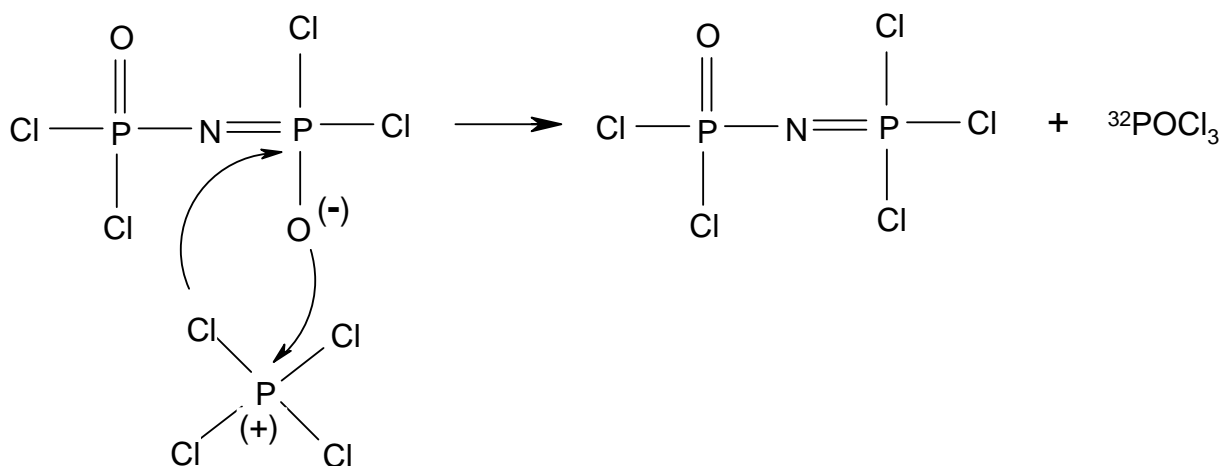
4.6 Calculate the solubility for $\text{Mg}(\text{NH}_4)\text{PO}_4$ at pH equal to 10 under idealized conditions (activity coefficients can be neglected).

SOLUTION

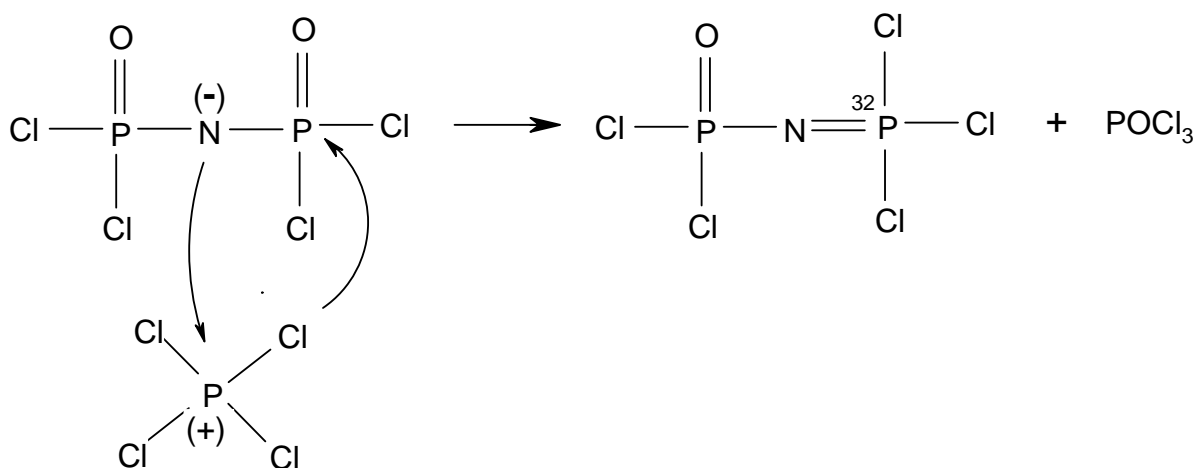


$$t = \frac{\ln A \ln A_0}{\lambda} = \frac{\ln 10^3}{\frac{\ln 2}{14.3}} \text{ d} = 142.5 \text{ d}$$

4.4



1st mechanism



2nd mechanism

- 4.5 Specific activities $A_{\text{sp}}(\text{II}) = 18.6 \text{ Bq/mg}$,
 $A_{\text{sp}}(\text{III}) = 0.18 \text{ Bq/mg}$,
 $A_{\text{sp}}(\text{IV}) = 18.5 \text{ Bq/mg}$.

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

- 4.6 Given data: $K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}] = 10^{-12.6}$; $[\text{NH}_4^+] = 0.1$; $\text{pH} = 10$; $\text{p}K_1 = 2.2$;
 $\text{p}K_2 = 7.2$; $\text{p}K_3 = 12.4$.

Exact solution:

$$2 [\text{Mg}^{2+}] + [\text{NH}_4^+] + [\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-] + 2 [\text{HPO}_4^{2-}] + 3 [\text{PO}_4^{3-}] + [\text{OH}^-]$$

$$[\text{HPO}_4^{2-}] = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{K_3}$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{K_2} = \frac{[\text{PO}_4^{3-}][\text{H}^+]^2}{K_2 K_3}$$

$$[\text{PO}_4^{3-}] = \frac{K_{\text{sp}}}{[\text{NH}_4^+][\text{Mg}^{2+}]}$$

$$\Rightarrow 2 [\text{Mg}^{2+}] = \left(\frac{[\text{H}^+]^2}{K_1 K_3} + \frac{2 [\text{H}^+]}{K_3} + 3 \right) \frac{K_{\text{sp}}}{[\text{NH}_4^+]} - [\text{Mg}^{2+}] ([\text{NH}_4^+] + [\text{H}^+] - [\text{OH}^-])$$

etc.

A simpler solution:

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

$$[\text{HPO}_4^{2-}] = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{K_3} = 10^{2.4} [\text{PO}_4^{3-}]$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{K_2} = 10^{-2.8} [\text{HPO}_4^{2-}]$$

$$S = [\text{Mg}^{2+}] [\text{HPO}_4^{2-}] \text{ and } K_{sp} = [\text{NH}_4^+] \times S \times K_3 \times \frac{S}{[\text{H}^+]}$$

$$pS = 0.5 (pK_{sp} + pH - pK_3 - p[\text{NH}_4^+]) = 0.5 (12.6 + 10.0 - 12.4 - 1.0) = 4.6;$$

$$S = 2.5 \times 10^{-5} \text{ mol dm}^{-3}$$

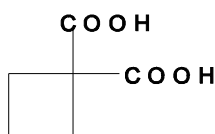
PROBLEM 5

Carboxylic acids are a chemically and biologically important class of organic compounds.

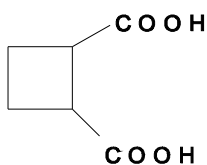
- 5.1 Draw the constitutional (structural) formulae of all isomeric cyclobutanedicarboxylic acids and give the systematic names for these compounds.
- 5.2 There are three stereoisomers, I, II and III, of cyclobutane-1,2-dicarboxylic acid. Draw perspective or stereo formulas of I, II and III indicating the relative configuration of each molecule.
- 5.3 Which pairs of stereoisomers I, II and III are diastereoisomers and which are enantiomers of each other?
- 5.4 Which reaction can be used to determine the relative configuration of diastereoisomers?
- 5.5 How may the enantiomers of cyclobutane-1,2-dicarboxylic acid be separated?
- 5.6 Indicate the absolute configurations of each asymmetric centre on the structures of the stereoisomers I, II and III using the Cahn-Ingold-Prelog rules (*R,S* system).

SOLUTION

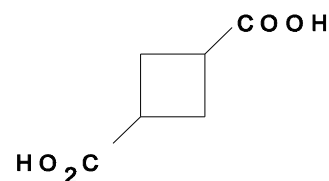
5.1 Constitutional isomers:



1,1 - cyclobutane -
dicarboxylic acid

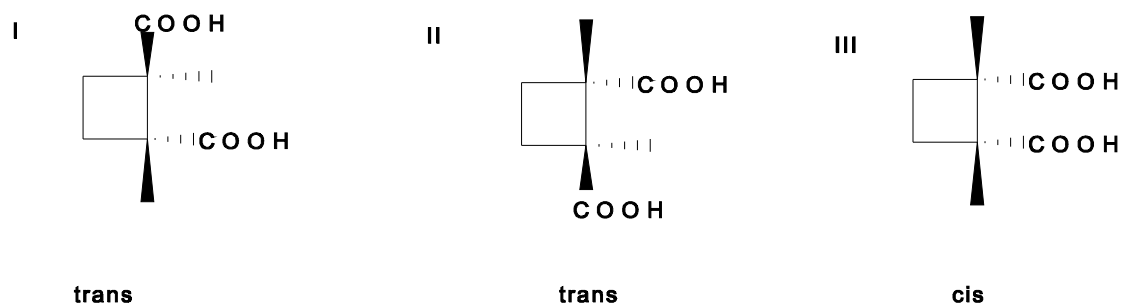


1,2 - cyclobutane -
dicarboxylic acid



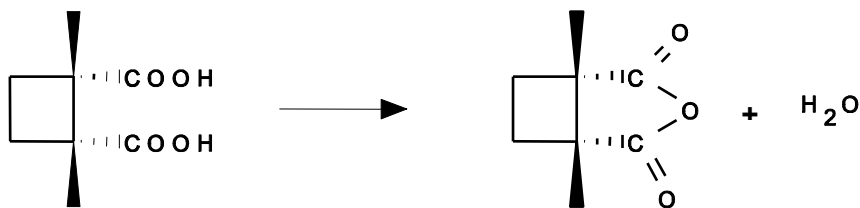
1,3 - cyclobutane -
dicarboxylic acid

5.2 Stereoisomers:



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

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



5.5 The trans-diastereomer can be precipitated with an optically active base.

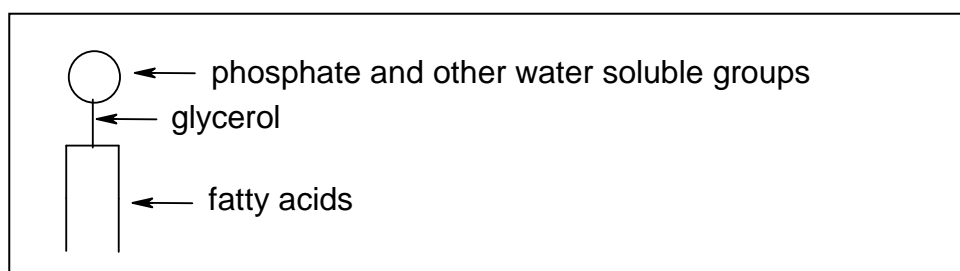
5.6 Stereoisomers absolute configuration:

I: *R,R*; II: *S,S*; III: *R,S*

PROBLEM 6

Fats (lipids) contain a non-polar (hydrophobic) and a polar (hydrophilic) group. The lipids insoluble in water, have important biological functions.

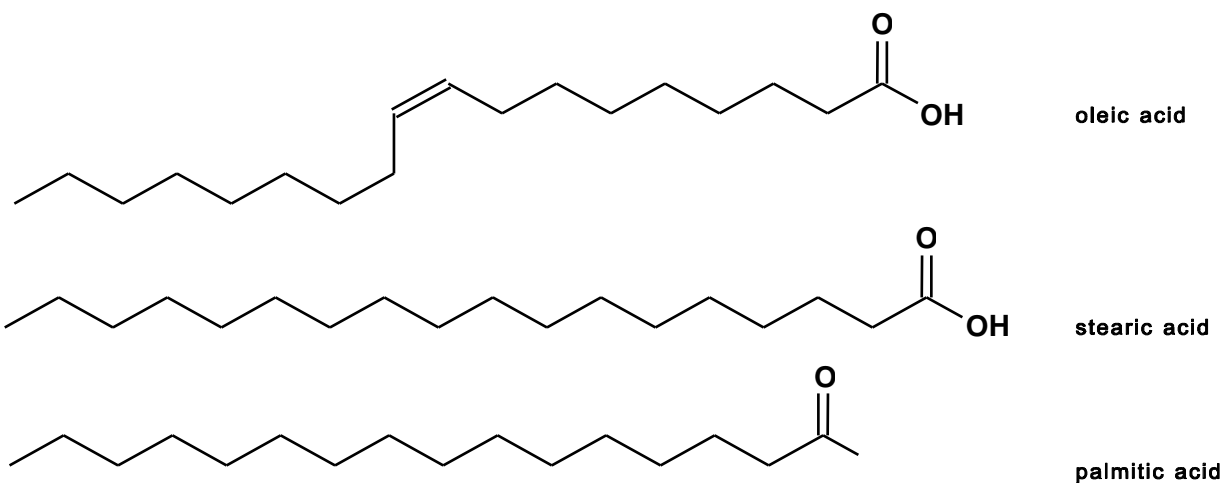
- 6.1 Draw the structures of *Z*-octadec-9-enoic acid (oleic acid), octadecanoic acid (stearic acid), and hexadecanoic acid (palmitic acid).
- 6.2 Using these three fatty acids in part 6.1 draw one possible structure of a triacyl glyceride.
- 6.3 Write the equation for the hydrolysis reaction of your triacyl glyceride in part 6.2 in aqueous NaOH solution. Give the mechanism of the hydrolysis of one of the fatty acids from your glyceride.
- 6.4 Which of the following fatty acids, $C_{21}H_{43}COOH$, $C_{17}H_{35}COOH$ or $C_5H_{11}COOH$, is the least soluble in water?
- 6.5 Phospholipids are an important class of bioorganic compounds. Draw the structure of the phosphatidic acid derived from your triacyl glyceride in part 6.2.
- 6.6 Phospholipids are frequently characterized by the diagram:



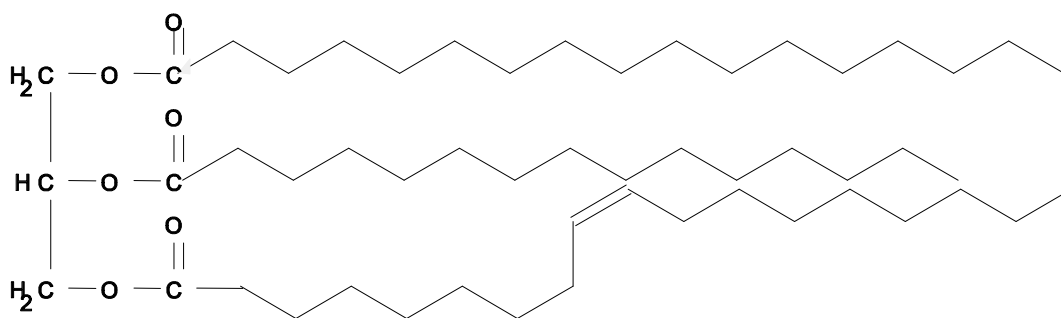
- Mark the hydrophilic and hydrophobic groups on a copy of the above diagram.
- Draw two possibilities for the association of six identical molecules of a phospholipid in water using the above diagram.
- Biomembranes consist of a phospholipid bi-layer. Draw such a model for a membrane using the above diagram.
- Such a model (iii) is incomplete. What other bio-macromolecules are contained in such biomembranes?

SOLUTION

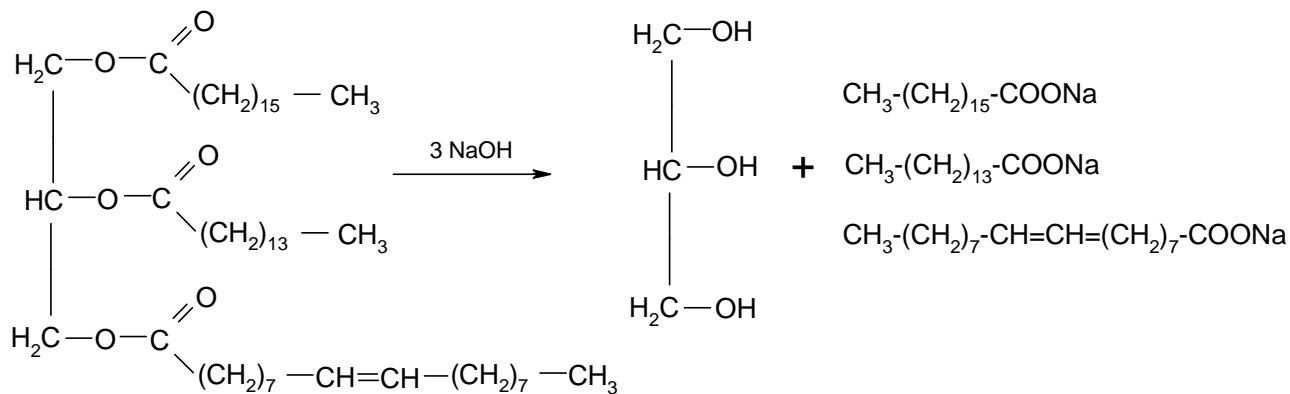
6.1

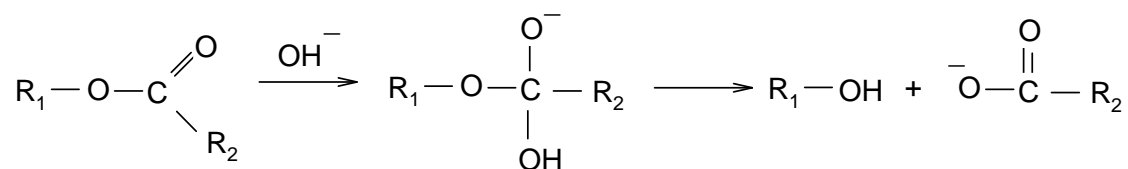


6.2 A possible structure of a triacyl glyceride with the fatty acids mentioned is:



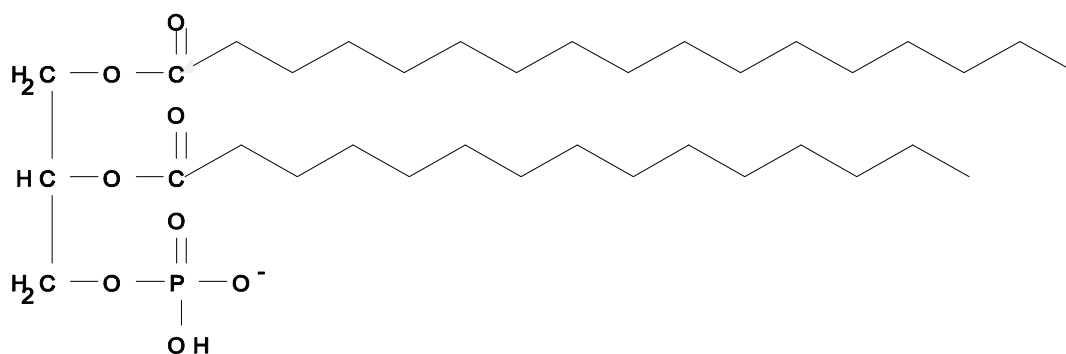
6.3



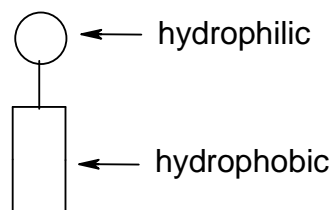


6.4 It is C₂₁H₄₃COOH.

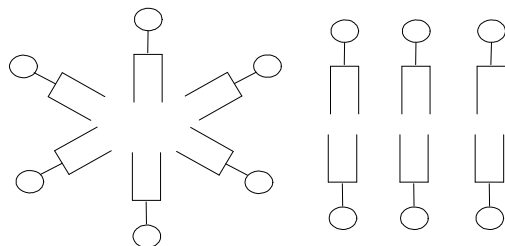
6.5 An example for a phospholipid is:



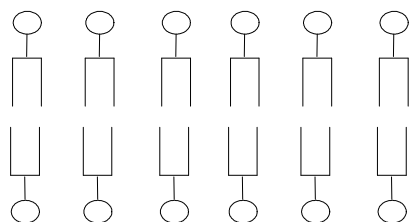
6.6 i)



ii)



iii)



phospholipid bilayer

iv) For example, proteins (enzymes)

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Synthesis**

Preparation of 2-Ethanoxybenzoic Acid (Acetylsalicylic Acid, also known as Aspirin) by Ethanoylation (Acetylation) of 2-Hydroxybenzoic Acid (Salicylic Acid) with Ethanoic Anhydride (acetic anhydride).

Relative atomic masses: C: 12.011; O: 15.999; H: 1.008

Reagents

2-hydroxybenzoic acid (melting point 158 °C)

Ethanoic anhydride (boiling point 140 °C)

Phosphoric acid (85 % H₃PO₄)

Ethanol

Deionised/distilled water

Procedure

In a 100 cm³ Erlenmeyer flask mix 2.760 g of 2-hydroxybenzoic acid (from weighing bottle A) with 5.100 g of ethanoic anhydride (from flask B), and with cautious swirling add 5 – 7 drops of 85 % phosphoric acid. Heat the flask to 70 – 80 °C in a beaker of near boiling water and maintain the mixture at this temperature for 15 minutes. Remove the flask from the water bath and, with gentle swirling, add dropwise 1 cm³ of deionised water to the still hot flask; then immediately add 20 cm³ of the cold deionised water all at once to the reaction flask. Place the flask in an ice bath. If no crystals are deposited, or if oil appears, gently scratch the inner surface of the flask with a glass rod while the flask remains in the ice bath.

Using a Büchner funnel, filter the product under suction. Rinse the flask twice with a small amount of cold deionised water. Recrystallize the crude product in the 100 cm³ Erlenmeyer flask using suitable amounts of water and ethanol. If no crystals form or if oil appears, scratch gently the inner surface of the flask with a glass rod. Filter the crystals under suction and wash with a small amount of cold deionised water. Place the

crystals on the porous plate to draw water from them. When the crystals have been air dried, transfer the product to the small glass dish labeled C. This dish has previously been weighed. The dish containing the product should be given to a technician who will dry it in an oven for 30 minutes at 80 °C.

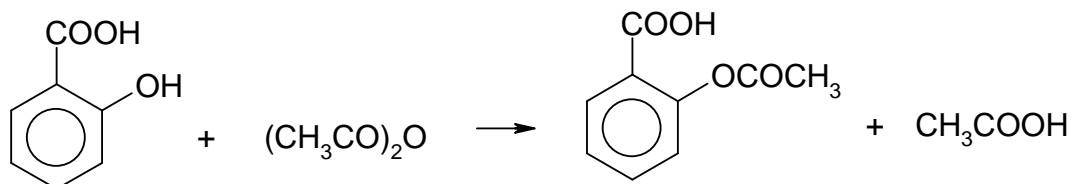
A technician should then weigh the cooled dish containing your product in your presence. Record the mass. The melting point will subsequently be taken by a technician to check the purity of your product.

Questions:

1. Write the balanced chemical equation for the reaction using structural formulae.
2. What is the percentage yield?

SOLUTION

1.



PROBLEM 2 (Practical)**Analysis**

Determination of Mass of a given Sample of 2-Ethanoyl-oxybenzoic Acid (Acetylsalicylic Acid, or Aspirin) by Volumetric Back Titration after Hydrolysis with Excess of Sodium Hydroxide.

Reagents

Aqueous solution of sodium hydroxide (about 0.5 mol dm^{-3})

Standard aqueous solution of hydrochloric acid ($0.4975 \text{ mol dm}^{-3}$)

Ethanolic phenolphthalein solution (indicator dropping bottle II)

Deionised/distilled water

Part 1:

Determine accurately the concentration of the about 0.5 mol dm^{-3} sodium hydroxide solution using the standard hydrochloric acid solution. (Record the answer as mol dm^{-3} with four places after decimal point.)

Procedure:

Pipette 20.00 cm^3 of the sodium hydroxide solution into a 300 cm^3 Erlenmeyer flask and dilute it to about 100 cm^3 with deionized water. Titrate the obtained solution with the standard $0.4975 \text{ mol dm}^{-3}$ hydrochloric acid solution using the phenolphthalein indicator. Repeat the procedure to produce three acceptable values and calculate the mean volume.

Part 2:

Determine accurately the mass of aspirin in Erlenmeyer flask I. Record your answer in g with three places after the decimal point.

Procedure:

Pipette 50.00 cm^3 of your standardized sodium hydroxide solution into the Erlenmeyer flask I (with a ground glass joint) which contains your unknown mass of aspirin. Add 3 – 5 boiling stones to the flask and boil the reaction mixture for 15 minutes using a reflux condenser and the electrical hot plate. After cooling, remove the reflux

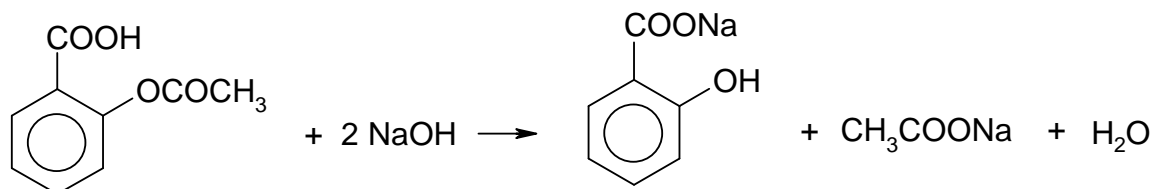
condenser and rinse it with a small quantity of deionised water into Erlenmeyer flask I. Pour the whole solution into a 100.0 cm³ volumetric flask and fill it exactly to the mark with deionised water. Pipette 20.00 cm³ of this solution into a 300 cm³ Erlenmeyer flask and dilute to about 100 cm³ with deionised water. Back titrate the residual sodium hydroxide with the standard hydrochloric acid solution (0.4975 mol dm⁻³) using a 10 cm³ burette and phenolphthalein indicator. Repeat the volumetric procedure to produce three acceptable values and calculate the mean volume.

Questions:

- 1) Write the balanced chemical equation for the ester hydrolysis of aspirin by sodium hydroxide using structural formulae. Note that 1000 cm³ aqueous solution of 0.5000 mol dm⁻³ sodium hydroxide is equivalent to 0.0450 g of aspirin.
- 2) Calculate the mass of aspirin that you were given.

SOLUTION

1.



22nd



International Chemistry Olympiad

**7 theoretical problems
4 practical problems**

THE TWENTY-SECOND INTERNATIONAL CHEMISTRY OLYMPIAD 8-17 JULY 1990, PARIS, FRANCE

THEORETICAL PROBLEMS

PROBLEM 1

PHOSPHORIC ACID

The elemental phosphorus is present in the nature as phosphate in a complex mineral apatite. This mineral contains, in addition to phosphate, silica and the following ions: Ca^{2+} , CO_3^{2-} , SO_4^{2-} , SiO_3^{2-} , and F^- .

Let us assume that this mineral is a mixture of tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, calcium sulphate, calcium fluoride, calcium carbonate and silica.

For uses as fertilizer the calcium bis(dihydrogenphosphate), $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which is soluble in water, has been prepared. For this purpose, apatite is treated with a mixture of phosphoric and sulphuric acid. At the same time this operation eliminates the majority of impurities.

The elemental analysis of an apatite gave the following results in which, except of fluorine, the elemental composition is expressed as if the elements were in the form of oxides:

	CaO	P ₂ O ₅	SiO ₂	F	SO ₃	CO ₂
% by mass	47.3	28.4	3.4	3.4	3.5	6.1

Operation 1 - A sample of m_0 of this mineral is treated with 50.0 cm³ of a solution containing 0.500 mol dm⁻³ phosphoric and 0.100 mol dm⁻³ sulphuric acids. The mixture is completely dehydrated by heating up to about 70 °C avoiding temperature rising above 90 °C. This operation is carried out under the hood since toxic gaseous substances are emitted. The dry residue is ground and weighed; m_1 is the mass of the residue obtained.

In these conditions only dihydrogenphosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, is formed while silica and silicate do not react.

Operation 2 - 1.00 g of this residue is treated with 50.0 cm^3 of water at $40 \text{ }^\circ\text{C}$, then filtered, dried and weighed. The mass of the residue obtained is m_2 . This new residue is mainly containing gypsum, $\text{CaSO}_4 \cdot 2 \text{ H}_2\text{O}$, whose solubility can be considered as constant between $20 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$ and is equal to 2.3 g dm^{-3} .

- 1.1 Write the balanced equations for the reactions that are involved.
 1.2 From what mass of apatite should one start if all the reactions are stoichiometric?

Starting with m_0 of obtained apatite, $m_1 = 5.49 \text{ g}$ of residue are obtained.

- 1.3 What mass should theoretically be obtained?
 1.4 This result is due to the presence of products that are not expected to be found in the residue. Give two of them that under these experimental conditions can plausibly account for the data.

Traditionally, in industry the analysis and the yield are expressed as percentage of oxide. The phosphorous content is expressed as if it were P_2O_5 .

If n_2 is the amount of a soluble product obtained, n_1 the amount of a substance added as acid, n_0 the amount of apatite added, the yield is:

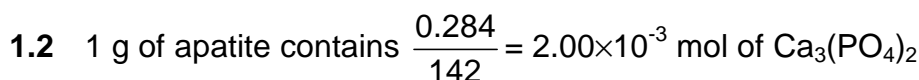
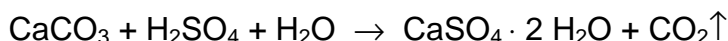
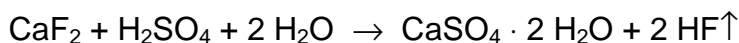
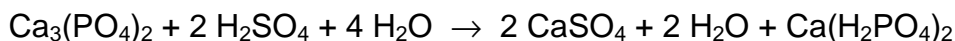
$$r_{\text{exp}} = \frac{n_2}{n_1 + n_0} 100$$

$m_2 = 0.144 \text{ g}$ of residue is obtained on the filter.

- 1.5 Calculate r_{exp} .
 1.6 The experimental yield is over 100 %. Calculate a value of r nearer to the real yield.

Relative atomic masses of P: 31; Ca: 40; O: 16; H: 1; F: 19; C: 12; Si: 28;
 S: 32.

Values of pK : $\frac{\text{HSO}_4^-}{\text{SO}_4^{2-}} = 2$ $\frac{\text{HF}}{\text{F}^-} = 3$ $\frac{\text{H}_3\text{PO}_4}{\text{H}_2\text{PO}_4^-} = 2$ $\frac{\text{H}_2\text{PO}_4^-}{\text{HPO}_4^{2-}} = 7$ $\frac{\text{HPO}_4^{2-}}{\text{PO}_4^{3-}} = 12$

SOLUTION

$$\frac{0.034}{2 + 19} = 0.89 \times 10^{-3} \text{ mol of } \text{CaF}_2$$

$$\frac{0.061}{44} = 1.39 \times 10^{-3} \text{ mol of } \text{CaCO}_3$$

$$\frac{0.035}{80} = 0.44 \times 10^{-3} \text{ mol of } \text{CaSO}_4$$

$$\frac{0.473}{56} - \frac{3 \times 0.284}{142} - \frac{0.034}{38} - \frac{0.061}{44} - \frac{0.035}{80} = 2.72 \times 10^{-4} \text{ mol CaO that remain.}$$

The amount of H_3PO_4 needed to react with 1 g of apatite is equal to $n(\text{H}_3\text{PO}_4) = 4 n(\text{Ca}_3(\text{PO}_4)_2) + 2 n(\text{CaF}_2) + 2 n(\text{CaCO}_3) = 12.56 \times 10^{-3} \text{ mol}$.

50 cm^3 of the acid contains $25 \times 10^{-3} \text{ mol}$ of H_3PO_4 , therefore $25 / 12.56 = \underline{1.99 \text{ g}}$ apatite is needed to neutralize the H_3PO_4 present.

The amount of H_2SO_4 needed to react with 1 g of apatite can be calculated in the same way:

$n(\text{H}_2\text{SO}_4) = 2 n(\text{Ca}_3(\text{PO}_4)_2) + n(\text{CaF}_2) + n(\text{CaCO}_3) = 6.28 \times 10^{-3} \text{ mol}$. 50 cm^3 of the acid contains $5.00 \times 10^{-3} \text{ mol}$ of sulphuric acid. Therefore $5 / 6.28 = 0.80 \text{ g}$ of apatite is needed to neutralize the H_2SO_4 .

The total amount of apatite is $m_0 = 1.99 + 0.80 = \underline{2.79 \text{ g}}$

1.3 Formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$:

1.99 g of apatite needed to neutralize the H_3PO_4 contains $1.9 \times 2.00 \times 10^{-3} \text{ mol}$ of $\text{Ca}_3(\text{PO}_4)_2$, thus $3 \times 2 \times 2 \times 10^{-3} = 1.2 \times 10^{-2} \text{ mol}$ of dihydrogen phosphate is being formed.

From CaF_2 , $1.99 \times 0.89 = 1.80$ mol and from CaCO_3 , $1.99 \times 1.39 = 2.77$ mol of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ are formed.

0.8 g of apatite that reacts with 50 cm^3 of the sulphuric acid yields $2 \times 0.8 \times 10^{-3} = 1.6 \times 10^{-3}$ mol of $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

$$m(\text{Ca}(\text{H}_2\text{PO}_4)_2) = 18.07 \times 10^{-3} \text{ mol} = 4.230 \text{ g}$$

Formation of gypsum: $n(\text{CaSO}_4) = n(\text{H}_2\text{SO}_4) = 5.00 \times 10^{-3} \text{ mol} \hat{=} 0.86 \text{ g}$

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

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

1.4 The difference of 0.1 g may be due to water and unreacted CaF_2 in the residue.

1.5 The second reaction is intended to dissolve $\text{Ca}(\text{H}_2\text{PO}_4)_2$, while all the other products remain on the filter.

According to the yielded residue of 0.144 g, 1 g of residue contains $1 - 0.144 = 0.856$ g of soluble product. If it were all $\text{Ca}(\text{H}_2\text{PO}_4)_2$ it would correspond to $0.856 / 234 = 3.66 \times 10^{-3}$ mol. For 5.49 g of residue it is 0.0201×10^{-3} mol of soluble product (n_2). The amount of acid used is $0.500 / 20 = 0.025$ mol H_3PO_4 (equals 0.0125 mol P_2O_5) and 0.005 mol H_2SO_4 . The amount of $\text{Ca}_3(\text{PO}_4)_2$ in 2.79 g apatite is 0.00558 mol (equals 0.00558 mol P_2O_5). So, $r_{\text{exp}} = 100 \times [0.0201 / (0.0125 + 0.00558)] = \underline{111 \%}$

Since 50 cm^3 water dissolve 0.115 g of gypsum, the real quantity of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is $0.856 - 0.115 = 0.741$ mol, so that the real yield gives: $r_{\text{exp}} = 100 \times [0.0174 / (0.0125 + 0.00558)] = \underline{96 \%}$.

1.6 The theoretical value for r_{exp} is: $r_{\text{exp}} = 100 \times [4.23 / 234 / (0.0125 + 0.00558)] = 100 \%$, so this calculation makes sense.

PROBLEM 2**IONIC SOLUTIONS – AQUEOUS SOLUTIONS OF COPPER SALTS**

This part is about the acidity of the hydrated Cu^{2+} ion and the precipitation of the hydroxide.

Consider a $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ solution of copper(II) nitrate. The pH of this solution is 4.65.

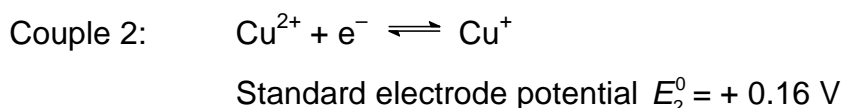
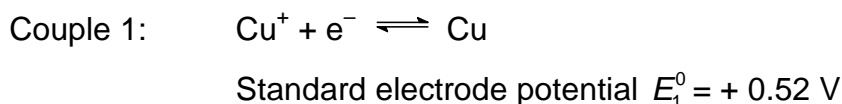
- 2.1** Give the equation for the formation of the conjugate base of the hydrated Cu^{2+} ion.
2.2 Calculate the pK_a of the corresponding acid-base pair.

The solubility product of copper(II) hydroxide is $K_{sp} = 1 \times 10^{-20}$.

- 2.3** At what pH value hydroxide $\text{Cu}(\text{OH})_2$ precipitates from the solution under consideration? Justify your calculation showing that the conjugate base of this hydrated Cu^{2+} ion is present in negligible quantity.

Disproportionation of copper(I) ions

The Cu^+ ion is involved in two redox couples:



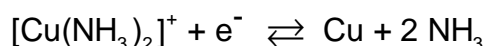
- 2.4** Write down the equation for the disproportionation of copper(I) ions and calculate the corresponding equilibrium constant.
2.5 Calculate the composition of the solution (in mol dm^{-3}) obtained on dissolving $1.00 \times 10^{-2} \text{ mol}$ of copper(I) in 1.0 dm^3 of water.
2.6 Apart from Cu^+ ions, name two chemical species which also disproportionate in aqueous solution; write down the equations and describe the experimental conditions under which disproportionation is observed.

Consider the stability of copper(I) oxide, Cu_2O , in contact with a $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ solution of Cu^{2+} ions. The solubility product of copper(I) oxide is $K_{sp} = [\text{Cu}^+][\text{OH}^-] = 1 \times 10^{-15}$

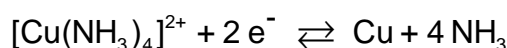
2.7 Calculate the pH value at which Cu_2O becomes stable. Quote a simple experiment allowing the observation of the precipitation of Cu_2O .

Complex formation involving Cu^+ and Cu^{2+} ions

2.8 The dissociation constant of the complex ion $[\text{Cu}(\text{NH}_3)_2]^+$ is $K_D = 1 \times 10^{-11}$. Calculate the standard electrode potential of the couple:



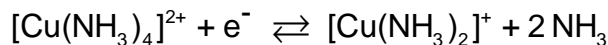
2.9 The standard electrode potential of the couple



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

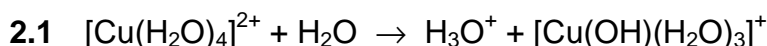
Calculate the dissociation constant for the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

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



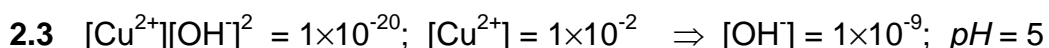
Does the disproportionation of the cation $[\text{Cu}(\text{NH}_3)_2]^+$ take place?

SOLUTION

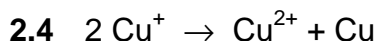


$$2.2 \quad K_a = \frac{[\text{H}_3\text{O}^+][[\text{Cu}(\text{OH})(\text{H}_2\text{O})_3]^+]}{[[\text{Cu}(\text{H}_2\text{O})_4]^{2+}]} = \frac{[\text{H}_3\text{O}^+]^2}{[[\text{Cu}(\text{H}_2\text{O})_4]^{2+}]} = \frac{(2.24 \times 10^{-5})^2}{1 \times 10^{-2}} = 5.01 \times 10^{-8}$$

$$pK_a = 7.30$$



$$[[\text{Cu}(\text{OH})(\text{H}_2\text{O})_3]^+] : [[\text{Cu}(\text{H}_2\text{O})_4]^{2+}] = K_a : 10^{-pH} = 1 \times 10^{-7.3} : 1 \times 10^{-5} = 1 : 200$$



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

$$0.52 - 0.16 = 0.059 \log K \text{ (Nernst equation)} \Rightarrow K = 1 \times 10^6$$

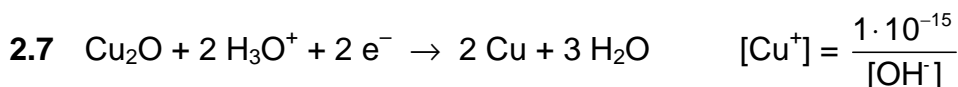
2.5 At equilibrium: $[\text{Cu}^+] + 2 [\text{Cu}^{2+}] = 1 \times 10^{-2}$ and $[\text{Cu}^{2+}] = 1 \times 10^6 [\text{Cu}^+]$ so that the following equation is obtained:

$$2 \times 10^6 [\text{Cu}^+]^2 + [\text{Cu}^+] - 1 \times 10^{-2} = 0$$

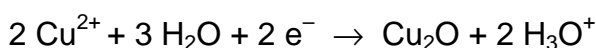
with the solution

$$[\text{Cu}^+] = \underline{7.07 \times 10^{-5}} \text{ and } [\text{Cu}^{2+}] = \underline{4.96 \times 10^{-3}} .$$

2.6 Other disproportionation reactions:



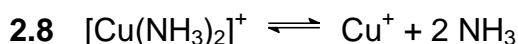
$$E_1 = 0.52 + \frac{0.059}{2} \log ([\text{Cu}^+][\text{H}_3\text{O}^+]^2) = 0.49 - 0.0885 \text{ pH}$$



$$E_2 = 0.16 + \frac{0.059}{2} \log \frac{1 \times 10^{-4}}{[\text{Cu}^+][\text{H}_3\text{O}^+]^2} = 0.07 + 0.0885 \text{ pH}$$

Cu_2O is stable when $E_2 > E_1$ i.e. $0.42 < 0.177 \text{ pH}$, or $\text{pH} > 2.4$

Cu_2O can be obtained by the reduction of Cu^{2+} in acid or basic media, e.g. by Fehling's solution or reducing sugars.



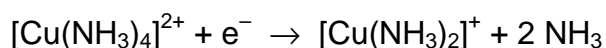
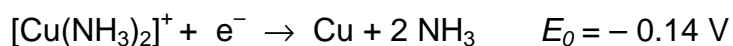
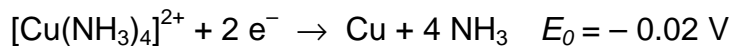
$$K_D = \frac{[\text{Cu}^+][\text{NH}_3]^2}{[\text{Cu}(\text{NH}_3)_2^+]} = 1 \times 10^{-11}$$

Knowing $E_0(\text{Cu}^+/\text{Cu}) = 0.52 \text{ V}$, the $E^0([\text{Cu}(\text{NH}_3)_2]^+ / \text{Cu}^+)$ becomes:

$$E_{f1} = 0.52 - 0.06 \text{ p}K_D = \underline{-0.14 \text{ V}}$$

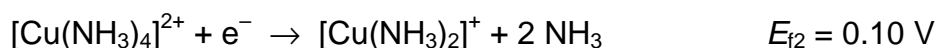
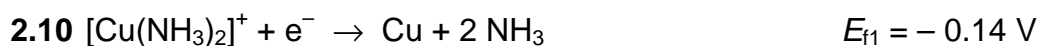
2.9 The standard *emf* of a Cu^{2+}/Cu cell is thus: $E^0 = (0.5 + 0.16)/2 = 0.33 \text{ V}$ and $E_3^0 = 0.33 - 0.03 \text{ p}K_2$.

$$\text{Thereout: } \text{p}K_2 = (0.33 - E_3^0) / 0.03 = (0.33 - (-0.02)) / 0.03 = \underline{12}$$



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

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



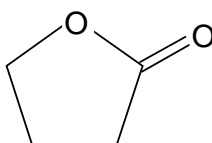
Since $E_{f1} < E_{f2}$ the $[\text{Cu}(\text{NH}_3)_2]^+$ ion doesn't disproportionate (the *emf* would be $-0.14 - 0.10 = -0.24 \text{ V}$)

PROBLEM 3**ORGANIC SYNTHESIS – SYNTHESIS OF HALOPERIDOL**

Haloperidol is a powerful neuroleptic prescribed in cases of psychomotoric disorder and for the treatment of various psychoses. A synthesis of this compound is proposed.

3.1 Give a scheme for the preparation of methyl 4-chlorobenzoate starting from benzene and all necessary inorganic substances. Diazomethane (H_2CN_2) must be used in your synthesis.

γ -Butyrolactone (**J**) is a cyclic ester represented below.

**J**

3.2 How can γ -butyrolactone **J** be converted into 4-hydroxybutanoic acid (**K**)?

3.3 Convert **K** into 4-chlorobutanoyl chloride (**L**).

The reactions described below do not correspond to those used in the industrial synthesis of haloperidol for which the route is quite complex.

Methyl 4-chlorobenzoate is treated with an excess of vinylmagnesium bromide in anhydrous ether. **M** is obtained after hydrolysis. When **M** is treated with an excess of hydrogen bromide in anhydrous conditions in the presence of benzoyl peroxide, **N** is obtained. **N** reacts with ammonia to form 4-(4-chlorophenyl)-4-hydroxypiperidine (**O**).

3.4 Write down the structure of **M**, **N** and **O** and indicate the mechanism of the reaction leading to **M**.

In the presence of a moderate amount of aluminium chloride, **L** reacts with fluorobenzene to yield mainly a ketone **P** ($\text{C}_{10}\text{H}_{10}\text{OFCl}$).

3.5 Sketch the structure of **P** and indicate the mechanism.

3.6 Give a chemical and physical test method for the determination of the carbonyl group. How can you make sure that the carbonyl group does not belong to an aldehyde group?

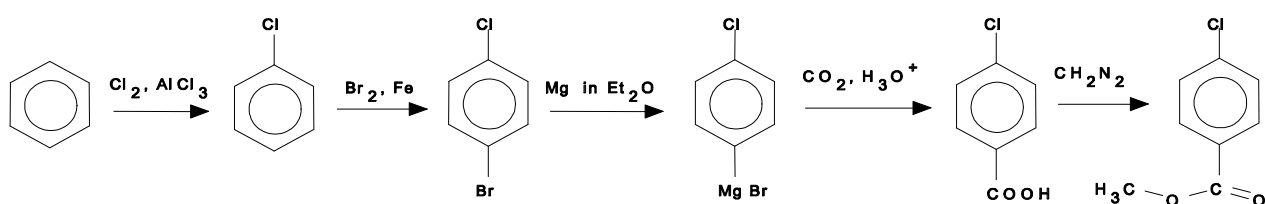
P reacts with **O** in basic media in a 1 : 1 molar ratio to give **H** that contains only one chlorine atom on the aromatic ring.

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

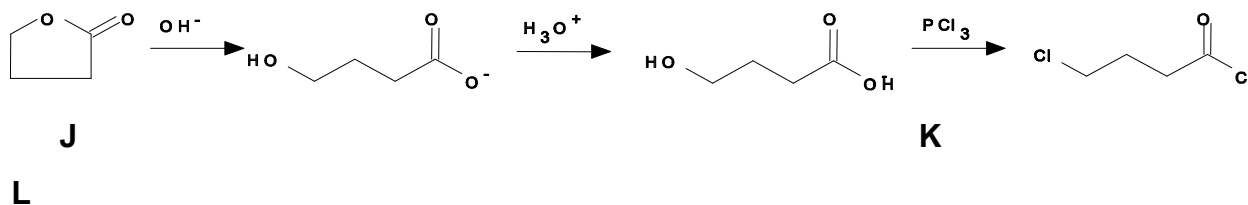
3.8 State the multiplicity of each resonance in the ¹H NMR spectrum of **K**. Assume that all coupling constants between protons and adjacent carbons are identical.

SOLUTION

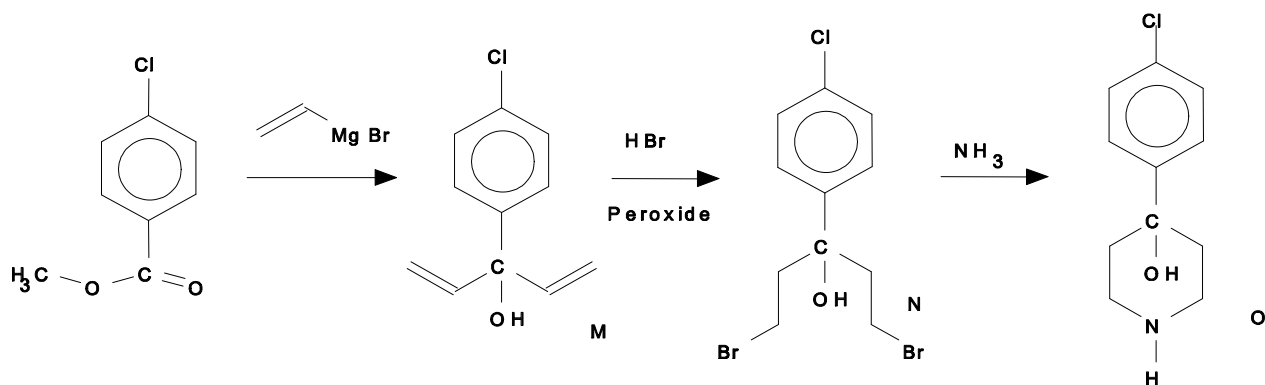
3.1



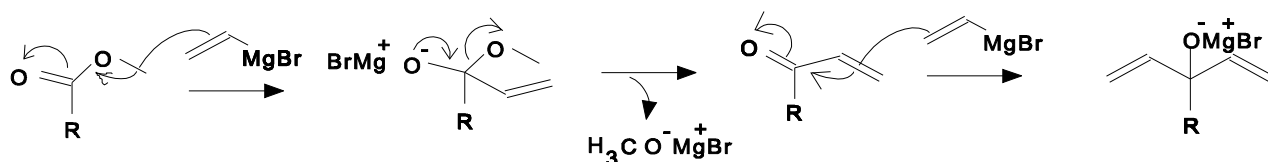
3.2 and 3.3



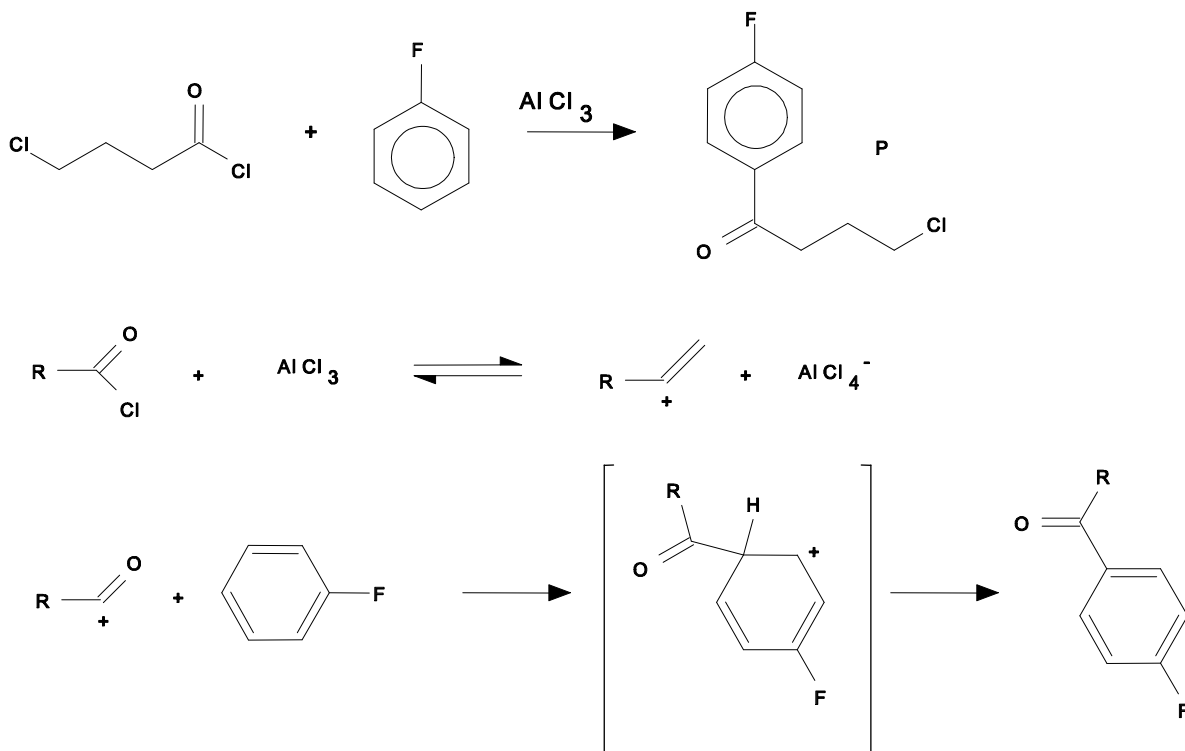
3.4



Mechanism of the Grignard reaction:



3.5

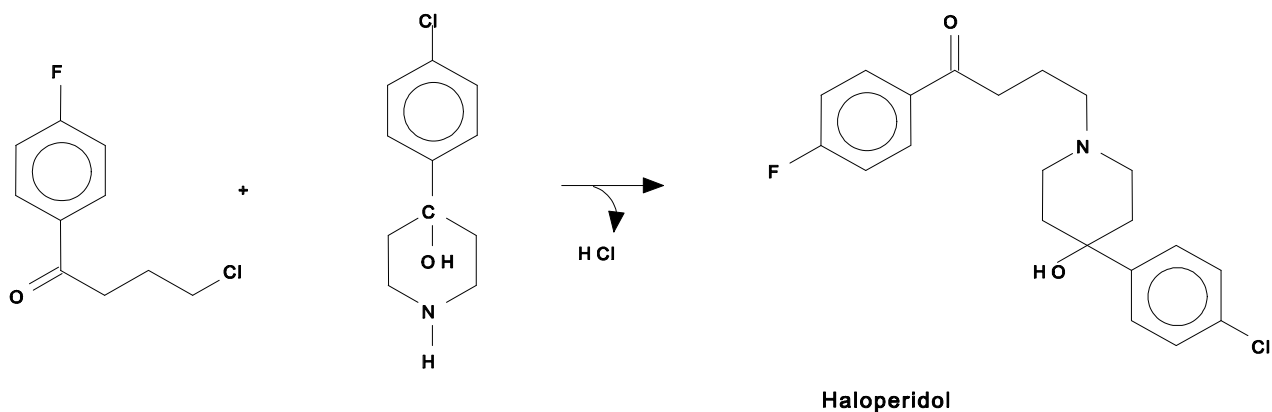


3.6 Chemical test: carbonyl groups react with phenylhydrazines to phenylhydrazones with a sharp, specific melting point.

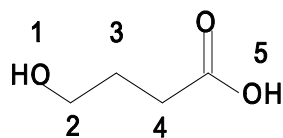
Physical test: IR-absorption at 1740 cm^{-1}

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

3.7



3.8

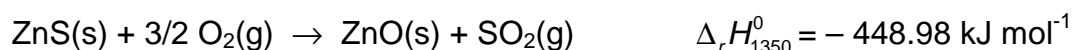


proton1:singulet
 proton2:triplet
 proton3:quintuplet
 proton4:triplet
 proton5:singulet

PROBLEM 4**CHEMICAL THERMODYNAMICS**

The production of zinc from zinc sulphide proceeds in two stages: the roasting of zinc sulphide in the air and the reduction of the zinc oxide formed by carbon monoxide. In this problem we will consider the roasting of zinc sulphide.

This operation consists in burning zinc sulphide in the air. The equation of the reaction taking place is as follows:



Industrially this reaction is carried out at 1350 K.

4.1 Show that the reaction can be self-sustaining, i.e. that the heat produced is sufficient to bring the reactants from ambient temperature to the reaction temperature.

Suppose that the zinc containing mineral contains only zinc sulphide, ZnS.

4.2 Starting with a stoichiometric mixture of one mole zinc blend only and a necessary quantity of the air at 298 K, calculate the temperature to which the mixture will raise by the heat evolved during the roasting of the mineral at 1350 K under standard pressure. Is the reaction self-sustaining? Air is considered to be a mixture of oxygen and nitrogen in a volume ratio equal to 1 : 4.

In fact, zinc blend is never pure and is always mixed with a gangue that can be assumed to be entirely silica SiO₂.

4.3 Assuming that the gangue does not react during the roasting, calculate the minimum ZnS content of the mineral for which the reaction would be self-sustaining at 1350 K despite the presence of silica. Give the answer in grams of ZnS per hundred grams of zinc blend.

Data:

Standard molar heat capacities averaged over the temperature range considered (in J K⁻¹ mol⁻¹):

ZnS (solid):	58.05	ZnO (solid):	51.64
SO ₂ (gas):	51.10	O ₂ (gas):	34.24
N ₂ (gas):	30.65	SiO ₂ (solid):	72.50
Molar masses (in g mol ⁻¹):		ZnS: 97.5	SiO ₂ : 60.1

SOLUTION

4.1 The heat given off heats 1 mol of ZnS, 1.5 mol of O₂ and 6 mol of N₂. Therefore:

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

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

4.2 If n denotes the quantity (in moles) of SiO₂ per mol of ZnS, the heat given off heats 1 mol of ZnS, n mol of SiO₂, 1.5 mol of O₂ and 6 mol of N₂ from 298 to 1350 K:

$$\Delta_r H^0 = \int_{298}^{1350} \sum (n_i \times c_{p(i)}) dT = \int_{298}^{1350} (293.3 + 72.5n) dT$$

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

4.3 By mass, we have 110.6 g of SiO₂ per 97.5 g of ZnS, or 46.9 g of ZnS per 100 g of mineral. Thus, the minimum tolerated ZnS content in the mineral is 46.9 %.

PROBLEM 5**CHEMICAL KINETICS**

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



The experimental kinetic law is as follows:

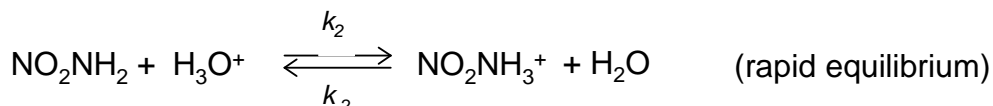
$$\frac{d[\text{N}_2\text{O}]}{dt} = k \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

- 5.1** What is the apparent order of this reaction in a buffered solution?
- 5.2** Which of the following mechanisms is the most appropriate for the interpretation of this kinetic law? Justify your answer.

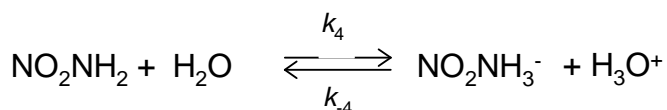
Mechanism 1:



Mechanism 2:



Mechanism 3:



- 5.3** Show the relationship between the experimentally observed rate constant and the rate constants of the selected mechanism.
- 5.4** Show that hydroxyl ions catalyze the decomposition of nitramide.

The decomposition is studied in a buffered solution of a constant volume V at a constant temperature by measuring the partial pressure of the gas N_2O , considered to be insoluble in water, in a constant volume of the same value V above the solution. The following results are obtained:

$t(\text{min})$	0	5	10	15	20	25
$p(\text{Pa})$	0	6800	12400	17200	20800	24000

After a sufficiently long time, the pressure stabilises at 40000 Pa.

5.5 Express the pressure p as a function of time and the constant k' such that

$$k' = \frac{k}{[\text{H}_3\text{O}^+]}$$

5.6 Verify graphically that the kinetic law is confirmed by these experimental results.

5.7 Calculate k' giving its units.

SOLUTION

5.1 In a buffer solution $[\text{H}_3\text{O}^+]$ is constant and the reaction is of the first order:

$$v = k' [\text{NO}_2\text{NH}_2]$$

5.2 The rate laws of the three mechanisms proposed are:

$$v_1 = k_1 [\text{NO}_2\text{NH}_2]$$

$$v_2 = k_3 [\text{NO}_2\text{NH}_3^+] = \frac{k_3 k_2}{k_{-2}} [\text{NO}_2\text{NH}_2] [\text{H}_3\text{O}^+]$$

$$v_3 = k_5 [\text{NO}_2\text{NH}^-] = \frac{k_5 k_4}{k_{-4}} \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

Thus, it is the third mechanism that is correct.

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

5.4 Noting that $[\text{H}_3\text{O}^+] = K_e / [\text{OH}^-]$ it follows that $v = k / K_e [\text{NO}_2\text{NH}_2] [\text{OH}^-]$, which shows the catalytic role of OH^- .

5.5 $d[\text{N}_2\text{O}]$ can be expressed by the change of pressure $dp(\text{N}_2\text{O})/RT$ (according to $pV = nRT$). We obtain:

$$v = \frac{d[\text{N}_2\text{O}]}{dt} = \frac{1}{RT} \frac{dp(\text{N}_2\text{O})}{dt} = \frac{1}{RT} \frac{dp}{dt} = k \frac{[\text{NO}_2\text{NH}_2]}{[\text{H}_3\text{O}^+]}$$

We also know that $V[\text{NO}_2\text{NH}_2] = n(\text{NO}_2\text{NH}_2)_{\text{init}} - n(\text{N}_2\text{O}) = n(\text{N}_2\text{O})_{\infty} - n(\text{N}_2\text{O})$ from which

$$\frac{dp}{dt} = \frac{k}{[\text{H}_3\text{O}^+]} \times \frac{RT}{V} \times (n(\text{N}_2\text{O})_{\infty} - n(\text{N}_2\text{O}))$$

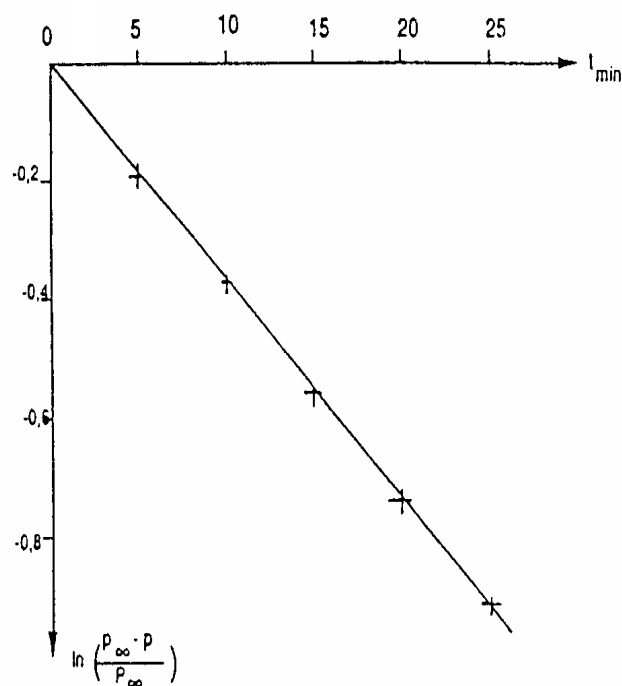
and thus

$$\frac{dp}{dt} = \frac{k}{[\text{H}_3\text{O}^+]} \times (p_{\infty} - p) = k'(p_{\infty} - p)$$

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

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

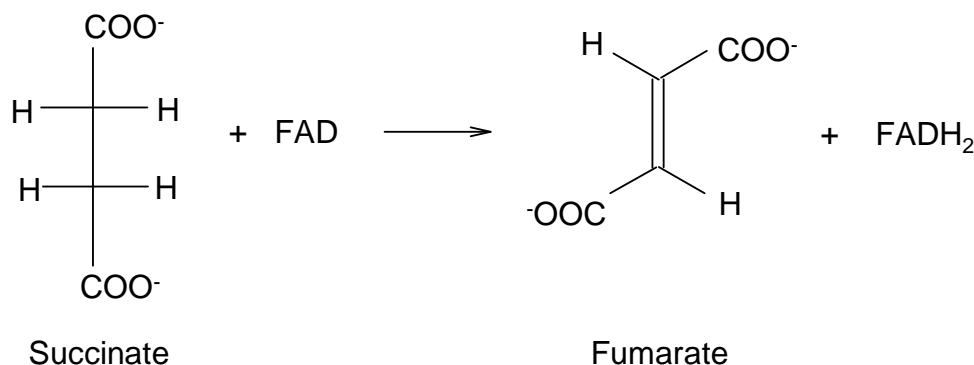
5.6



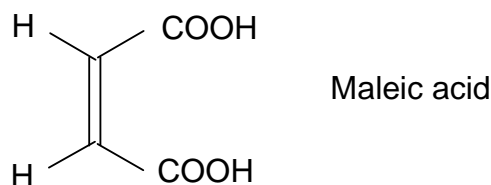
5.7 The graph of $f(x) = \ln(1 - p/p_{\infty}) = -k't$ is a straight line with the slope k' shown in Fig. k' was determined to be $3.7 \times 10^{-2} \text{ min}^{-1}$.

PROBLEM 6**BIO-ORGANIC CHEMISTRY**

The reaction of dehydrogenation of succinate to fumarate is a one step in the tricarboxylic Krebs cycle, catalysed by the enzyme succinic dehydrogenase. Flavine-adenine-dinucleotide, FAD, acts as a coenzyme. The equation of the process:



The stereochemistry of the dehydrogenation of succinate to fumarate has been studied. Consider the enzymatic reaction with the 2,3-dideuteriosuccinates related to the acids or obtained by catalytic deuteration (in the presence of palladium on coal) of fumaric and maleic acids.



6.1 Using Fischer formulae, write down structures for all the possible stereoisomers obtained by catalytic deuteration of maleic and fumaric acids. How many isomers are there? Indicate those that are optically active. Establish a stereochemical relationship between them (compare the isomers two by two). Using Newman projections show the most stable conformation of each isomer.

The proportion of dideuterated fumarate (obtained when each of the above 2-3 dideuterated succinates is submitted to the enzymatic reaction) is 4 % when using fumaric acid as starting molecule, but 48.5 % when using maleic acid.

It is assumed that at the active site, the enzymatic dehydrogenation occurs on the succinate, in the most stable conformation as proposed in 6.1. The dehydrogenation stereochemistry can be *syn* or *anti*.

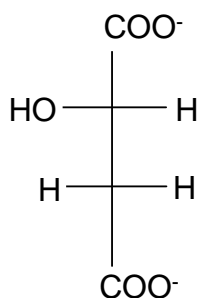
6.2 On the basis of the Newman projections of the most stable conformations of each isomer and the above facts, determine the percentage of dideuterated fumarate formed by *syn* and *anti* dehydrogenation.

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

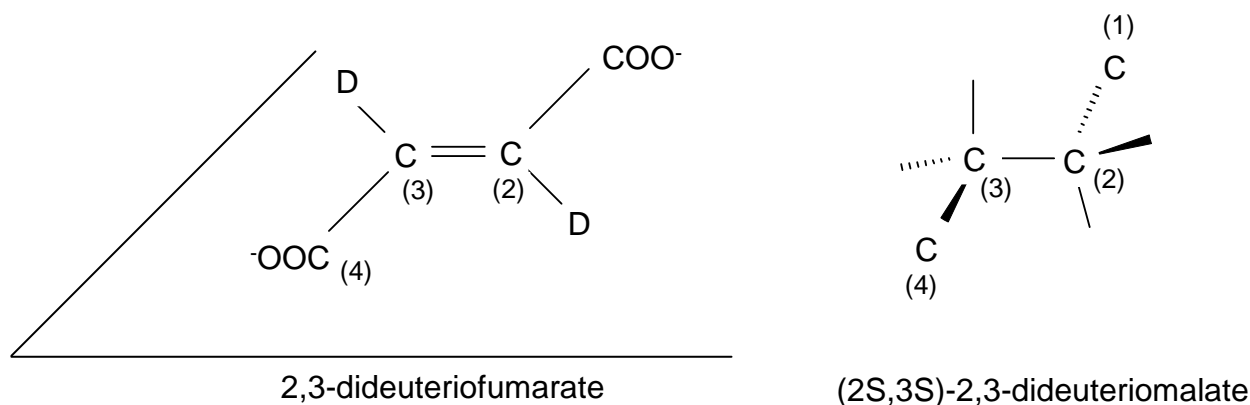
6.3 Show the stereochemistry of the enzymatic dehydrogenation.

In the following step of the Krebs cycle and in the presence of fumarase enzyme, fumarate adds on a water molecule to yield (*S*)-malate (also called as L-malate).

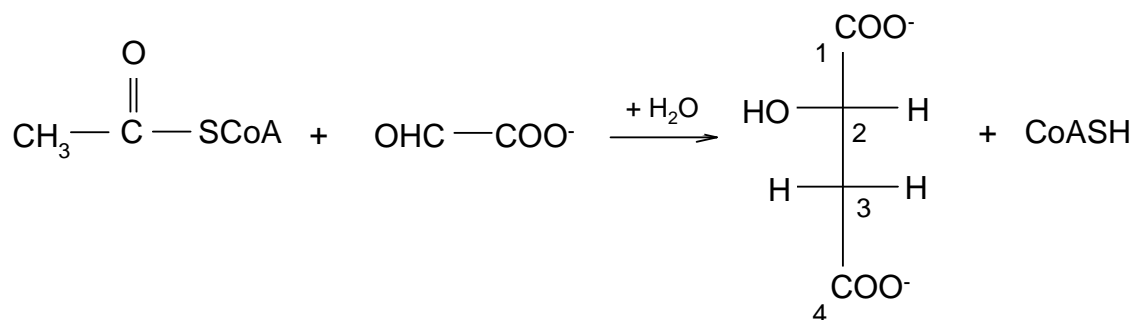
Fischer projection of (*S*)-malate:



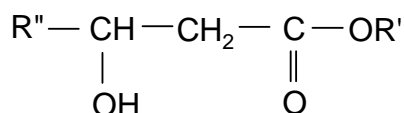
6.4 The 2,3-dideuterofumarate reacts with fumarase to (*2S,3S*)-2,3-dideuteromalate (through addition of water). Show the stereochemical pathway of the reaction. Use the schematic drawing below to answer this question.



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



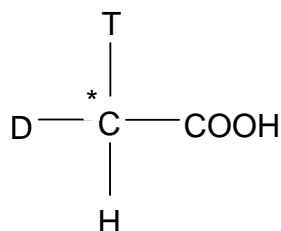
A similar reaction can proceed between an ester $\text{CH}_3\text{COOR}'$ (similar to the thioester CH_3COSCoA) and an aldehyde $\text{R}''\text{CHO}$ (similar to the glyoxylate) in the presence of $\text{R}'\text{-O}^-$ ions. It leads to a β -hydroxyester.



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

6.5 Write the steps of the mechanism.

The enzymatic reaction is carried out using acetylcoenzyme A which is obtained from acetic acid CH_3COOH having *R*-configuration.



(tritium $\text{T} = {}^3_1\text{H}$, deuterium $\text{D} = {}^2_1\text{H}$)

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

6.6 What enzyme can be used?

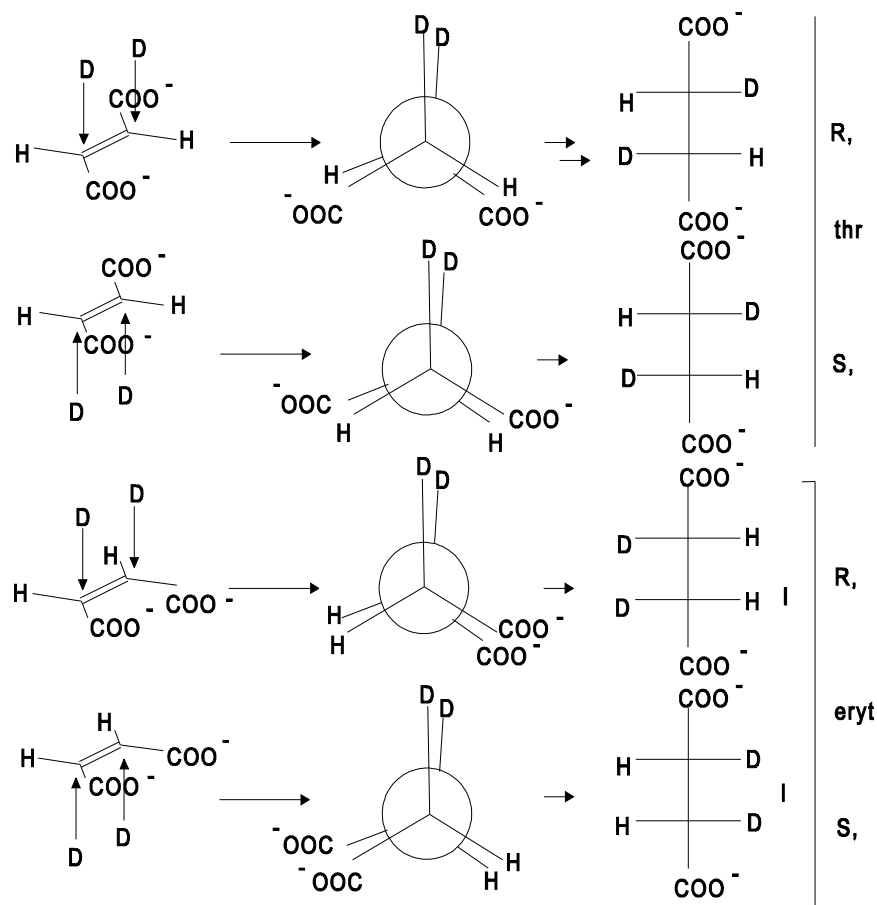
The major product is monotrinitated fumarate (79%) with 21 % untritiated fumarate.

6.7 Write down the Fischer projections of the two possible structures of the major product (*S*)-malate arising from the acetylcoenzyme A which has a labelled acetyl group with *R*-configuration.

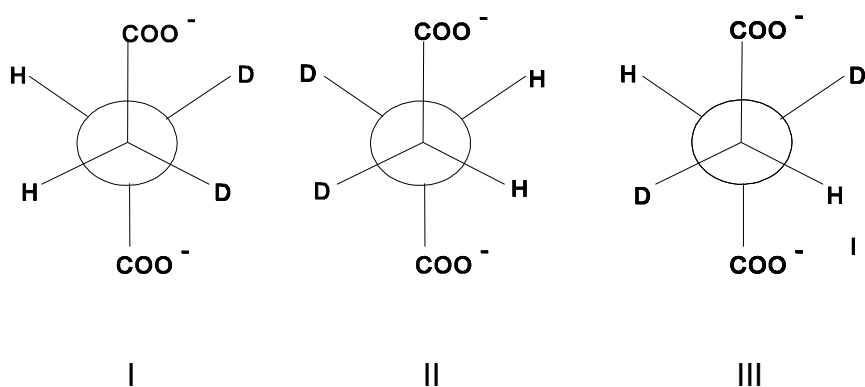
6.8 What would be the products if the starting material has a labelled acetyl group with *S*-configuration?

SOLUTION

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



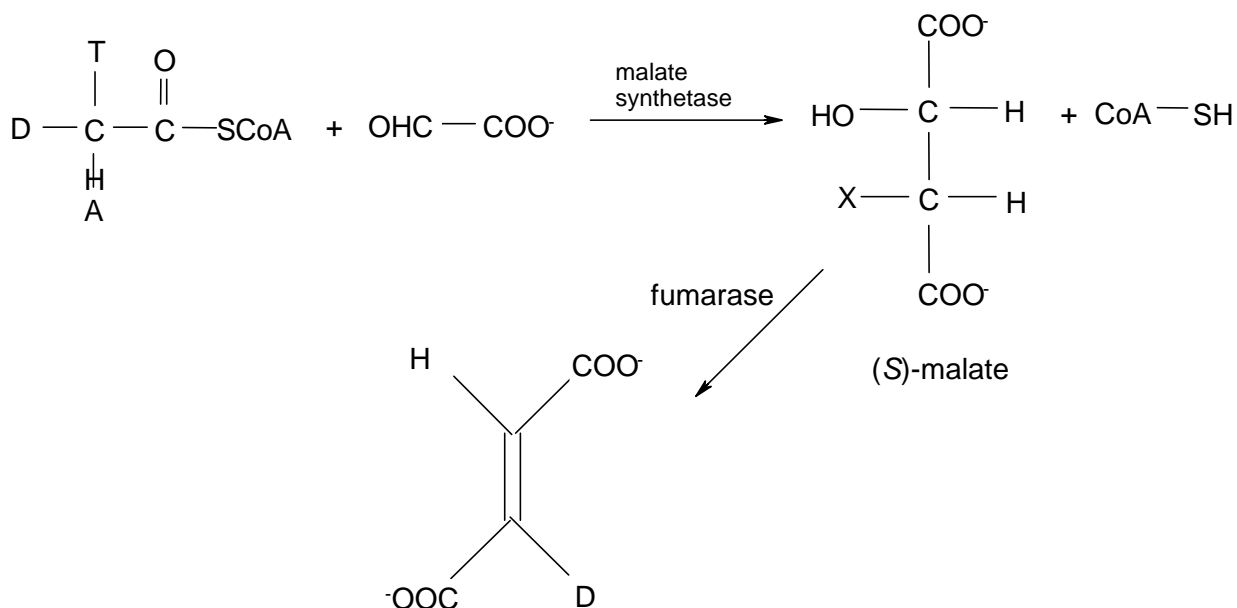
The most stable conformation for succinates is the anti form, since the distance between the bulky COO^- groups is maximal:



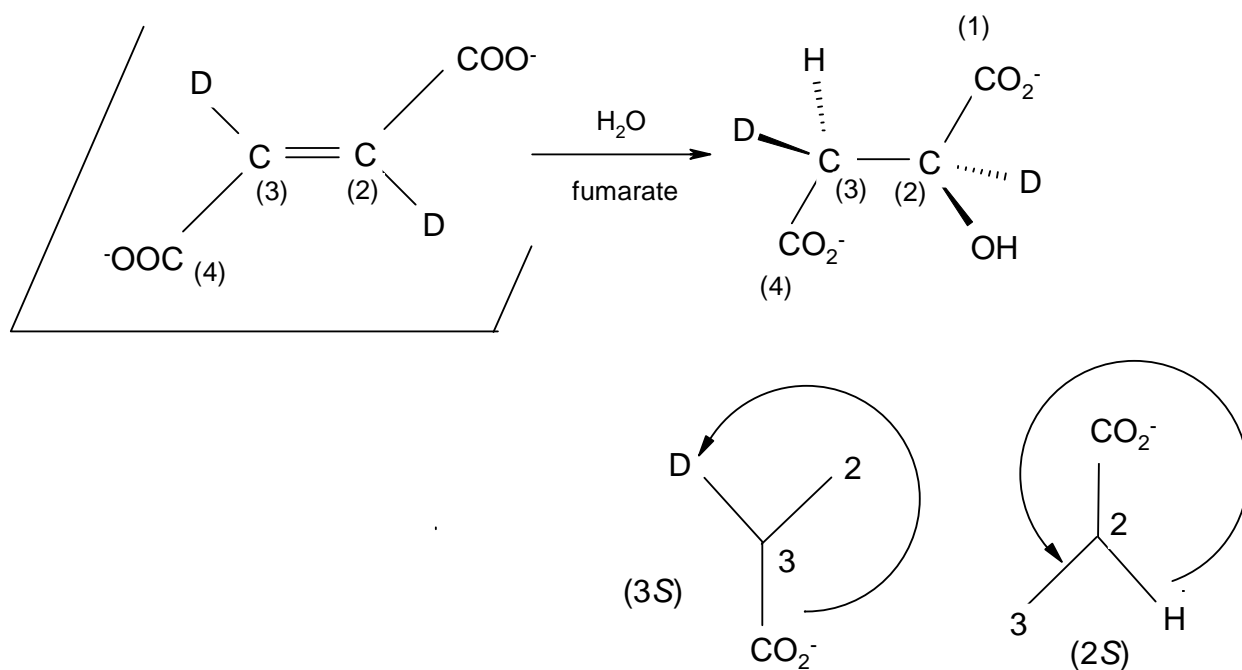
I and II are enantiomers, II and III are a meso isomer, thus there are in total three isomers (two enantiomers and one meso form). Each threo and the meso form are diastereomers.

6.2 Considering the Newman projections of the three isomers it is clear that *syn* elimination of I and II leads either to fumarate containing no D or to dideuterated fumarate (percentage of dideuterated fumarate is thus 50 %) whereas *anti* elimination leads to monodeuterated fumarate. Concerning the experiment 4 % of dideuterated fumarate indicates that *anti* elimination occurs. *Syn* - elimination of the meso-form only leads to monodeuterated fumarate, whereas *anti*-elimination gives 50 % normal and 50% dideuterated fumarate. This is in accordance with the experiment where 48.5% of dideuterated fumarate are obtained after enzymatic dehydrogenation of the meso isomer formed from maleic acid.

6.3 The enzymatic dehydrogenation is a anti elimination as shown above.

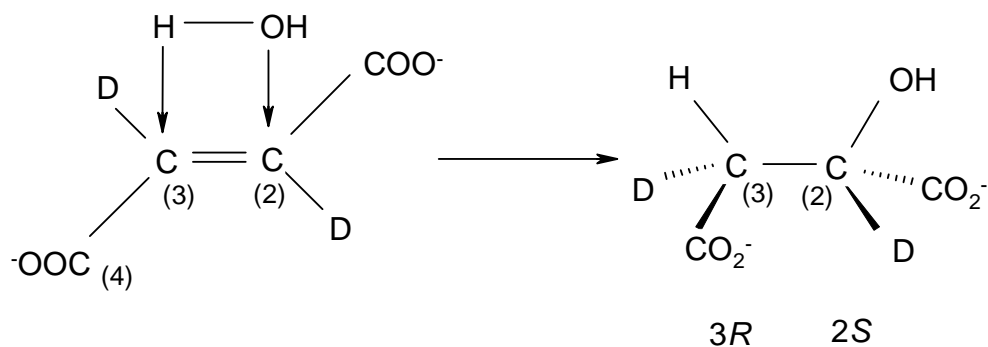


6.4



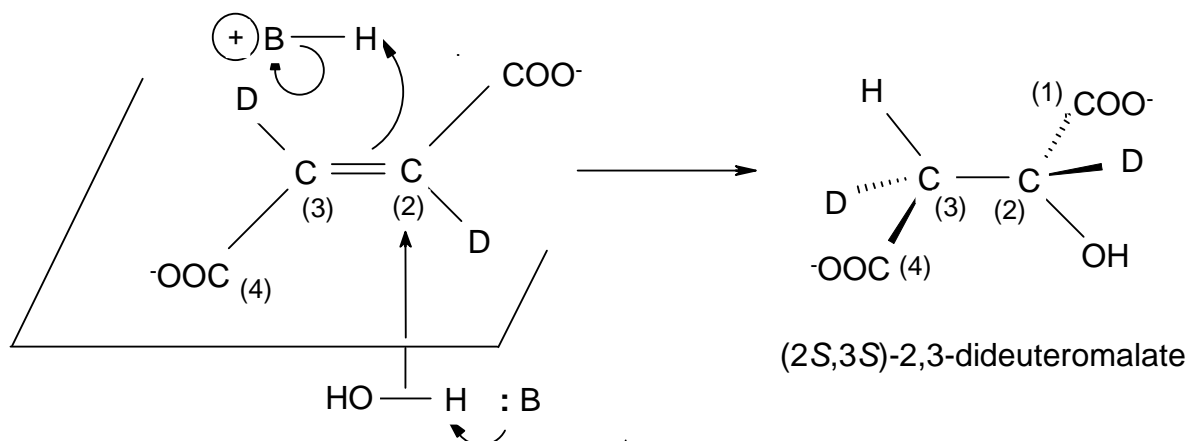
Stereospecific addition, *syn* or *anti*

Syn addition:

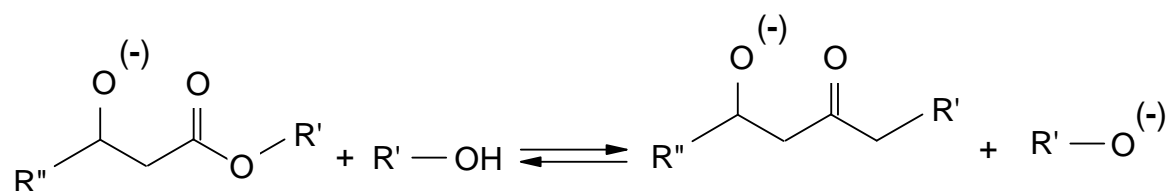
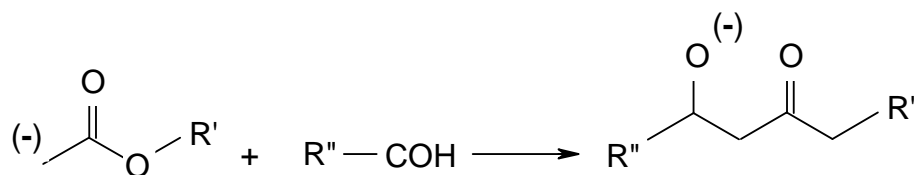
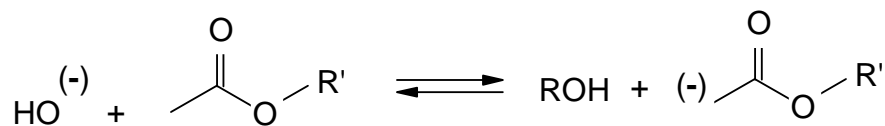


Syn addition would yield 2S, 3R or 2R, 3S

Anti addition:

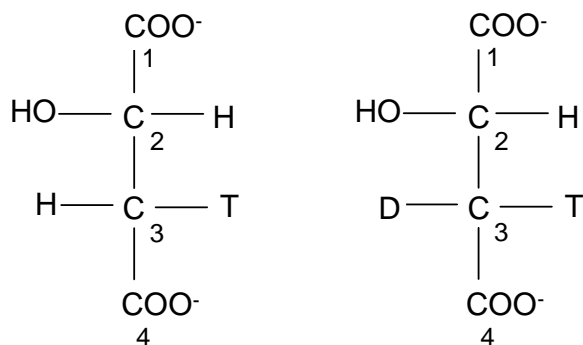


6.5

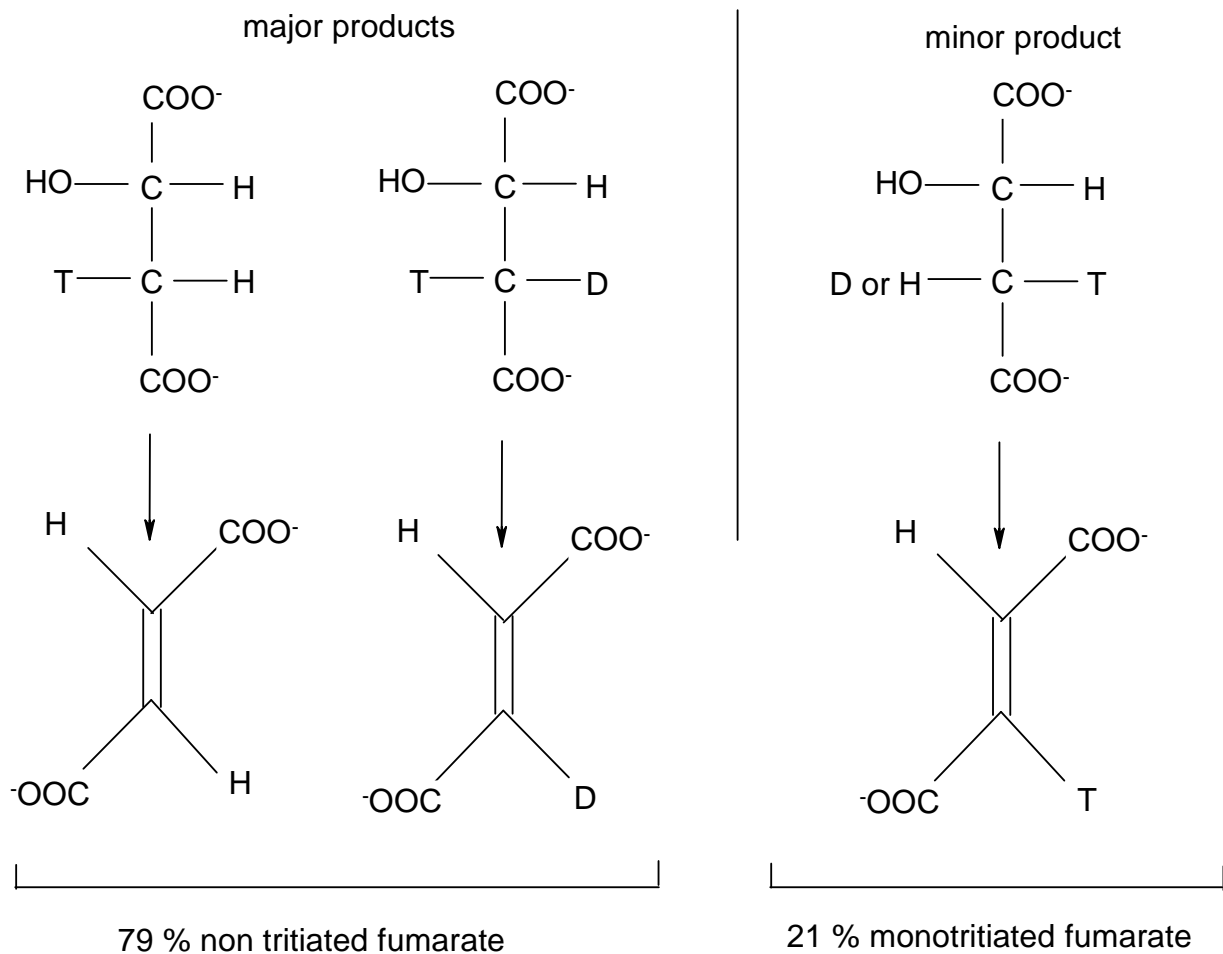


6.6 We would have (2*R*) (3*R*) if the enzyme did not produce enantiospecific addition.
Thus: enantiospecific addition *anti*.

6.7 Thus Y = T and X = H or D; then the two Fischer projections are:



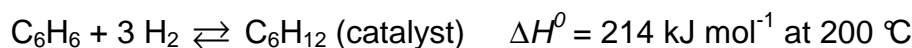
6.8 Starting from an acetyl group of *S* configuration one obtains a configuration inversion of carbon 3 for L-malate and two possible structures are:



PROBLEM 7

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

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



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

The continuous plug flow reactor (Fig. 1)

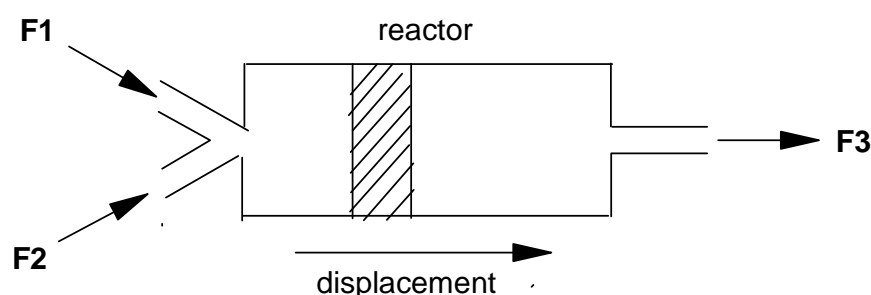


Fig. 1

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

The continuous stirred reactor (Fig. 2)

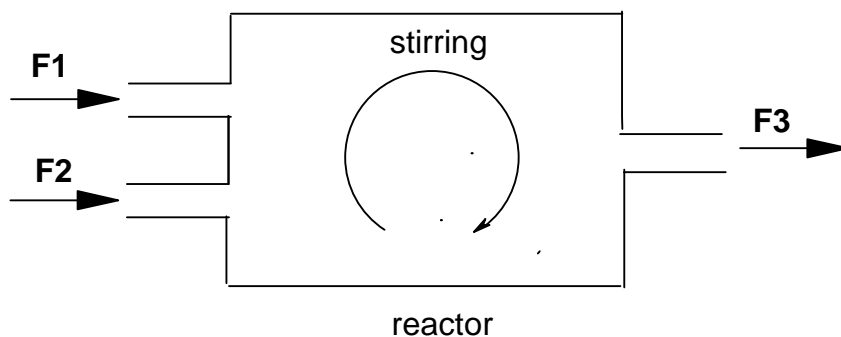


Fig. 2

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

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

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

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

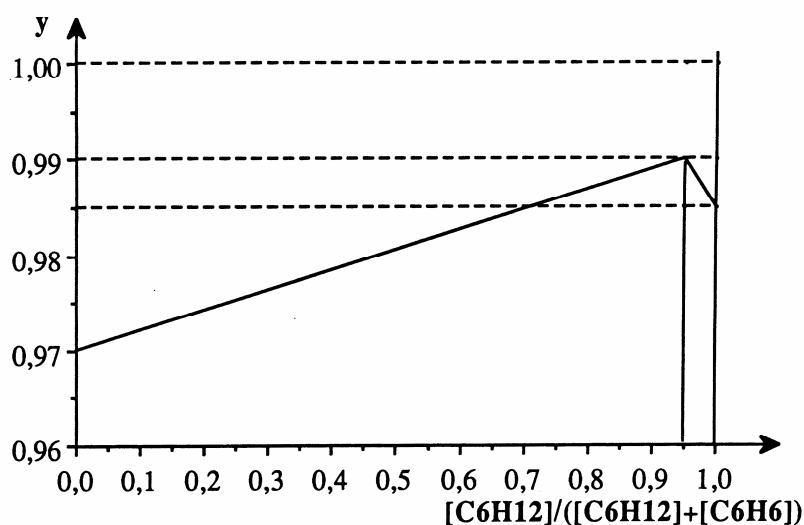


Fig. 3

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

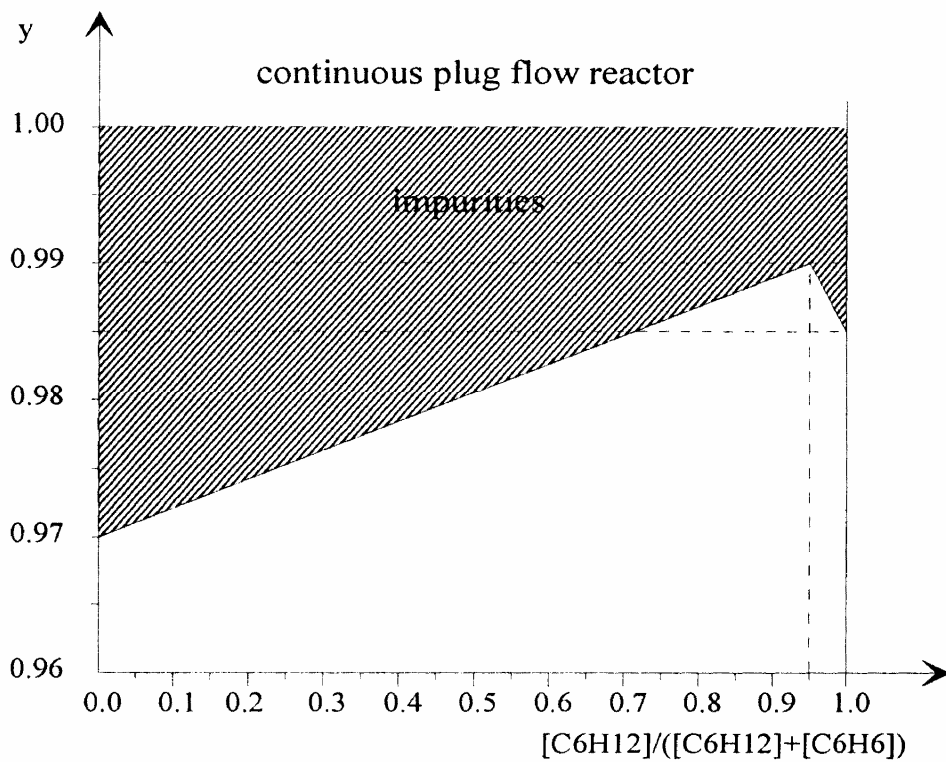
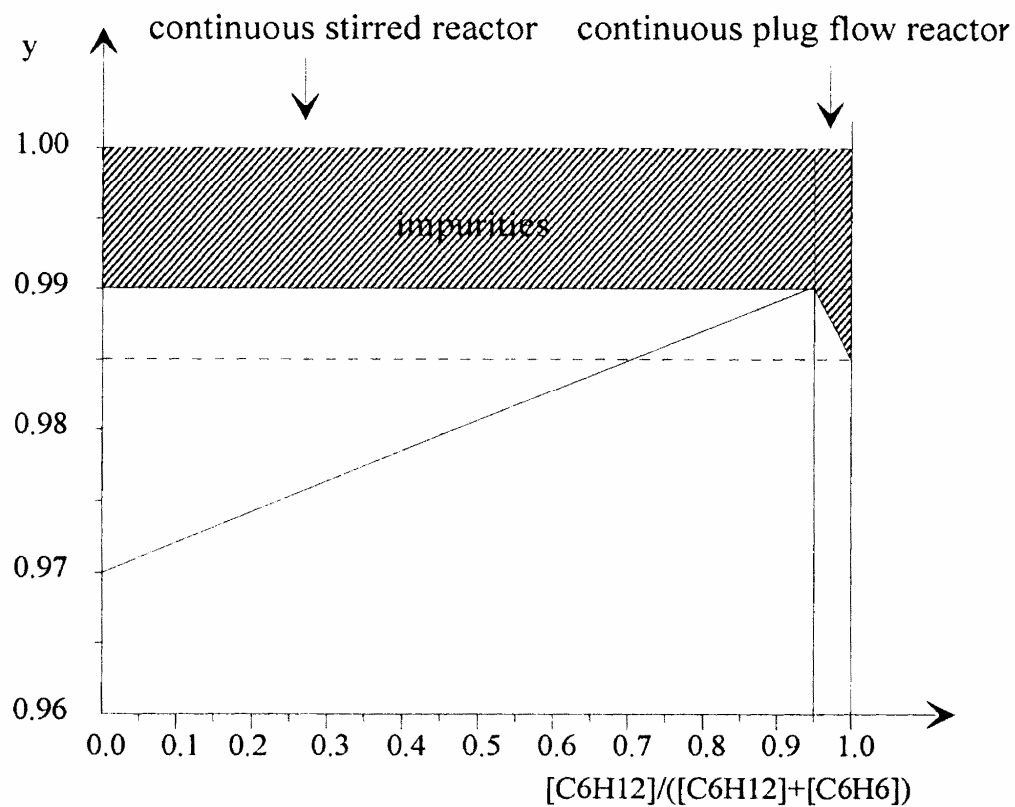
$$Y = -\frac{\Delta[C_6H_{12}]}{\Delta[C_6H_6]}$$

- 7.1** What is the value of p in a continuous stirred reactor leading to the maximal mean yield of hydrogenation? What is the maximal value of Y ?
- 7.2** For a continuous plug flow reactor, give a rough value of Y for $0.9 \leq p \leq 1$:
 $Y = 0.97, 0.98, 0.99$ or 1.00 ?
- 7.3** Represent by grey shading in the graph (Fig. 3) the quantities of benzene lost in installation P (plug flow reactor) and installation MP (stirred reactor + plug flow reactor).
- 7.4** Give the amount of annual benzene lost in installation P and MP assuming an annual consumption of 100 000 tons of benzene.

SOLUTION

- 7.1** In the continuous stirred reactor, concentrations are time independent and identical at every point. This means that the differential yield y for a given p is identical to the mean yield Y . A maximum mean yield is therefore obtained for y_{\max} . From the Fig. 1 it's seen that $y_{\max} = 0.99$ with $p = 0.95$.
- 7.2** In a continuous plug flow reactor concentrations are time-independent but dependent upon the location in the reactor. We shall consider a thin slice dx of the reactor at the entrance and at the end of the reactor. At the entrance $[C_6H_6] = 1$ and $[C_6H_{12}] = 0$, thus $p = 0$ and $y = 0.97$. At the outlet of the reactor we have: $[C_6H_6] = 0$ and $[C_6H_{12}] = 1$. So, $p = 1$ and $y = 0.985$. The mean yield is now the average of y over all p , which is 0.98, as one can easily see from the Fig. 1.
- 7.3** In the plug flow reactor, the quantity of benzene lost (not hydrogenated) is $1 - p$. Fig. 1 shows the area that represents the amount of benzene that is not hydrogenated and therefore lost. For the installation MP we first have the amount of benzene lost in the continuous stirred reactor which is always $1 - 0.99 = 0.01$ independent from p up to a point $p = 0.95$. At $p > 0.95$ to the continuous plug reactor has the same loss of benzene as already indicated in the Fig 1 below.
- 7.4** In the plug reactor the percentage of benzene lost is 2 % (the best mean yield is 0.98), therefore the amount of benzene annually lost is 2000 tons.
In a MP installation, the yield of hydrogenation is 0.99 (except for $0.95 < p < 1$ where it slightly decreases to 0.985, but this can be neglected) and therefore, the overall mean yield of hydrogenation is also 0.99.
The amount of benzene annually lost is therefore 1000 tons.

Figure 1

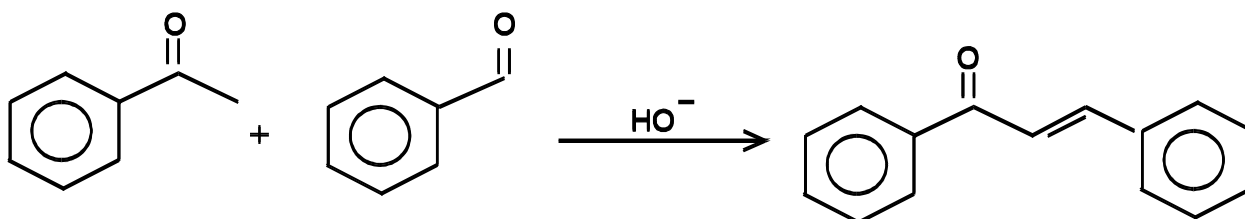


PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis involving Carbanions Chalcone

The aim of this experiment is to condense acetophenone and benzaldehyde in a mixed aldol condensation. After spontaneous dehydration, an α,β - unsaturated ketone is obtained: the chalcone, 1,3-diphenylprop-2-en-1-on.



a) *Starting the condensation reaction*

In a 250 cm³ ground neck Erlenmeyer (conical) flask, dissolve about 5 g of potassium hydroxide, KOH, (50 pellets) in 30 cm³ of water, then add slowly under stirring 20 cm³ of ethanol. From the automatic dispensers, add 9.6 g (0.08 mol = 9.5 cm³) of acetophenone and 8.5 g (0.08 mol = 8.5 cm³) of benzaldehyde. Set up a condenser in the vertical reflux position and reflux vigorously while stirring the mixture with the magnetic stirrer for an hour.

b) *Isolation of the crude chalcone*

After refluxing, cool the contents of the Erlenmeyer flask in an ice bath. The chalcone should crystallize. If crystals do not appear, scratch the inside wall of the flask with a glass rod. Collect the crystals in a Büchner funnel, wash them with a little ice cold ethanol, then air dry and weigh the crystals.

c) *Recrystallization of the chalcone*

Recrystallize this crude chalcone from ethanol, using a 100 cm³ beaker. Use the heating plate located in the hood (fume chamber). When the crystallization is over (wait long enough and scratch if necessary), collect the crystals in a Büchner funnel, and air dry them.

Give your entire product to the supervisor who will measure its mass and melting-point.

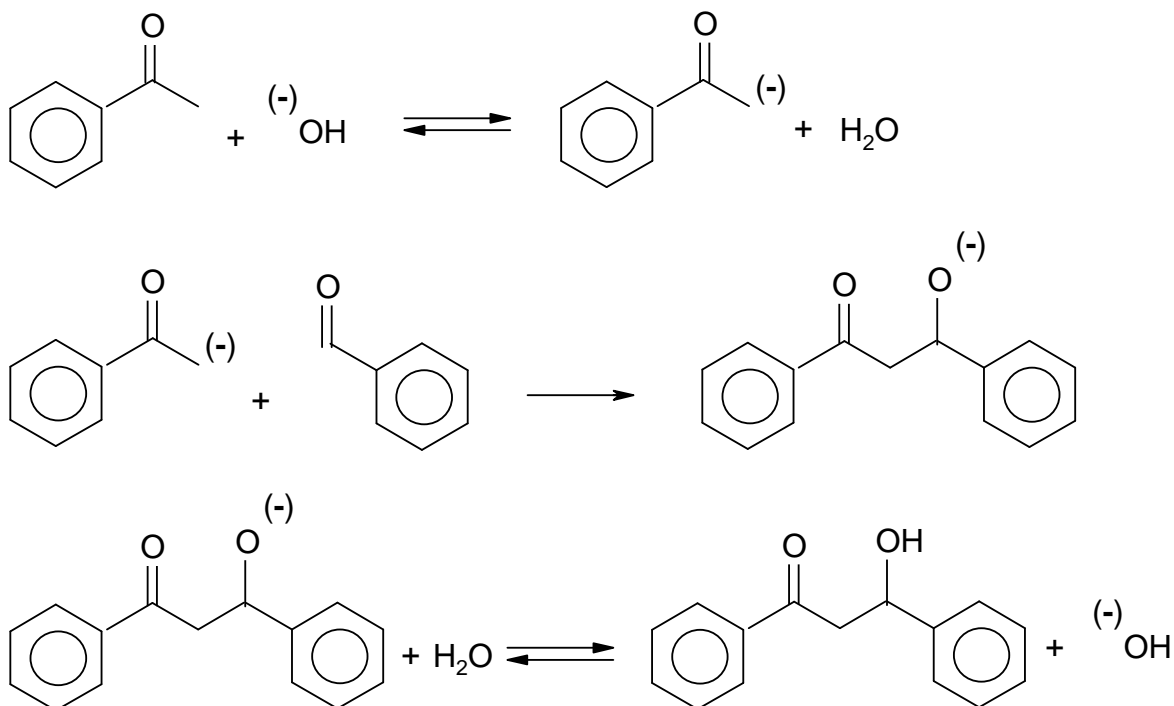
Do not breathe the vapour while recrystallizing and measuring the melting point. It contains irritating chalcone!!!

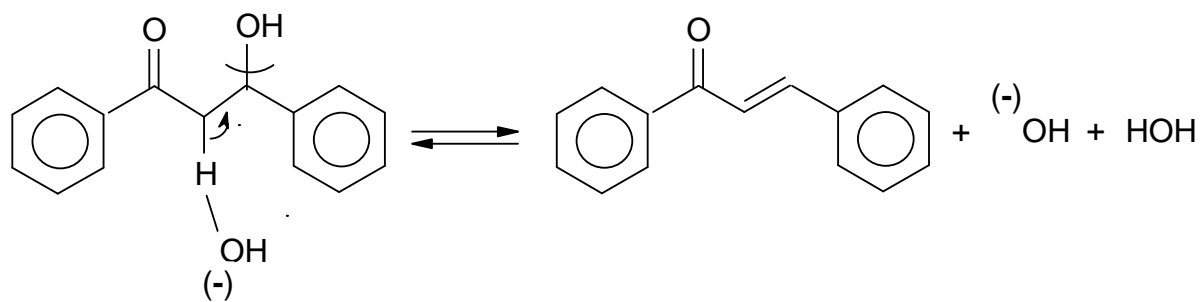
Questions:

- 1.1 Write the mechanism for this reaction.
- 1.2 Give the mass of the crystals of the crude chalcon obtained and calculate the yield of crude product.
- 1.3 Calculate the yield of recrystallized product based on starting material and calculate the efficiency of the recrystallization process.

SOLUTION

1.1





PROBLEM 2 (Practical)Qualitative Analysis

Equipment:

Five flasks are labelled 2.1 through 2.5. Each contains an aqueous solution of a colourless metal nitrate. Except for silver nitrate, the concentrations of the nitrates used to prepare these solutions, are all 0.1 mol dm^{-3} .

The solutions are: aluminium(III) nitrate
calcium(II) nitrate
lead(II) nitrate
silver(I) nitrate
zinc(II) nitrate

Moreover, available are pH indicator paper and the following three reagents of a concentration of about 5 mol dm^{-3} , contained in flasks labelled 2.6 through 2.8.

2.6 : hydrochloric acid,

2.7 : aqueous ammonia solution,

2.8 : sodium hydroxide solution.

Beware: these solutions are all concentrated and corrosive.

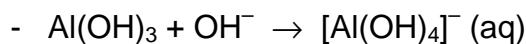
Tasks:

- 2.1 Carry out reactions between each reagent and each solution. For each of the solutions 2.1 through 2.5, record your observations for each reaction observed.
- 2.2 Write the name of the cation contained in each of the solutions 2.1 through 2.5 in the corresponding space on the answer sheet.
- 2.3 For each cation identified, write the equation for each reaction observed.

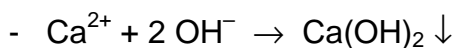
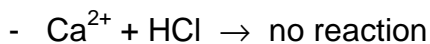
SOLUTION

2.1 Aluminium(III) nitrate

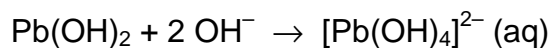
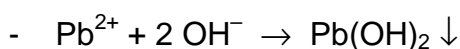
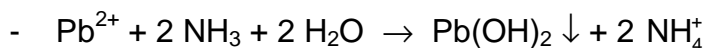
- $\text{Al}^{3+} + \text{HCl} \rightarrow \text{no reaction}$
- $\text{Al}^{3+} + 3 \text{NH}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 \downarrow + 3 \text{NH}_4^+$
- $\text{Al}^{3+} + 3 \text{OH}^- \rightarrow \text{Al}(\text{OH})_3 \downarrow$



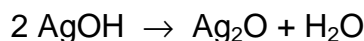
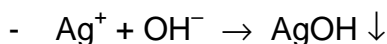
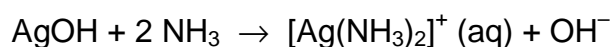
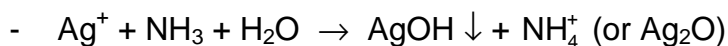
calcium(II) nitrate



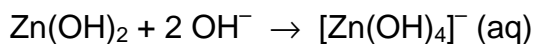
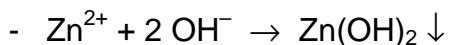
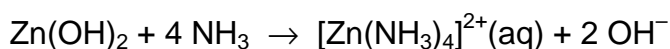
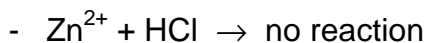
lead(II) nitrate



silver(I) nitrate



zinc(II) nitrate



PROBLEM 3 (Practical)Titration of Oxygen Dissolved in Water

(Winkler's method)

In aqueous alkaline solution, dissolved oxygen oxidizes manganese(II) hydroxide to hydrated manganese(III) oxide (written as $\text{Mn}(\text{OH})_3$ for simplification). In acidic solution, manganese(III) ions oxidize iodide ions to iodine. The iodine formed is titrated with a sodium thiosulphate solution.

Data:

Redox couple	Electrode potentials (in V)	
	at $pH = 0$	at $pH = 14$
$\text{Mn}^{3+} / \text{Mn}^{2+}$	1.51	
$\text{Mn}(\text{OH})_3 / \text{Mn}(\text{OH})_2$		0.13
$\text{O}_2 / \text{H}_2\text{O}$	1.23	0.39
I_2 / I^-	0.62	0.62
$\text{S}_4\text{O}_6^{2-} / \text{S}_2\text{O}_3^{2-}$	0.09	0.09

Solubility products: $K_{sp}(\text{Mn}(\text{OH})_2) = 1 \times 10^{-13}$ $K_{sp}(\text{Mn}(\text{OH})_3) = 1 \times 10^{-36}$ Gas constant: $R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$ *Procedure:*

Preliminary remarks: To reduce volume variations, the reagents are added either as solids (sodium hydroxide pellets ...), or as concentrated solutions (sulphuric acid).

- The water to be tested is stored in a large container located on the general-use bench. Place two glass beads into a 250 cm^3 ground top Erlenmeyer (conical) flask. Fill it to the rim with the water to be tested. At this stage of the manipulation the

Erlenmeyer flask should be standing in the basin provided to avoid overflow of water onto the bench. Measure the temperature of the water.

2. Add to the water, avoiding any loss of reagent:
 - a) 2 g of manganese(II) chloride, preweighed within a decigram and contained in the bag.
 - b) about 8 pellets of sodium hydroxide (yielding a basic medium, $pH = 14$). The pellets will be found on the general-use bench.
3. Stopper the Erlenmeyer flask, avoiding air bubbles, and swirl it until complete dissolution of the sodium hydroxide and of the manganese chloride has occurred. A brown precipitate forms.
4. Let the flask stand for at least 30 minutes.
5. Open the Erlenmeyer flask, add concentrated sulphuric acid dropwise, stirring with a glass rod until the solution is definitely acidic (check with the pH indicator paper); make sure that nearly all the precipitate has disappeared.
Sulphuric acid will be found on the general-use bench.
6. Add to the Erlenmeyer flask 3 g of potassium iodide, preweighed within a decigram and contained in a bag. Stopper the flask and shake it until the potassium iodide has dissolved. The solution should now be clear.
7. Remove a 50 cm^3 sample of the solution and titrate it with a $X\text{ mol dm}^{-3}$ sodium thiosulphate solution (the numerical value of X will be shown on the board). For this titration, the endpoint can be determined using the indicator thiodene which is equivalent to starch. A small quantity of this solid indicator should be dissolved in the solution being titrated just prior to the endpoint.

Questions:

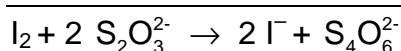
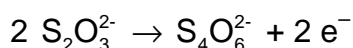
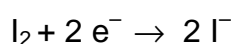
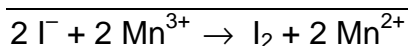
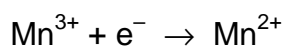
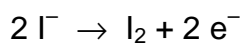
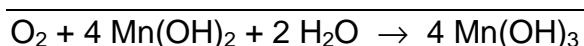
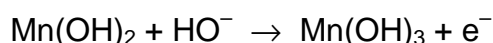
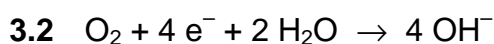
- 3.1 Justify that the oxidation of manganese(II) by dissolved oxygen is possible only in alkaline solution.
- 3.2 Write the equation of the reaction between:
 - dissolved oxygen and manganese(II) hydroxide (in alkaline solution),
 - manganese(III) ions and iodide ions,
 - iodine and thiosulphate.
- 3.3 Record the volume of thiosulphate required to reach the endpoint.

- 3.4 Derive an expression that relates the dissolved oxygen concentration in water (expressed as mol dm⁻³) to the volume in cm³ of thiosulphate added at the endpoint. Determine that concentration for the water tested.

Deduce the volume of oxygen (in cm³), determined at 0 °C and at a pressure of 101,325 Pa, contained in a litre of water (measured at ambient temperature). Give the temperature of the water.

SOLUTION

3.1 $E^0(\text{O}_2/\text{H}_2\text{O}) > E^0(\text{Mn(III)/Mn(II)})$ at $\text{pH} = 14$



3.4 $1 \text{ mol O}_2 \hat{=} 4 \text{ mol Mn(II)} \hat{=} 4 \text{ mol Mn(III)}$

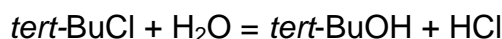
$$4 \text{ mol Mn(III)} \hat{=} 4 \text{ mol I}^- \hat{=} 2 \text{ mol I}_2$$

$$2 \text{ mol I}_2 \hat{=} 4 \text{ mol S}_2\text{O}_3^{2-}$$

$$c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-}) = 4 \times c(\text{O}_2) \times 50$$

PROBLEM 4 (Practical)Kinetics of an S_N1 Reaction

In an aqueous ethanolic solution, *tert*-butyl chloride (2-chloro-2-methylpropane) undergoes an S_N1 nucleophilic substitution reaction leading to the formation of 2-methylpropan-2-ol and hydrochloric acid:



The rate of the reaction is given by

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

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

Procedure:

- Using a pipette transfer 2.0 cm³ of *tert*-butyl chloride (flask 4.1 on the general-use bench) into a clean and dry 250 cm³ ground neck Erlenmeyer (conical) flask.
- As soon as possible add 148 cm³ (measure with the graduated cylinder) of the aqueous ethanol solution standing on the general-use bench (flask 4.2).
- Stopper the Erlenmeyer flask and stir vigorously using the magnetic stirrer. Start your timer. Note carefully the temperature, T(0), of the solution.
- After approximately 5, 15, 25, 35, 45, 55 min (determined accurately), transfer 10.0 cm³ samples using a pipette into 20 cm³ of a mixture of ice and acetone (propanone).

Add 2 drops of bromothymol blue and titrate the liberated acid with a solution of Y mol dm⁻³ aqueous sodium hydroxide (Y will be shown on the board).

Questions:

- 4.1** The concentrations of *tert*-BuCl at time $t = 0$ and at time t are linked by the following relationship:

$$\ln \frac{[\textit{tert}\text{BuCl}]_0}{[\textit{tert}\text{BuCl}]_t} = k_1 \cdot t$$

Establish the theoretical expression:

$$\ln \frac{V_\infty}{V_\infty - V} = k_1 t$$

where V stands for the volume of sodium hydroxide used at time t and $V(8)$ for the corresponding value at $t(8)$.

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

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

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

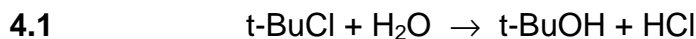
$$t(\text{min}), \quad V(\text{cm}^3), \quad V_{\infty}, \quad V, \quad \frac{V_{\infty}}{V_{\infty} - V}, \quad \ln \frac{V_{\infty}}{V_{\infty} - V}$$

Draw the curve

$$\ln \frac{V_{\infty}}{V_{\infty} - V} = f(t)$$

4.4 Determine the value of k_1 (give the value of $t(0)$).

SOLUTION



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

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

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

t :

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

$t(8)$:

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

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

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

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

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

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

23rd



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

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

THEORETICAL PROBLEMS

PROBLEM 1

- 1.1 Show that 0.1 mol of Ti_2S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.
- 1.2 Show that 0.1 CuS dissolves in a 1 M HNO_3 but not in a 1 M HCl solution.

Information:

Assume that Cu^{2+} ions do not form stable complexes with chloride ions in aqueous solutions.

$$E^0(\text{S}/\text{S}^{2-}) = -0.48 \text{ V} \quad E^0(\text{NO}_3^-/\text{NO}_{(\text{aq})}) = 0.96 \text{ V}$$

$$pK_a(\text{H}_2\text{S}) = 7 \quad pK_a(\text{HS}^-) = 13$$

$$K_{sp}(\text{Ti}_2\text{S}) = 1 \times 10^{-20} \quad K_{sp}(\text{CuS}) = 1 \times 10^{-35}$$

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

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

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

SOLUTION

- 1.1 Solubility condition: $[\text{Ti}^+]^2 [\text{S}^{2-}] \leq 1 \times 10^{-20}$

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

$$c(\text{S}^{2-}) = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}] = [\text{S}^{2-}] \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right) = 0.1 \text{ mol dm}^{-3}$$

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

For a strong monoprotic acid (1 mol dm⁻³) and [H⁺] ≈ 1.

Then

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

$$[\text{Ti}^+]^2 [\text{S}^{2-}] = \frac{(0.2)^2 \times 0.1}{1 \times 10^{20}} = 4 \times 10^{-23} < K_s(\text{Ti}_2\text{S})$$

Thus, 0.1 mol of Ti₂S dissolves in a 1 M solution of any strong monoprotic non-coordinating acid.

1.2

- Dissolving CuS in 1 M solution HCl (non-oxidizing and non-complexing acid):

$$c(\text{Cu}^{2+}) = 0.1 \text{ mol dm}^{-3}$$

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

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

Similarly as in part (1.1):

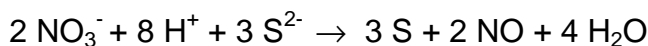
$$[\text{S}^{2-}] = \frac{0.1}{1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2}}$$

$$[\text{S}^{2-}] \approx \frac{0.1}{1 \times 10^{20}}$$

$$[\text{Cu}^{2+}] [\text{S}^{2-}] = \frac{(0.1)^2 \times 0.1}{1 \times 10^{20}} \approx 1 \times 10^{-23} > K_s(\text{CuS})$$

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

- When dissolving 0.1 mol CuS in 1 M HNO₃ an additional redox process occurs: the oxidation of S²⁻ to S.



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

$$\log K = \frac{\Delta G}{RT} = \frac{nF}{RT} \Delta E = \frac{n_1 n_2 (E_1^0 - E_2^0)}{0.0591} \cong 144 \quad K = 1 \times 10^{144}$$

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

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

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

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

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

$c_{\text{CuS}} = [\text{S}] + [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$

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

However

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

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

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

Conclusion: CuS dissolves in 1 M solution of HNO₃.

PROBLEM 2

A polymer **X** contains 88.25 % C and 11.75 % H. In dilute solutions it reacts with bromine and ozone. The thermal degradation of **X** produces a volatile liquid **Y** in 58 % yield. **Y** starts boiling at 34 °C and contains 88.25 % C and 11.72 % H. Some higher boiling products are formed both from the cracking of **X** and from Diels-Alder type cyclization of **Y**. The vapour of **Y** was 34 times as dense as hydrogen.

The product of bromination of **Y** yields a compound containing 82.5 % bromine by mass. Ozonolysis of **Y** followed by mild reduction gave **A** and **B** in a molar ratio **A** : **B** = 2 : 1. Only compound **B** gave a positive result for the iodoform reaction.

2.1 Determine the molecular formula and the molar mass of **Y**.

2.2 Show the structures of compounds **Y**, **A**, and **B**.

2.3 Give an equation for the reaction of **Y** with bromine.

In the catalytic hydrogenation of 13.6 g of **X**, 0.2 mole of hydrogen was absorbed. Ozonolysis of **X** followed by mild reduction yielded compound **Z** (60.0 % C, 8.0 % H).

2.4 Give the molecular formula of **Z** and the degree of unsaturation of **X**.

Compound **Z** gave a positive reaction with Fehling's solution. Mild oxidation of **Z** gave an acid **C**. A solution of acid **C** was titrated with aqueous KOH solution (phenolphthalein as indicator). 0.001 mol KOH was necessary for neutralization of 0.116 g of **C**.

In the iodoform reaction a probe 2.90 g of **C** yielded 9.85 g of iodoform. In addition, the alkaline filtrate yielded compound **D** upon acidification.

2.5 What is the molar mass of **C** and what functional groups are present in **Z**?

When heated, **D** loses water to form **E**. Both **D** and **E** react with an excess of acidified ethanol to **F** (C₈H₁₄O₄).

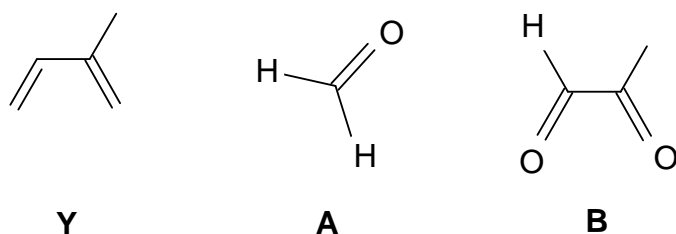
2.6 Sketch the structures of **C**, **D**, **E**, **F** and **Z**.

2.7 **X** exists in isomeric forms which are stereoregular. Show the structure (containing at least 3 monomer units) for two possible stereoisomers of **X**.

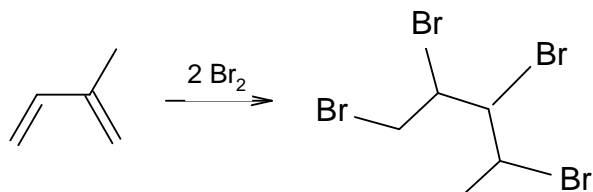
SOLUTION

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

2.2



2.3

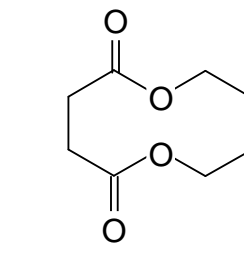
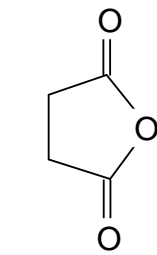
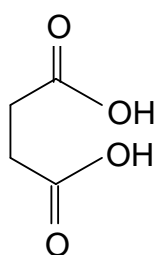
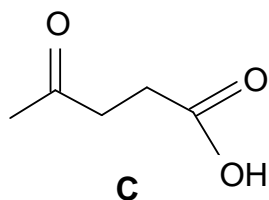


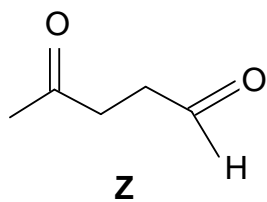
2.4 $Z = C_5H_8O_2$

There is one double bond per monomer unit.

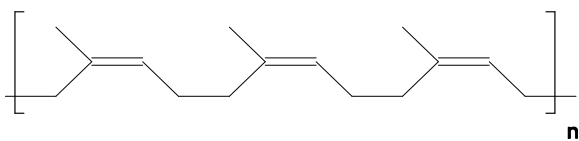
2.5 The molar mass of **C** is 116 g mol^{-1} . **Z** must be a keto aldehyde since it contains an aldehyde functional group and a methyl group next to the carbonyl group.

2.6

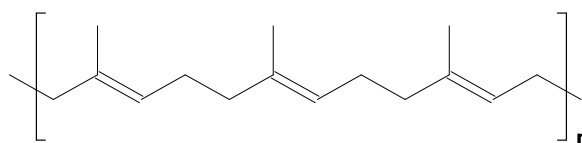




2.7 There are two isomeric form (all cis or all trans) possible:



all-cis (natural caoutchouc)



all-trans

PROBLEM 3

Type II electrodes that are made of a metal covered with a sparingly soluble salt of the metal are dipped into a soluble salt solution containing an anion of the sparingly soluble salt. The silver/silver chloride (Ag, AgCl/Cl⁻) and the calomel electrode (Hg, Hg₂Cl₂/Cl⁻) are examples of such electrodes. The standard emf of a cell built of those electrodes (-) Ag,AgCl/Cl⁻ || Hg₂Cl₂/Hg (+) is $E^0 = 0.0455 \text{ V}$ at $T = 298 \text{ K}$. The temperature coefficient for this cell is $dE^0/dT = 3.38 \times 10^{-4} \text{ V K}^{-1}$.

3.1 Give the equations of the reactions taking place at both the cell electrodes and the overall cell reaction.

3.2 Calculate the Gibbs free energy change (ΔG^0) for the process taking place in the cell at 298 K. What does its sign imply?

3.3 Calculate the enthalpy change for the process taking place at 298 K.

$$\Delta S = n F \Delta E / \Delta T.$$

3.4 Knowing the standard potential of Ag/Ag⁺ electrode is $E^0 = 0.799 \text{ V}$ and the solubility product of AgCl $K_{sp} = 1.73 \times 10^{-10}$, calculate the standard electrode potential value of the silver/silver chloride electrode. Derive an expression showing the dependence between $E^0(\text{Ag}/\text{Ag}^+)$ and $E^0(\text{Ag}, \text{AgCl}/\text{Cl}^-)$.

3.5 Calculate the solubility product of Hg₂Cl₂ knowing that the standard potential of the calomel electrode is $E^0 = 0.798 \text{ V}$.

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

SOLUTION

3.1 Reduction (calomel electrode (+)): $1/2 \text{ Hg}_2\text{Cl}_2 + e^- \rightarrow \text{Hg} + \text{Cl}^-$
 Oxidation (silver/silver chloride electrode (-)): $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + e^-$
 Summary reaction: $\text{Ag} + 1/2 \text{ Hg}_2\text{Cl}_2 \rightarrow \text{Hg} + \text{AgCl}$

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

Since ΔG^0 is negative, the reaction is spontaneous.

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

$$\begin{aligned}\Delta H &= \Delta G + T\Delta S = -nFE + TnF\left(\frac{\Delta E^0}{\Delta t}\right) = -nF\left(E - T\left(\frac{\Delta E^0}{\Delta t}\right)\right) = \\ &= -96487 \text{ C mol}^{-1} (0.0455 \text{ V} - 298 \text{ K} \times 3.38 \times 10^{-4} \text{ V K}^{-1}) = 5.36 \text{ kJ mol}^{-1}\end{aligned}$$

3.4 For the Ag | Ag⁺ electrode: $E = E^0 + 0.0591 \log[\text{Ag}^+]$

For the Ag, AgCl | Cl⁻ electrode [Ag⁺] is determined by the solubility product:

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

$$E^0(\text{Ag, AgCl} | \text{Cl}^-) = E^0(\text{Ag} | \text{Ag}^+) + 0.0591 \log K_{sp} = 0.799 - 0.577 = 0.222 \text{ V}$$

3.5 $E^0(\text{Hg, Hg}_2\text{Cl}_2 | \text{Cl}^-) = E^0(\text{Hg} | \text{Hg}^{2+}) + \frac{0.0591}{2} \log K_{sp}(\text{Hg}_2\text{Cl}_2)$

The standard potential of the calomel electrode is equal to $0.0455 + 0.222 = 0.2675 \text{ V}$.

Thus, $\log K_{sp}(\text{Hg}_2\text{Cl}_2)$ can be calculated as:

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

$$K_{sp} = 1.03 \times 10^{-18}$$

PROBLEM 4

The energy of stable states of the hydrogen atom is given by: $E_n = -2.18 \times 10^{-18} / n^2$ [J] where n denotes the principal quantum number.

4.1 Calculate the energy differences between $n = 2$ (first excited state) and $n = 1$ (ground state) and between $n = 7$ and $n = 1$.

4.2 In what spectral range is the Lyman series lying?

4.3 Can a single photon, emitted in the first and/or sixth line of the Lyman series, ionize:

- another hydrogen atom in its ground state?
- a copper atom in the Cu crystal?

The electron work function of Cu is $\Phi_{\text{Cu}} = 7.44 \times 10^{-19}$ J.

4.4 Calculate the de Broglie wavelength of the electrons emitted from a copper crystal when irradiated by photons from the first line and the sixth line of the Lyman series.

$$h = 6.6256 \times 10^{-34} \text{ J s}; \quad m_e = 9.1091 \times 10^{-31} \text{ kg}; \quad c = 2.99792 \times 10^8 \text{ m s}^{-1}$$

SOLUTION

4.1 $\Delta E_{n \rightarrow 1} = E_n - E_1 = 2.18 \times 10^{-18} (1 - n^2)$

$$\Delta E_{2 \rightarrow 1} = 1.635 \times 10^{-18} \text{ J}$$

$$\Delta E_{7 \rightarrow 1} = 2.135 \times 10^{-18} \text{ J}$$

4.2 The Lyman series is due to $\Delta E_{n \rightarrow 1}$ varying from 1.635×10^{-18} J ($n = 1$) to 2.135×10^{-18} J ($n \rightarrow \infty$), which corresponds to 121.5 nm and to 93.0 nm, respectively. This is in the UV-region.

4.3 a) The ionisation energy is equal to $\Delta E_{\infty \rightarrow 1} = 2.18 \times 10^{-18}$ J. Both $\Delta E_{2 \rightarrow 1}$ and $\Delta E_{7 \rightarrow 1}$ are smaller than $\Delta E_{\infty \rightarrow 1}$ and a single photon emitted from these transitions is not able to ionize a hydrogen atom.

b) Ionization of copper in a Cu-crystal is related to the photoelectric effect:

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

Because $\Delta E_{2 \rightarrow 1} > \Phi_{\text{Cu}}$ and $\Delta E_{7 \rightarrow 1} > \Phi_{\text{Cu}}$ both photons are indeed able to ionize a Cu-atom in the crystal.

The kinetic energy of the emitted electrons is:

$$\Delta E_{\text{kin}}(2 \rightarrow 1) = \Delta E_{2 \rightarrow 1} - \Phi_{\text{Cu}} = 8.91 \times 10^{-19} \text{ J}$$

$$\Delta E_{\text{kin}}(7 \rightarrow 1) = \Delta E_{7 \rightarrow 1} - \Phi_{\text{Cu}} = 13.91 \times 10^{-19} \text{ J}$$

4.4 The wavelength of an electron is:

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

$$(p = m_e v_e \text{ and } E_{\text{kin}} = \frac{p^2}{2 m_e})$$

$$\Delta E_{2 \rightarrow 1}: \quad \lambda_1 = 4.16 \times 10^{-10} \text{ m} = 4.16 \text{ \AA}$$

$$\Delta E_{7 \rightarrow 1}: \quad \lambda_2 = 5.20 \times 10^{-10} \text{ m} = 5.20 \text{ \AA}$$

PROBLEM 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 dm³ of hydrogen, (295 K, 102 kPa) were obtained.

B and hydrogen are the only products. A mixture of halogen derivatives **C**, **D**, **E**, **F** and **G** is produced from **B** by reaction with a halogen in presence of a Lewis acid. Compounds **C** to **G** contain each one halogen atom more than 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:
 - $^{19}\text{F} = 100\%$;
 - $^{35}\text{Cl} = 75.53\%$; $^{37}\text{Cl} = 24.47\%$;
 - $^{79}\text{Br} = 50.54\%$; $^{81}\text{Br} = 49.46\%$;
 - $^{127}\text{I} = 100\%$.

5.1 Give the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G**₁, **G**₂ and **G**₃.

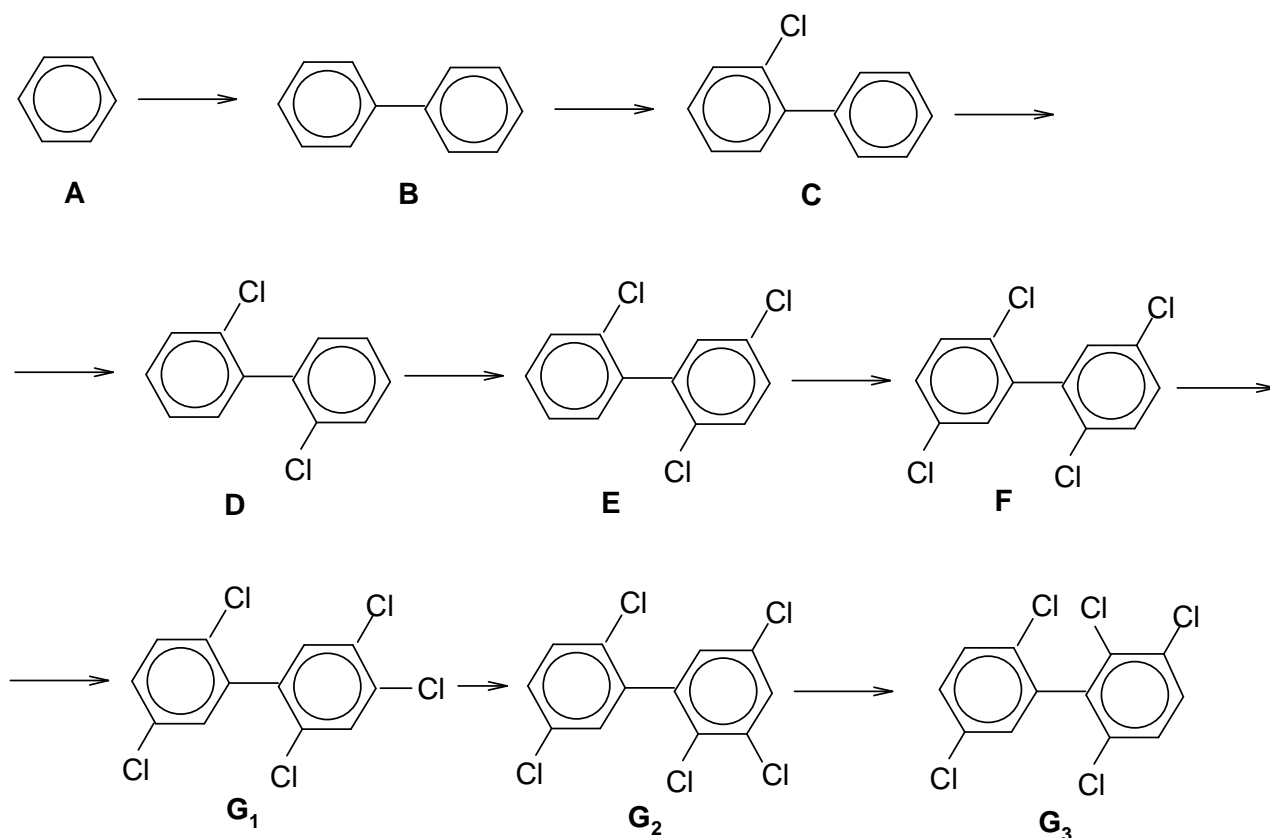
5.2 Explain your choice for the halogen.

5.3 Draw and label stereo-formulas of the rotational isomers of **D** for $\Phi = 0, \pi/2, \pi,$ and $3\pi/2$, where Φ denotes the dihedral or torsional angle in radians and $\vartheta = 0$ describes the configuration with maximal energy.

- 5.4 Draw profiles of the energy changes as a function of the angle of rotation around the C-C bond for compounds **C** and **D**.
- 5.5 Give a sequence of **G**₁, **G**₂, **G**₃ according to their increasing difficulty of racemization. Explain your answer.
- 5.6 Draw stereo-formulas of the enantiomers of **G**₃.
- 5.7 Suggest a chemical reaction or a biological method by which compounds like these can be destroyed.

SOLUTION

5.1



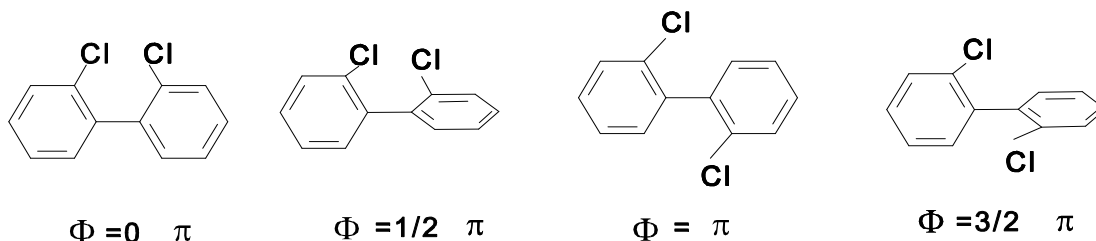
5.2 For the determination of the halogen of **E** we consider the ratio of the isotopic peaks in the mass spectrum.

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

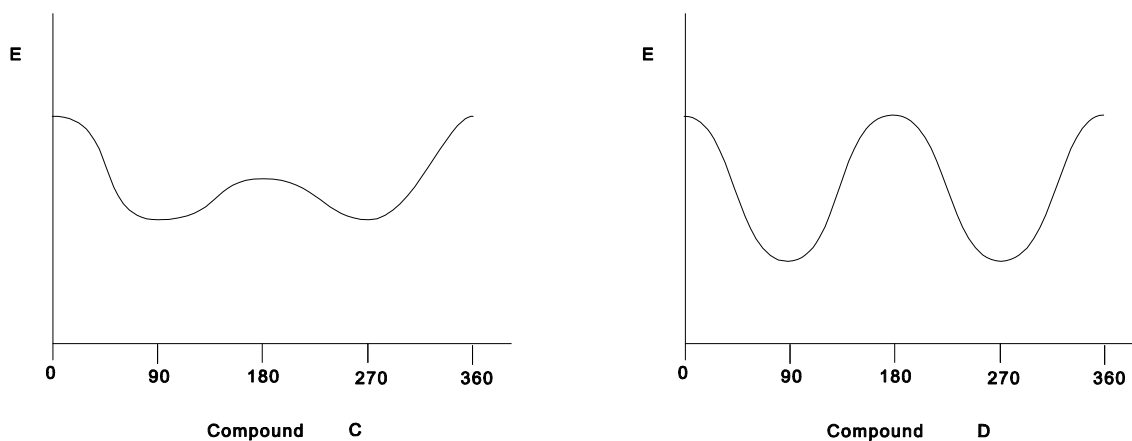
Therefore, with Br we would obtain: $x : y = 50.54 : 49.46 \cong 1 : 1$ hence $(x + y)^3 = 1 + 3 + 3 + 1$ and the ratio would be 1 : 3 : 3 : 1 which is not in agreement with the text.

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

5.3



5.4

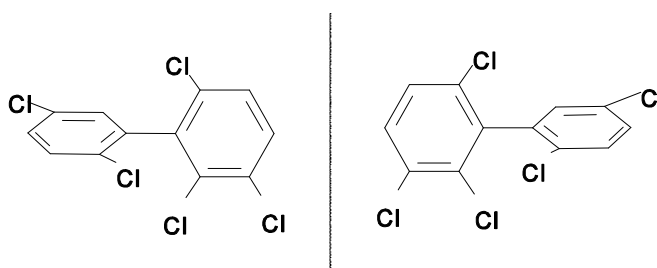


5.5

$$G_1 < G_2 < G_3.$$

Due to the increasing steric hindrance as a result of the interference of the big Van der Waals radii of chlorine, the rotation around the C-C single bond becomes more and more difficult. Therefore racemization is most likely to occur with G_1 , less with G_2 and least with G_3 . This kind of isomerism is called atropisomerism.

5.6



- 5.7** - Complete combustion in chemical incinerator equipped with an afterburner and scrubber.
- Addition of a strong base to obtain corresponding phenols.
 - Transformation into ArOH by OH-radicals in water.
 - Bacteria metabolizing polychlorobiphenyls.
-
-

PROBLEM 6

Sulphuric acid is produced by catalytic oxidation of SO_2 to SO_3 , absorption of SO_3 in concentrated sulphuric acid forming oleum (containing 20 % SO_3 by mass) and appropriate dilution hereafter. The gas leaving the catalyst chamber contains nitrogen, oxygen, a trace of SO_2 and 10 % (by volume) of SO_3 . Sulphur trioxide, SO_3 , is converted into sulphuric acid (98 % by mass) and/or oleum.

- 6.1** Assuming that oleum is the only product formed, calculate the mass of water which is required for 1000 m^3 of gas leaving the catalyst chamber (273 K, 101.3 kPa).
- 6.2** Assuming that only 98 % sulphuric acid is produced, calculate the necessary mass of water and the mass of product produced thereby.
- 6.3** In the industry both oleum and 98 % sulphuric acid are produced in a mass ratio of $x = m_1/m_2$, where m_1 denotes the mass of oleum, m_2 the mass of 98 % sulphuric acid. Find an expression $y = f(x)$ to describe the relation between the mass of water consumed for 1000 m^3 gas (denoted y) and the value of x . Show that the results of 6.1) and 6.2) are in good agreement with your mathematical expression.

SOLUTION

- 6.1** 1000 m^3 of gas contain 4.462 kmol SO_a
 100 kg 20 % oleum contain 0.2498 kmol SO_3 and 0.8157 kmol H_2SO_4
 1.0655 kmol SO_a and 0.8157 kmol (14.70 kg) H_2O are necessary for production of 100 kg 20 % oleum.
 61.56 kg H_2O are necessary for 1000 m^3 of gas.
- 6.2** Assumption that only 98 % sulphuric acid is produced:
 100,0 kg 98 % H_2SO_4 contain 0,9992 kmol H_2SO_4 and 1,1102 kmol H_2O .
 100,0 kg 98 % H_2SO_4 contain 0.9992 kmol SO_3 and 1,1102 kmol (20,01 kg) H_2O .
 89.36 kg H_2O are necessary for 1000 m^3 of gas and 446.56 kg 98 % H_2SO_4 are obtained.
- 6.3** To obtain 1 kg 20 % oleum, 0,1470 kg H_2O are necessary,
 To obtain 1 kg 98 % H_2SO_4 , 0,2001 kg H_2O are necessary.

Thus, for mass of water for production of m_1 kg 20 % oleum and m_2 kg 98 % H_2SO_4 :
 $y = 0,1470 m_1 + 0,2001 m_2$.

Analogically for mass balance of SO_a :

$$4,462 = 1,0655 m_1 + 0,9992 m_2$$

Then:
$$\frac{y}{4.462} = \frac{14.70 m_1 + 20.01 m_2}{1.0655 m_1 + 0.9992 m_2}$$

After substitution: $m_1/m_2 = x$ the above relation may written in the form of a function
 $y = f(x)$:

$$y = \frac{61.65 x + 83.79}{x + 0.9378}$$

Production of oleum: $m_2 = 0$, $y = 61,56$,

production of the acid: $m_1 = 0$, $y = 89,35$,

Results are similar to those obtained in parts **6.1** and **6.2**.

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**Determination of an acid dissociation constant

Reagents:

A solution of a weak monoprotic acid with a concentration of about 0.1 mol dm^{-3} ,
a solution of sodium hydroxide with a concentration of about 0.1 mol dm^{-3} ,
solutions of the indicators: methyl orange and phenolphthalein.

Equipment:

burette 25 cm^3 ,

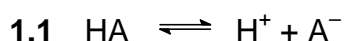
calibrated pipette 20 cm^3 ,

two conical flasks 200 cm^3 ,

access to the *pH*-meter. An assistant will make one measurement only for each participant.

Questions:

- 1.1 Give the expression for the concentration dissociation constant of the acid HA.
- 1.2 Give your reasons for the choice of the indicator.
- 1.3 Give the results of titrations.
- 1.4 Write down your *pH* value (measured by assistant).
- 1.5 Show how you calculate the concentration pK_a value for the acid. Write down the value.

SOLUTION

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

1.2 Since the HA is a weak acid the colour transition of the indicator is expected in the basic region ($pH > 7$), and thus phenolphthalein is suitable.

1.3 and 1.4

The results obtained by measuring volumes of the titrand and pH values were expected to be shown in the answer sheet.

1.5 The equation (a) can be transformed to equation (b) as follows:

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

When $[A^-] = [HA]$, then $pH = pK_a$

Since the concentration of the sodium hydroxide solution is approximate only, it is not possible to calculate the exact concentration of the acid. Nevertheless, the combination of titration and measuring pH values gives the possibility to find the value of dissociation constant K_a .

PROBLEM 2 (Practical)

Determination of the formation (stability) constants of the complex ions $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$

Equipment:

Two dry beakers with copper and zinc electrodes,
 three bottles with aqueous solutions of CuSO_4 , ZnSO_4 and NH_3 , respectively,
 one beaker with strips of filter paper for making a salt bridge,
 one beaker with an aqueous solution of KNO_3 ,
 three pipettes for delivering CuSO_4 , ZnSO_4 and NH_3 solutions,
 digital voltmeter for the EMF measurements,
 red and blue leads (conductors) for connecting cell electrodes to the digital voltmeter,
 rubber pipette filler,
 appropriately marked glass stirring rods.

a) Procedure for setting up the Daniell cell:

1. Into the dry beakers containing Cu and Zn electrodes deliver 20 cm³ of CuSO_4 and 20 cm³ of ZnSO_4 using marked pipettes in order to get Cu/Cu^{2+} and Zn/Zn^{2+} half-cells.
2. Wet the filter paper strip with KNO_3 solution. The strip should only be moisten with the solution. Then place the strip ends into the CuSO_4 and ZnSO_4 solutions.
3. Connect the leads to the electrodes (red to Cu electrode and blue to Zn electrode).

a)

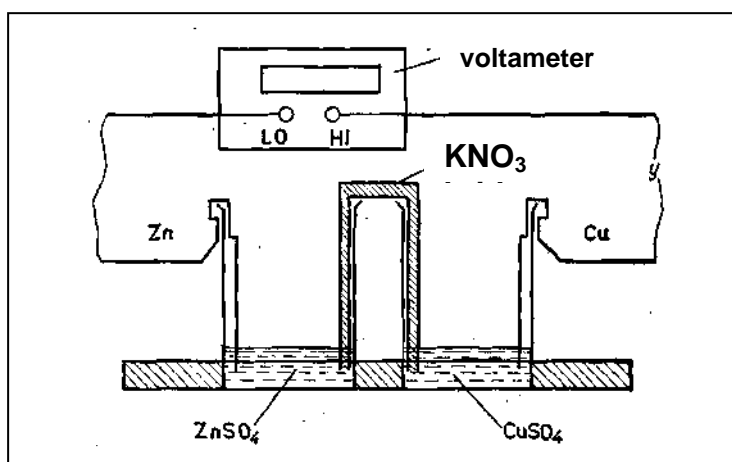


Fig. 1

b) Procedure for the EMF measurement of the Daniell cell (E_A):

Put the appropriately marked glass rods (red - Cu, blue - Zn) into the CuSO_4 and ZnSO_4 solutions. Having stirred the solutions gently with the rods, the rods should be left in the solutions throughout the course of the experiment. Start the EMF measurement of the cell by connecting the red lead to the voltmeter terminal (HI) and the blue one to the negative terminal (LO). If the EMF value changes by no more than 0.001 V, record the EMF (E_A).

c) Procedure for the EMF measurement of the cell (E_B) after the addition of the complexing agent (NH_3 solution) into the Cu/Cu^{2+} half-cell:

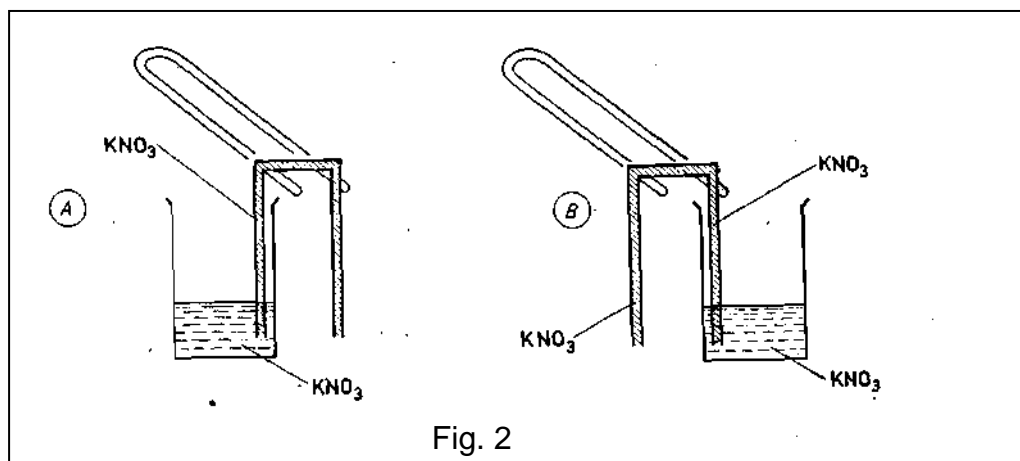


Fig. 2

Pipette 20 cm³ of aqueous NH_3 solution into the CuSO_4 solution. Stir the solution with a glass rod gently until it becomes a clear dark blue. Leave the rod in the solution. Measure and record the new EMF (E_B), in the way described in part b).

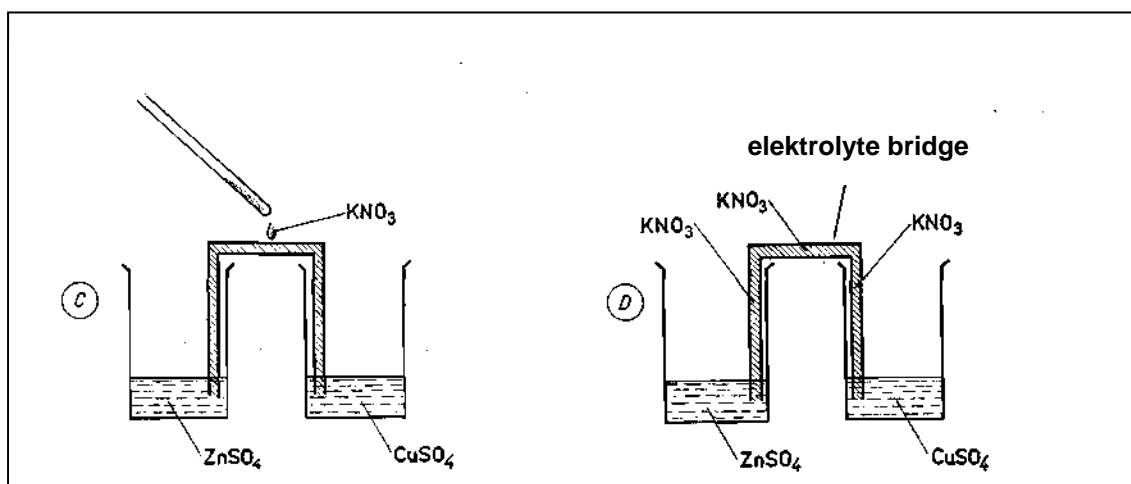


Fig. 3

- d) Procedure for the EMF measurement of the cell (E_C) after the addition of the complexing agent (NH_3 solution) to the Zn/Zn^{2+} half-cell:

Leave the $\text{Cu}/[\text{Cu}(\text{NH}_3)_4]^{2+}$ half-cell unchanged. Add 20 cm^3 of NH_3 solution to the ZnSO_4 half-cell. Carry out the EMF measurement of the cell in the way described in part b). Write down the result (E_C).

Theoretical considerations:

Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

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

- i) The concentrations of CuSO_4 , ZnSO_4 and NH_3 aqueous solutions written on the bottles are expressed in mol kg^{-1} . Therefore they must be converted into appropriate concentrations expressed in mol dm^{-3} . The densities (d) of the solutions as functions of temperature are respectively:
- CuSO_4 : $d_1 = 1.0923 (\text{kg dm}^{-3}) - 0.0002700 (\text{kg dm}^{-3}\text{K}^{-1}) T$
 ZnSO_4 : $d_2 = 1.0993 (\text{kg dm}^{-3}) - 0.0002900 (\text{kg dm}^{-3}\text{K}^{-1}) T$
 NH_3 : $d_3 = 1.0740 (\text{kg dm}^{-3}) - 0.0002800 (\text{kg dm}^{-3}\text{K}^{-1}) T$
- ii) In order to convert concentrations (c_i) into ionic activities (a_i), we need to calculate activities of the ions using the equation $a_i = f_i \cdot c_i$. The activity coefficient values, f_i , of the ions involved are given in the answer sheet. The activity coefficient of ammonia should be assumed to be 1.
- iii) To simplify the calculations it should be assumed that after the addition of the excess of complexing agent (NH_3) only $\text{Cu}^{2+}_{\text{aq}}$, $\text{Zn}^{2+}_{\text{aq}}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions exist in the respective solutions.
- iv) Any diffusion potential occurring between both half-cells when the salt bridge is applied may be neglected in practice.

Questions:

- 2.1** Calculate the values of the concentrations of Cu^{2+} and Zn^{2+} ions in the Daniell cell before the introduction of the complexing agent (NH_3).
- 2.2** Calculate the standard EMF value E^0 of your Daniell cell using the Nernst equation.

- 2.3 Calculate the concentrations of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and NH_3 in the B type cell, i.e. after the addition of NH_3 to the Cu/Cu^{2+} half-cell.
- 2.4 Determine the values of the thermodynamic formation (stability) constants K_B and $\ln K_B$ for the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions.
- 2.5 Calculate the concentrations of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and NH_3 in the type C cell, i. e. after the addition of NH_3 to the Zn/Zn^{2+} half-cell.
- 2.6 Determine the values of the thermodynamic formation (stability) constant K_C and $\ln K_C$ for $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions.

SOLUTION

2.1 The mass of the solutions (kg) can be transformed to volumes of the solutions (dm^3) using the given densities. The concentrations are then given in units mol dm^{-3} .

$$2.2 \quad E = \left(E^0(\text{Cu}^{2+}/\text{Cu}) + \frac{RT}{2F} \ln([\text{Cu}^{2+}] \times f_{\text{Cu}^{2+}}) \right) - \left(E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln([\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}}) \right) - E_{\text{diff}}$$

For $E_{\text{diff}} = 0$:

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

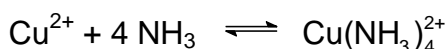
E_A can be measured. All other data required are given in the text of the problem or in the answer sheet.

2.3 Concentrations after the addition of NH_3 :

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

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

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



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

Then the Nernst equation has the form:

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

$$E_B = E_1' - E_2 = E^0(\text{Cu}^{2+}/\text{Cu}) - E^0(\text{Zn}^{2+}/\text{Zn}) + \frac{RT}{2F} \ln \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \times f_{\text{Cu}(\text{NH}_3)_4^{2+}}}{[\text{Zn}^{2+}] \times f_{\text{Zn}^{2+}} \times \beta_4 \times [\text{NH}_3]^4}$$

From the above equation β_4 or $\ln\beta_4$ can be calculated since E_B can be measured, and all other data required are given in the text of the problem or in the answer sheet.

2.5 and 2.6

The procedure in the calculation of β_4 or $\ln\beta_4$ for complex $\text{Zn}(\text{NH}_3)_4^{2+}$ is analogical as that shown in parts (2.3) and (2.4) for complex $\text{Cu}(\text{NH}_3)_4^{2+}$.

24th



International Chemistry Olympiad

**9 theoretical problems
1 practical problem**

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

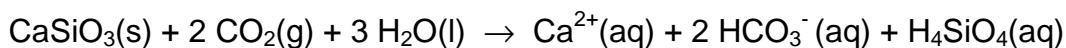
THEORETICAL PROBLEMS

PROBLEM 1

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



- 1.1** During the first five years of life blue whales gain 75 kg of mass per day by feeding on krill. The whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill. Assuming that the mass gain in the first years of a whale's life is due to the consumption of carbohydrates ($\text{C}_6\text{H}_{12}\text{O}_6$), calculate the volume of CO_2 at STP (0 °C, 101 kPa) that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.
- 1.2** There is 0.23 cm^3 of dissolved CO_2 per one litre sea water (at 24 °C and 101 kPa).
- If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life?
 - What fraction of the total volume of the oceans will be needed to supply the carbon dioxide for the first five years of growth of 1000 blue whales? The volume of the oceans is $1.37 \times 10^{18} \text{ m}^3$.
- 1.3** Three percent of the mass of a $9.1 \times 10^4 \text{ kg}$ adult whale is nitrogen. When a $9.1 \times 10^4 \text{ kg}$ blue whale dies, what is the maximum mass of NH_4^+ that can become available for other marine organisms?
- 1.4** Eighteen percent of a $9.1 \times 10^4 \text{ kg}$ whale's mass is carbon. Carbon can be returned to the atmosphere as CO_2 and then removed from the atmosphere by weathering of rocks containing calcium silicate.



What are the maximum number of grams of CaSiO_3 that can be weathered by the carbon dioxide produced from the decomposition of 1000 blue whales, the number estimated to die annually?

SOLUTION

1.1 In five years a whale eats carbohydrates coming from $5 \times 365 \times 75 \times 10 = 1.4 \times 10^6$ kg krill which themselves need 1.4×10^7 kg of carbohydrates coming from diatoms.

For 180 g $\text{C}_6\text{H}_{12}\text{O}_6$, 6×44 g CO_2 are necessary, and thus

for 1.4×10^7 kg carbohydrates $1.4 \times 10^7 \times (264/180) = 2.00 \times 10^7$ kg of CO_2 are needed,

i. e. 1.0×10^{10} dm³ CO_2

1.2 i) The amount of water is 4×10^{13} dm³.

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

1.3 The mass of nitrogen from a whale is $0.03 \times 9.1 \times 10^4$ kg = 2.7×10^6 g.

$$n(\text{N}) = n(\text{NH}_4^+) = \frac{2.7 \times 10^6 \text{ g}}{14 \text{ g mol}^{-1}} = 1.9 \times 10^5 \text{ mol}$$

$$m(\text{NH}_4^+) = 1.9 \times 10^5 \text{ mol} \times 18 \text{ g mol}^{-1} = 3 \times 10^6 \text{ g NH}_4^+ = 3 \times 10^3 \text{ kg NH}_4^+$$

1.4 One whale contains 1.6×10^4 kg of carbon. It corresponds to 1.3×10^6 mol of CO_2 .

From the equation: $n(\text{CaSiO}_3) = 6.5 \times 10^5$ mol

$$m(\text{CaSiO}_3) = 6.5 \times 10^5 \text{ mol} \times 116 \text{ g mol}^{-1} = 7.5 \times 10^7 \text{ g CaSiO}_3$$

1000 whales therefore produce 7.5×10^{10} g CaSiO_3 .

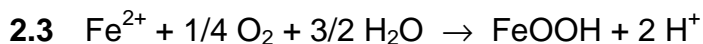
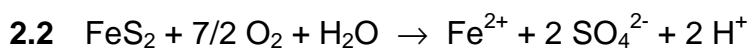
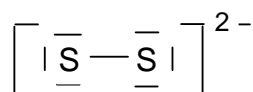
PROBLEM 2

Many streams drain in areas where coal or metallic ores are mined. These streams have become acidic and contain high concentrations of dissolved iron and sulphate, due to sulphur-containing ores being exposed to the atmosphere or to oxygenated waters. The most common sulphur-containing mineral is pyrite, FeS_2 , in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite, FeO(OH) , which coats the stream bottom while the water remains acidic.

- 2.1 Draw the electron dot structure that illustrates the bonding in the ion S_2^{2-} , showing all valence electrons.
- 2.2 Write a balanced chemical equation to show how hydrogen ions (H^+) are generated during the oxidation of pyrite to form a solution of iron(II) and sulphate ions.
- 2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, FeO(OH) .
- 2.4 Calculate how many moles of pyrite would be required to bring 1.0 dm^3 of pure water to a pH of 3.0 if the pyrite was completely converted into FeO(OH) and H^+ ions. Neglect the formation of HSO_4^- .
- 2.5 The concentration of iron as Fe(II) in a stream is 0.00835 M. At a very narrow point in the stream it empties into a large pond, with a flow rate of 20.0 l each minute. The water in this stream is sufficiently aerated that 75 % of the Fe(II) is oxidized to Fe(III). The pH of the pond is high enough (> 7) that the iron(III) precipitates immediately as Fe(OH)_3 which on aging becomes Fe_2O_3 . What mass of Fe_2O_3 will be deposited on the bottom of the pond in two years?

SOLUTION

2.1



2.4 $[\text{H}^+] = 1 \times 10^{-3}$

$n[\text{H}^+] = 1 \times 10^{-3} \text{ mol}$

From both equations: $n(\text{FeS}_2) = 2.5 \times 10^{-4} \text{ mol}$

2.5 Total flow into pond in 2 years =

$$2 \text{ yr} \times 365 \text{ days yr}^{-1} \times 24 \text{ h day}^{-1} \times 60 \text{ min h}^{-1} \times 20.0 \text{ dm}^3 \text{ min}^{-1} = \\ = 2.10 \times 10^7 \text{ dm}^3 \text{ of water}$$

$$n(\text{Fe}^{2+}) \text{ into pond} = 2.10 \times 10^7 \text{ dm}^3 \times 8.35 \times 10^{-3} \text{ mol dm}^{-3} = 1.76 \times 10^5 \text{ mol}$$

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

mass of deposited Fe_2O_3 :

$$m(\text{Fe}_2\text{O}_3) = 0.5 \times 1.32 \times 10^5 \text{ mol} \times 159.7 \text{ g mol}^{-1} = 1.05 \times 10^7 \text{ g}$$

PROBLEM 3

Coniferyl alcohol has the molecular formula $C_{10}H_{12}O_3$. It is isolated from pine trees. Coniferyl alcohol is not soluble in water or aqueous $NaHCO_3$. A solution of Br_2 in CCl_4 is decolorized when added to coniferyl alcohol forming **A** ($C_{10}H_{12}O_3Br_2$). Upon reductive ozonolysis coniferyl alcohol produces vanillin (4-hydroxy-3-methoxybenzaldehyd) and **B** ($C_2H_4O_2$). Coniferyl alcohol reacts with benzoyl chloride (C_6H_5COCl) in the presence of a base to form **C** ($C_{24}H_{20}O_5$). This product rapidly decolorizes $KMnO_4$ (aq) and is insoluble in dilute $NaOH$.

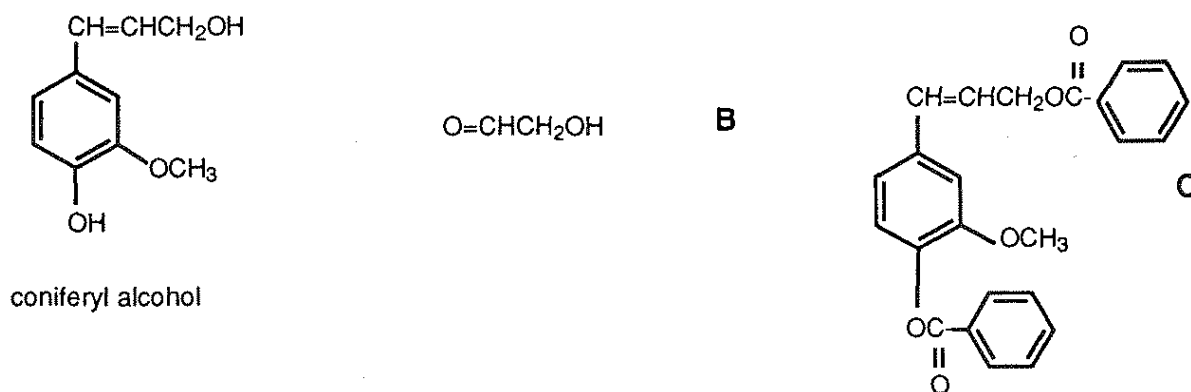
Coniferyl alcohol reacts with cold HBr to form **D** ($C_{10}H_{11}O_2Br$). Hot HI converts $ArOR$ to $ArOH$ and RI . Coniferyl alcohol reacts with excess hot HI to give **E** ($C_9H_9O_2I$) and CH_3I . CH_3I in aqueous base reacts with coniferyl alcohol to form **F** ($C_{11}H_{14}O_3$), which is not soluble in a strong base, but decolorizes Br_2/CCl_4 -solution.

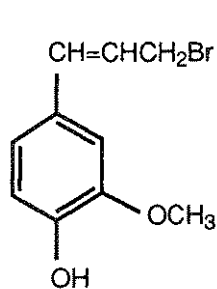
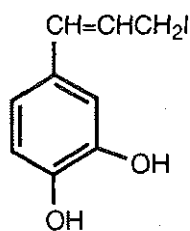
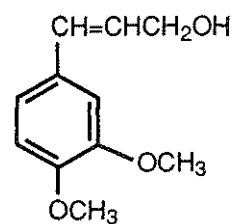
3.1 Draw the structures of coniferyl alcohol and compounds **A - F**.

3.2 There are a number of stereoisomers of compound **A**. Draw structure of compound **A**. Label each chiral centre in compound **A** with an asterisk (*). For all stereoisomers draw Fischer projections and label each chiral center with the proper *R* or *S* designation giving the absolute configuration about the chiral centre.

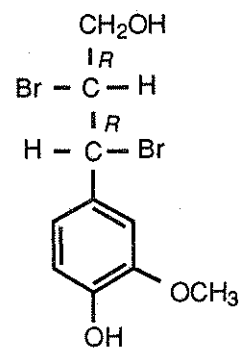
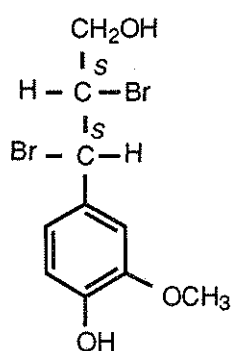
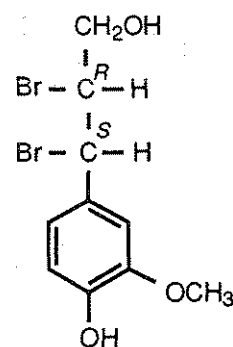
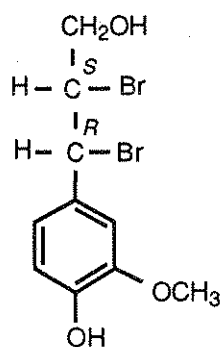
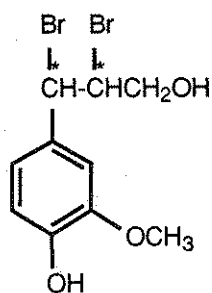
SOLUTION

3.1




D

E

F
I

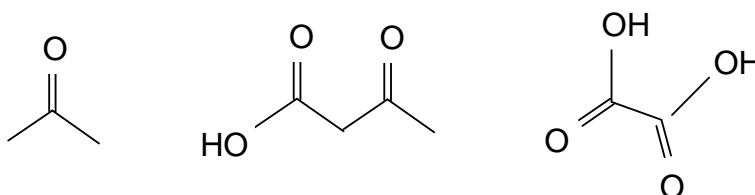
3.2 There are no geometric isomers of compound **A**, but there are 4 diastereomers (2 pairs of enantiomers).



PROBLEM 4

Rose oil is an essential oil obtained from the steam distillation of plant material from roses. It contains a number of terpenes, one of which is geraniol, $C_{10}H_{18}O$ (**A**). Upon oxidation, geraniol can either give a ten-carbon aldehyde or a ten-carbon carboxylic acid. Reaction with two moles of bromine gives a tetrabromide ($C_{10}H_{18}OBr_4$) (**B**). Geraniol reacts with HBr to give two bromides of formula $C_{10}H_{17}Br$.

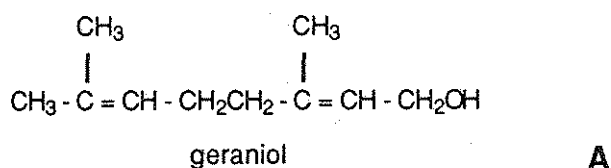
When geraniol is vigorously oxidized, three products are obtained:



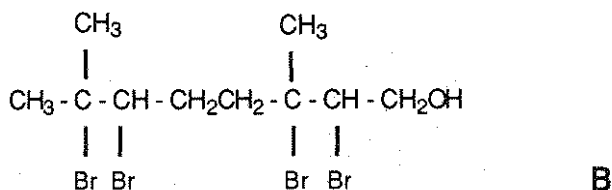
- 4.1 Give the structure of geraniol **A**.
- 4.2 Give the structure of compound **B**.
- 4.3 Give the structures of the two bromides of formula $C_{10}H_{17}Br$.
- 4.4 Indicate which of the two bromides is formed in greater proportions.

SOLUTION

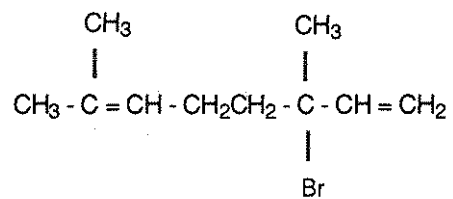
4.1



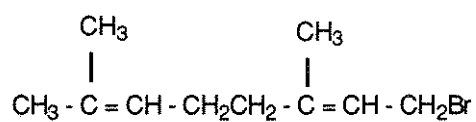
4.2



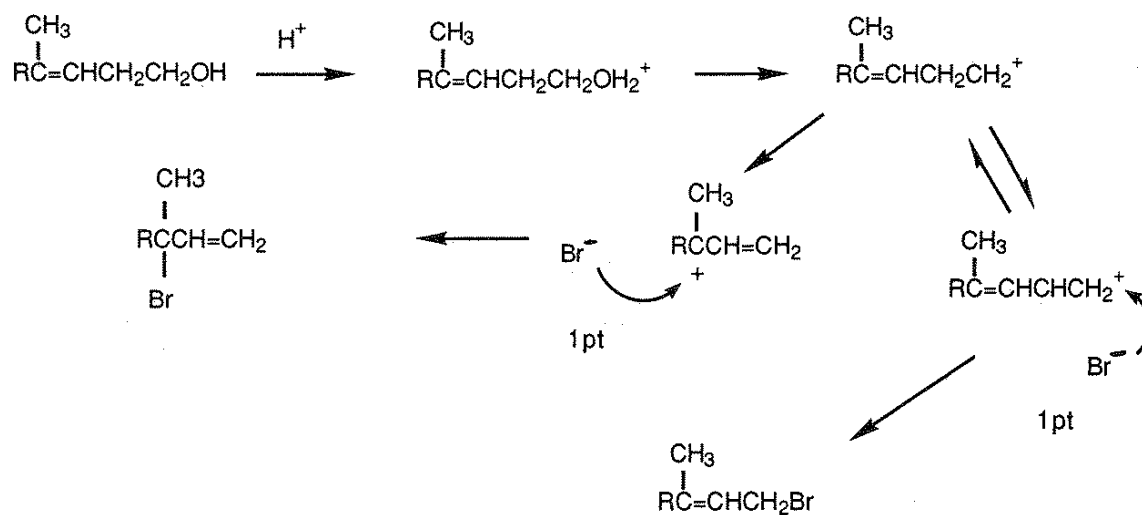
4.3



or

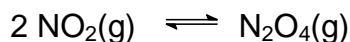


4.4



PROBLEM 5

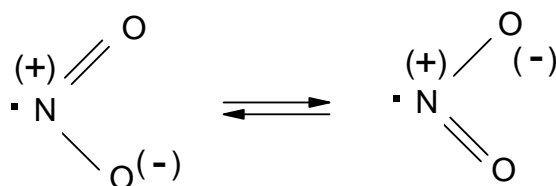
Nitrogen dioxide NO_2 is one of a number of oxides of nitrogen found in our atmosphere. It can dimerize to give N_2O_4 (g):



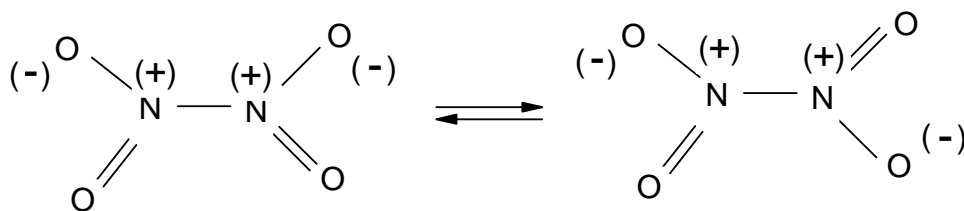
- 5.1** With a diagram, show the bonds present in NO_2 (g) using the concept of resonance if necessary. Nitrogen dioxide, NO_2 , is paramagnetic.
- 5.2** Show, with bonding diagrams, how two molecules of NO_2 (g) combine to give a molecule of N_2O_4 (g) which is not paramagnetic.
- 5.3** At 298 K, the ΔG° 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° for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?
- 5.5** The dissociation of N_2O_4 (g) to give NO_2 (g) is a first order process with a specific rate constant of $5.3 \times 10^4 \text{ s}^{-1}$ at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original N_2O_4 to decompose?
- 5.6** The association of NO_2 (g) to give N_2O_4 (g) is a second-order process with a specific rate constant of $9.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c , at 298 K for the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

SOLUTION

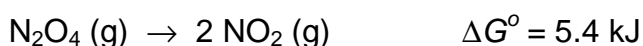
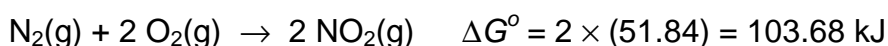
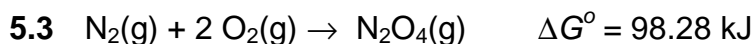
- 5.1** The structure of NO_2 :



- 5.2** The structure of N_2O_4 :



(At very low temperatures there is another structure of N_2O_4 possible: $\text{O}=\text{N}-\text{ONO}_2$, nitrosyl nitrate)



If x denotes the fraction of decomposed N_2O_4 and P_T the partial pressure and X the mole fraction of the corresponding species, we obtain:

$$\Delta G^\circ = -RT \ln K; \quad K = e^{(-5.4 \text{ kJ} / 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})}$$

$$K_p = 0.113 = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(P_T X_{\text{NO}_2})^2}{P_T X_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2x}{1+x}\right)^2}{\left(\frac{1-x}{1+x}\right)} = \frac{4x^2}{1-x^2}$$

wherefrom $x = 0.166$

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

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

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

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

$$T_2 = 318 \text{ K}$$

5.5 $\ln \frac{[\text{N}_2\text{O}_4]_t}{[\text{N}_2\text{O}_4]_0} = -kt$

$$\ln 0.80 = -(5.3 \times 10^4 \text{ s}^{-1}) t$$

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

5.6 $K = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{9.8 \times 10^6}{5.3 \times 10^4} = 1.8 \times 10^2$

PROBLEM 6

The concentration of carbon dioxide in the atmosphere has increased substantially during this century and is predicted to continue to increase. The $[\text{CO}_2]$ is expected to be about 440 ppm (440×10^{-6} atm) in the year 2020.

- 6.1** Calculate the concentration (in mol dm^{-3}) of CO_2 dissolved in distilled water equilibrated with the atmosphere in the year 2020.
- 6.2** Calculate the pH -value of the solution in 6.1.
- 6.3** Calculate the enthalpy of reaction between CO_2 (aq) and H_2O .
- 6.4** If the temperature of an equilibrated solution of CO_2 is increased and the concentration of dissolved carbon dioxide is maintained constant, the pH of the solution may change. Predict whether the pH will increase or decrease.

Data:

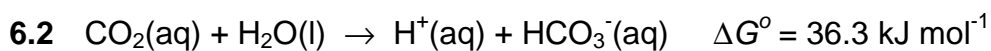
Henry's Law constant for CO_2 at 298 K: $0.0343 \text{ dm}^3 \text{ mol}^{-1} \text{ atm}^{-1}$

Thermodynamic values, in kJ/mol at 298 K are:

	$\Delta_f G^0$	$\Delta_f H^0$
CO_2 (aq)	-386.2	-412.9
H_2O (l)	-237.2	-285.8
HCO_3^- (aq)	-587.1	-691.2
H^+ (aq)	0.00	0.00

SOLUTION

$$6.1 \quad [\text{CO}_2(\text{aq})] = K_{\text{H}} p_{\text{CO}_2} = 0.0343 \text{ M atm}^{-1} \times 440 \times 10^{-6} \text{ atm} = \underline{1.51 \times 10^{-5} \text{ M}}$$



$$K = e^{-\Delta G^\circ / RT} = 4.37 \times 10^{-7}$$

Since $x = [\text{H}^+] = [\text{HCO}_3^-]$,

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x^2}{[\text{CO}_2]}$$

Solving for x yields $[\text{H}^+] = 2.57 \times 10^{-6}$; pH = 5.59

$$6.3 \quad \Delta H^\circ = \Delta H_f^\circ(\text{HCO}_3^-) - \Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ(\text{H}_2\text{O}) = \\ = -691.2 - (-412.9) - (-285.8) = \underline{7.5 \text{ kJ mol}^{-1}}$$

6.4 Since the reaction is endothermic, the equilibrium constant will increase with temperature. Therefore, $[\text{H}^+]$ will also increase and the *pH* will decrease.

PROBLEM 7

When the fresh-water rivers that run into the Chesapeake Bay flood after heavy rains in the spring, the increase in fresh water in the Bay causes a decrease in the salinity in the areas where oysters grow. The minimum concentration of chloride ions needed in oyster beds for normal growth is 8 ppm (8 mg dm^{-3}).

After one week of heavy rain, the following analysis is done on water from the bay. To a 50.00 cm^3 sample of bay water a few drops of a K_2CrO_4 solution are added. The sample is then titrated with 16.16 cm^3 of a 0.00164 M AgNO_3 solution. After AgNO_3 solution has been added to the sample a bright red-orange precipitate forms.

- 7.1 What is the molar concentration of chloride in the sample?
- 7.2 Does the water contain sufficient chloride for the normal growth of oysters? Show your calculation.
- 7.3 Write a balanced equation for the reaction of the analyte with the titrant.
- 7.4 Write a balanced net-ionic equation that describes the reaction responsible for the colour change at the endpoint of the titration. Which compound produces the brick-red colour?
- 7.5 The concentration of chromate at the endpoint is 0.020 M . Calculate the concentration of chloride ions in the solution when the red precipitate forms.
- 7.6 For this titration to work most effectively, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium that would influence the observed endpoint of this titration.

Typically, a buffer is added to the solution being titrated to control the pH if the initial sample is acidic. Suppose the *pH* of the sample of bay water was 5.10, thus too acidic to perform the analysis accurately.

- 7.7 Select a buffer from the list that would enable you to establish and maintain a *pH* of 7.20 in aqueous medium. Show the calculations which lead to your choice.

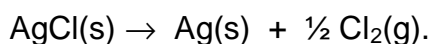
Buffer systems	K_a of weak acid
1. 0.10 M lactic acid / 0.10 M sodium lactate	1.4×10^{-4}
2. 0.10 M acetic acid / 0.10 M sodium acetate	1.8×10^{-5}

3. 0.10 M sodium dihydrogen phosphate /
/ 0.10 M sodium hydrogen phosphate 6.2×10^{-8}
4. 0.10 M ammonium chloride / 0.10 M ammonia 5.6×10^{-10}

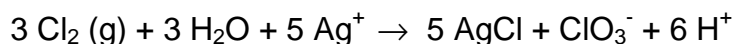
7.8 Using the selected buffer system, calculate the mass (in g) of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 cm³ of a stock solution buffered at a pH of 7.2.

7.9 The chloride concentration in another 50.00 cm³ sample of bay water was determined by the Volhard method. In this method an excess of AgNO₃ is added to the sample. The excess Ag⁺ is titrated with standardized KSCN, forming a precipitate of AgSCN. The endpoint is signalled by the formation of the reddish-brown FeSCN²⁺ complex that forms when Ag⁺ is depleted. If the excess Ag⁺ from the addition of 50.00 cm³ of 0.00129 M AgNO₃ to the water sample required 27.46 cm³ of 1.41 10⁻³ M KSCN for titration, calculate the concentration of chloride in the bay water sample.

In natural waters with much higher concentration of Cl⁻, the Cl⁻ can be determined gravimetrically by precipitating the Cl⁻ as AgCl. A complicating feature of this method is the fact that AgCl is susceptible to photodecomposition as shown by the reaction:



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



If 0.010 g of a 3.000 g sample of AgCl contaminated with excess Ag⁺ undergoes photodecomposition by the above equations

7.10 Will the apparent weight of AgCl be too high or too low? Explain your answer showing by how many grams the two values will differ.

Data: $K_{sp}(\text{AgCl}) = 1.78 \times 10^{-10}$
 $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.00 \times 10^{-12}$

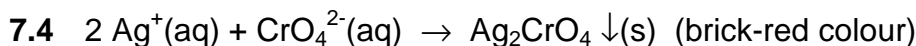
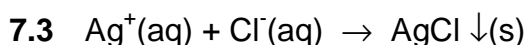
SOLUTION

$$7.1 \quad n(\text{Ag}^+) = n(\text{Cl}^-)$$

$$c(\text{Cl}^-) = \frac{0.01616 \text{ dm}^3 \times 0.00164 \text{ mol dm}^{-3}}{0.050 \text{ dm}^3} = 5.30 \times 10^{-4} \text{ mol dm}^{-3}$$

$$7.2 \quad \text{Concentration in mg dm}^{-3} = 5.30 \times 10^{-4} \text{ mol dm}^{-3} \times 35.5 \text{ g mol}^{-1} = 0.0188 \text{ g dm}^{-3} = 18.8 \text{ mg dm}^{-3}$$

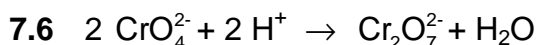
Thus the chloride concentration is sufficiently high for normal oyster growth.



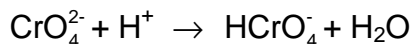
$$7.5 \quad K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 4x^3 \text{ if } x = [\text{Ag}^+] \Rightarrow$$

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

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



either/or



7.7 A buffer system has its maximum buffer capacity when $\text{pH} = \text{pK}_a$. So, the system 3 would be best since $\text{pK}_a = 7.2$

$$7.8 \quad m(\text{NaH}_2\text{PO}_4) = 0.10 \text{ mol dm}^{-3} \times 0.500 \text{ dm}^3 \times 119.98 \text{ g mol}^{-1} = 6.0 \text{ g}$$

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

$$7.9 \quad \text{mol Ag}^+ \text{ added: } n(\text{Ag}^+)_{\text{ad}} = 0.05 \text{ dm}^3 \times 0.00129 \text{ mol dm}^{-3} = 6.45 \times 10^{-5} \text{ mol}$$

$$\text{mol Ag}^+ \text{ left over: } n(\text{Ag}^+)_{\text{left}} = 0.02746 \text{ dm}^3 \times 0.0141 \text{ mol dm}^{-3} = 3.87 \times 10^{-5} \text{ mol}$$

mol Cl^- in sample:

$$n(\text{Cl}^-) = n(\text{Ag}^+)_{\text{ad}} - n(\text{Ag}^+)_{\text{left}} = (6.45 \times 10^{-5} \text{ mol}) - (3.87 \times 10^{-5} \text{ mol}) = 2.58 \times 10^{-5} \text{ mol}$$

$$\Rightarrow [\text{Cl}^-] = \frac{2.58 \times 10^{-5}}{0.050} = 5.16 \times 10^{-4} \text{ mol dm}^{-3}$$

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

$n(\text{Cl}_2)$ produced: $\frac{1}{2} (6.98 \times 10^{-5} \text{ mol}) = 3.49 \times 10^{-5} \text{ mol}$

$n(\text{AgCl})$ new prod.: $\frac{5}{3} (3.49 \times 10^{-5} \text{ mol}) = 5.82 \times 10^{-5} \text{ mol} \equiv 8.34 \text{ mg}$

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

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

The mass of the sample is equal to $3.0 \text{ g} - 0.010 \text{ g} + 0.00834 \text{ g} + 0.00753 \text{ g} = 3.006 \text{ g}$. Therefore the total mass of the solid (AgCl + Ag) will be too high and the difference is 6 mg.

PROBLEM 8

The Pourbaix diagrams for water, nitrogen and manganese are depicted in Fig. 1.

8.1 Write the formula of the species of nitrogen that is predominant

- i) in O₂-rich lakes of pH ≈ 6,
- ii) in highly O₂-depleted lakes that are strongly contaminated with acid rain (pH ≈ 3),

8.2 Which species of manganese is predominant

- i) in O₂-rich lakes of pH ≈ 6,
- ii) in highly O₂-depleted lakes that are strongly contaminated with bases (pH ≈ 12)?

8.3 People often find that clear, slightly acidic (pH ≈ 5) water drawn from wells deposits a black manganese-containing solid on standing in toilet bowls.

- 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 Mn²⁺(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 Pourbaix diagrams, some of the chemical forms of manganese should oxidize NH₃(aq) or NH₄⁺(aq) to N₂(g).

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

Mn, Mn(OH)₂, Mn²⁺, Mn₃O₄, Mn₂O₃, MnO₂, MnO₄²⁻, MnO₄⁻

8.6 Ammonium permanganate, NH₄MnO₄, is a well-known salt, but ammonium manganate, (NH₄)₂MnO₄, is a rarely known salt.

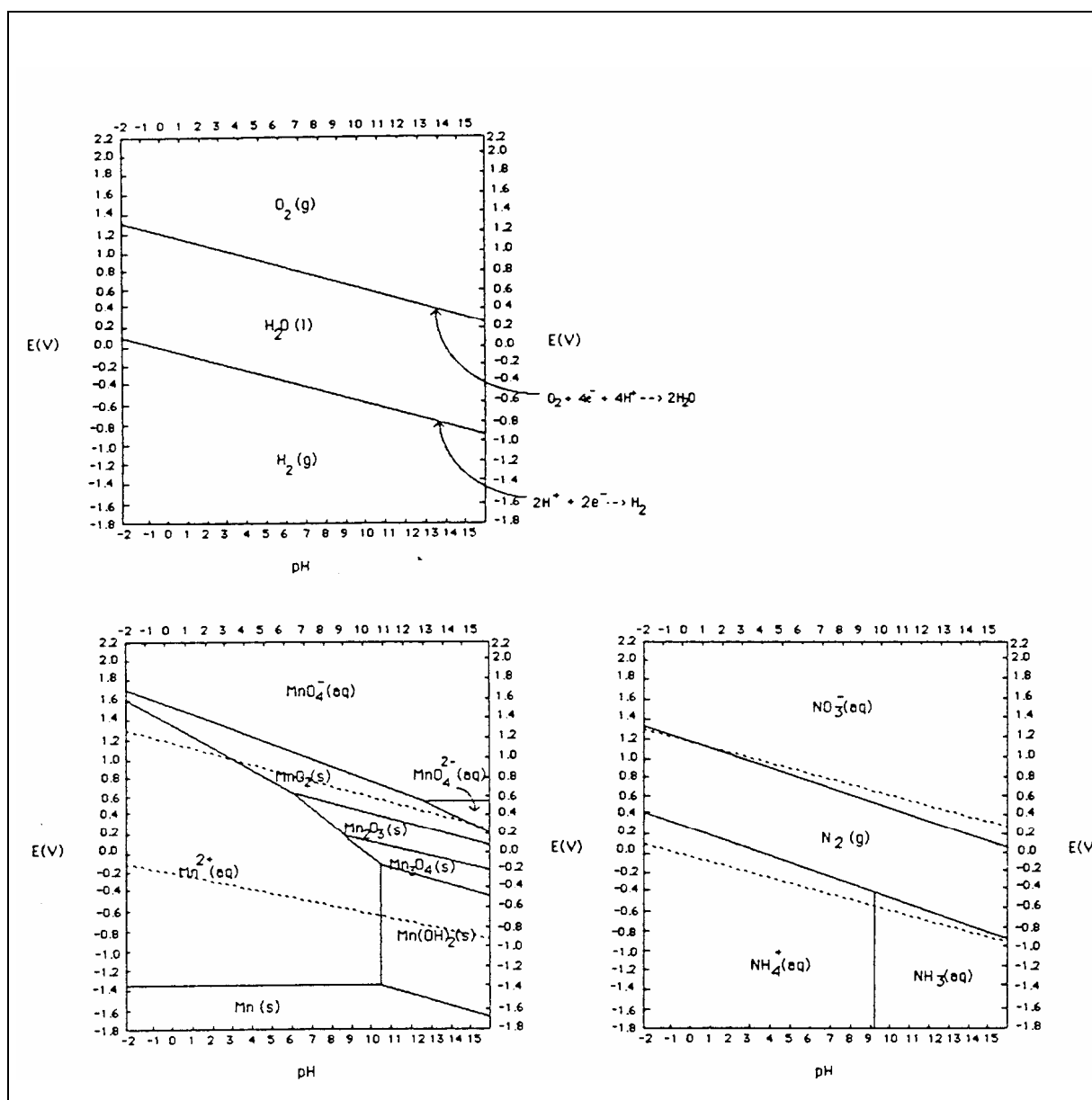
- i) Is NH₄MnO₄ expected to be thermodynamically stable? (YES or NO)
- ii) Is (NH₄)₂MnO₄ expected to be thermodynamically stable? (YES or NO)
- iii) Write and balance an equation for the decomposition of NH₄MnO₄ to give MnO₂ and N₂.
- iv) Write and balance an equation for the decomposition of (NH₄)₂MnO₄ to give Mn and N₂.

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

- i) potassium nitrate and manganese metal,
- ii) potassium nitrate and manganese dioxide?

8.8 The standard reduction potential, E^0 , for the reduction of MnO_4^- to MnO_2 is 1.692 V. Applying the Nernst equation calculate the reduction potential, E , for the reduction of 0.00100 M MnO_4^- solution at a $\text{pH} = 4.0$.

Figure 1



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.

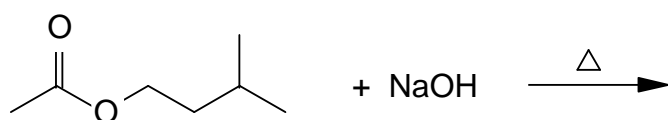
$$8.8 \quad E = E^\circ + \frac{0.0591}{3} \log[MnO_4^-] + \frac{0.0591}{3} \log[H^+]^4 =$$

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

PROBLEM 9

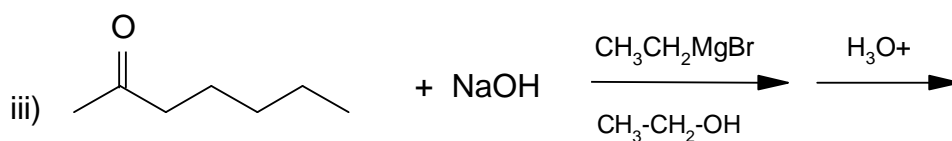
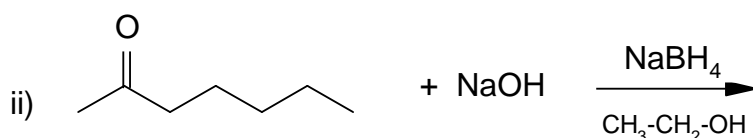
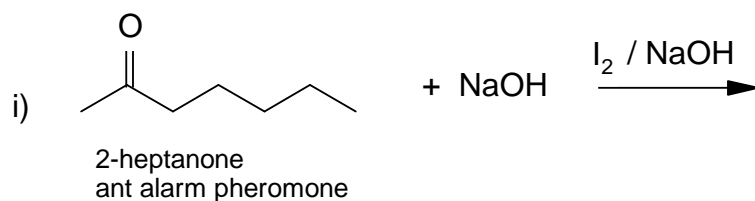
Pheromones are chemicals or mixtures of certain chemicals secreted by insects and some animals for communication. They bring about certain responses in another individual of the same species. In the problem below you will find a number of pheromones undergoing reactions which were used in determining 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

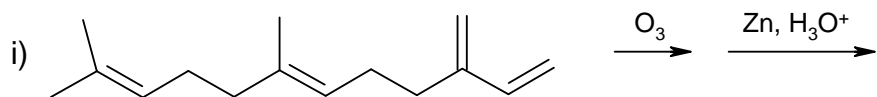


isoamyl acetate,
bee alarm pheromone

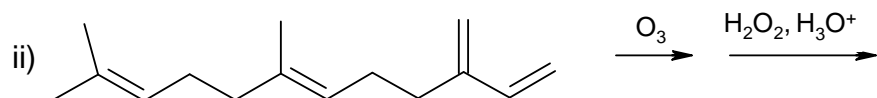
9.2



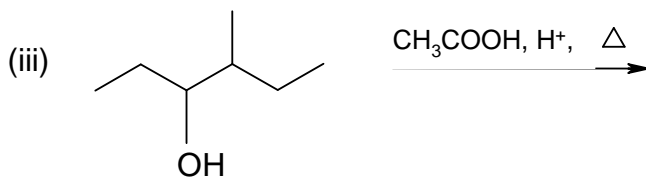
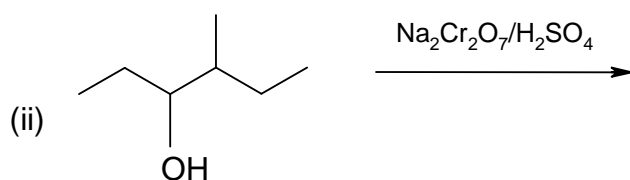
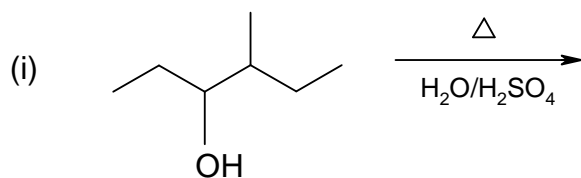
9.3



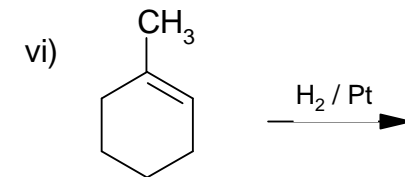
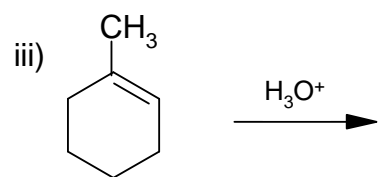
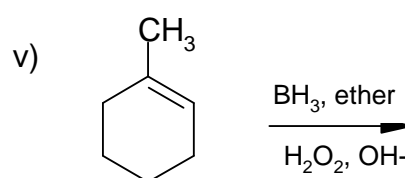
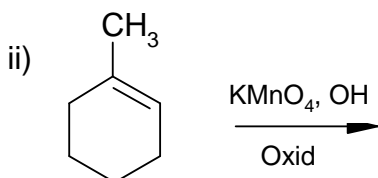
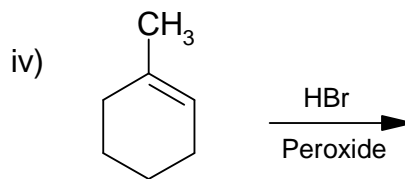
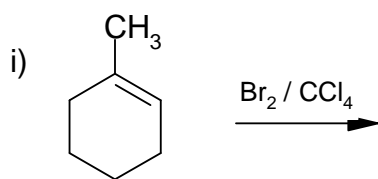
green peach -
aphid pheromone



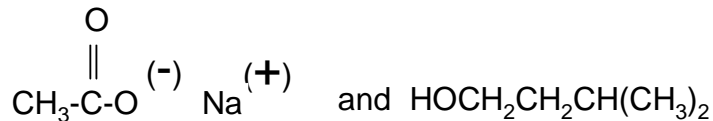
9.4



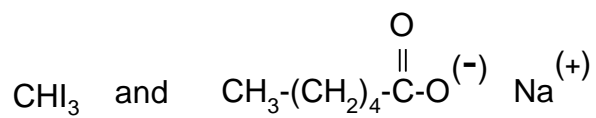
9.5


SOLUTION

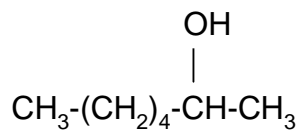
9.1



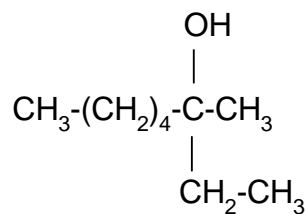
9.2 i)



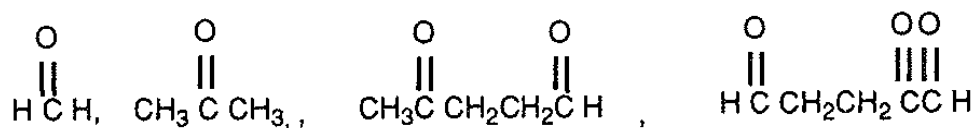
ii)



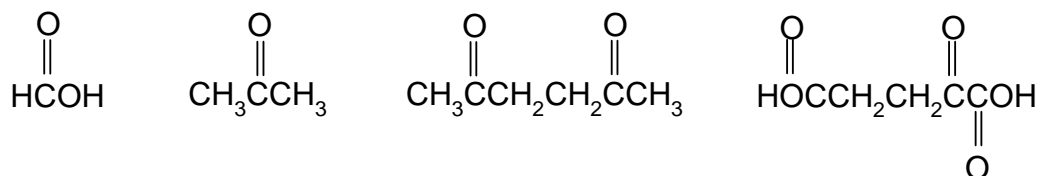
iii)



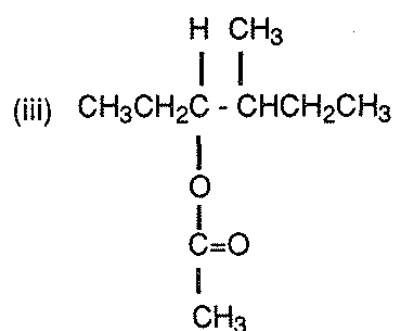
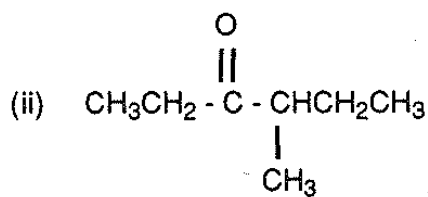
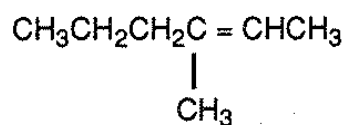
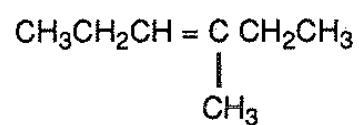
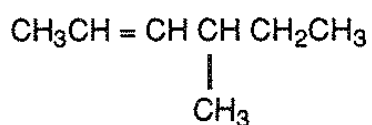
9.3 i)



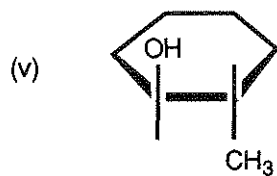
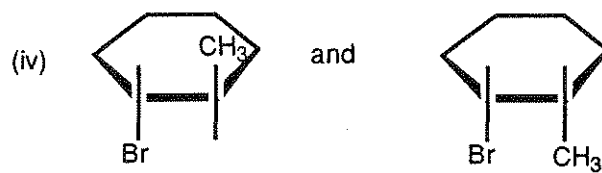
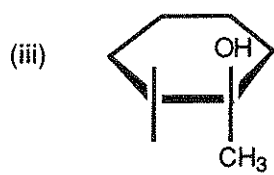
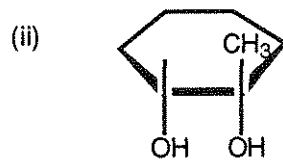
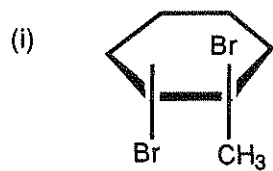
ii)



9.4 i)



9.5



PRACTICAL PROBLEMS**PROBLEM 1 (Practical)**Effects of CO₂ on Solubility

Calcium carbonate is a partially soluble material commonly known as limestone, marble, chalk, or calcite. In the presence of CO₂-rich groundwater, calcium carbonate dissolves to form cavities and caves in limestone formations.

In this experiment you will determine the solubility of calcium carbonate in an aqueous solution saturated with carbon dioxide and in solution free of carbon dioxide. The [Ca²⁺] will be determined by complexometric titration with EDTA (ethylenediamine-tetraacetic acid).

- a) Procedure for the determination of [Ca²⁺]
1. Calibrate your *pH* meter.
 2. Measure and record the *pH* of the sample equilibrated with solid CaCO₃ and CO₂ gas.
 3. Filter all your sample into a second 250 cm³ plastic bottle to remove any suspended CaCO₃. Quickly cap the bottle when the filtering is complete.
 4. Uncap the bottle long enough to measure and record the *pH* of the filtered solution and recap the bottle until you are ready for the next step.
 5. As rapidly as possible, transfer three 25 cm³ aliquots of this sample to three Erlenmeyer flasks. Recap the sample bottle after removing each 25 cm³ aliquot.
 6. Add 15 drops of 6 M HCl to each of the three flasks with stirring. Any CaCO₃ that may have formed should dissolve. Before proceeding with the next step, make sure there is no solid CaCO₃ in the Erlenmeyer flasks. If a flask has some solid present, then more stirring is necessary.
 7. To one, and only one flask, add 5 cm³ of a *pH* 10 NH₃ buffer. Proceed immediately with steps 8 - 10.
 8. Add 20 drops of 0.001 M Mg²⁺/EDTA⁴⁻ solution to the flask in order for the indicator to function properly.
 9. Add 5 drops of Calmagite indicator to the sample.

10. Titrate the sample with an approximately 0.01 M EDTA solution provided (to be standardized as directed below) to a colour change from red to blue. You may wish to make a reference for colour with water, buffer, two drops EDTA and indicator.
11. Quickly repeat steps 7 - 10 for each remaining flask, one at a time.
12. After steps 1 - 11 have been completed to your satisfaction, transfer the remaining filtered, saturated solution from step 3 to a suitable beaker. Heat this solution to 96 – 99 °C and allow it to remain at that temperature, with magnetic stirring, for 5 minutes. A stirrer setting on 6 is adequate, and an initial high setting of heat will be required. You should see CO₂ being evolved and some CaCO₃ may precipitate.
13. At the end of the five minutes heating period, use the beaker tongs to remove the beaker from the hot plate and place it in an ice bath. Allow the solution to cool to room temperature.
14. Measure and record the *pH* of the cooled solution.
15. Filter the solution to remove any suspended CaCO₃.
16. Transfer three 25 cm³ aliquots of this filtered solution to three Erlenmeyer flasks. Add about 25 cm³ of deionized water to each flask, followed by 15 drops of 6 M HCl.
17. Titrate each sample according to steps 7 - 11.

b) Procedure for standardization of EDTA

1. Weigh approximately 0.35 g of dried primary standard CaCO₃, (molar mass 100.09 g mol⁻¹) which will be found in the weighing bottle in the desiccator. Note: CaCO₃ is hygroscopic.
2. Add 25 cm³ of deionized water to the CaCO₃, then carefully add 5 cm³ of 6 M HCl. Quickly cover with a watch glass.
3. When the CaCO₃ has dissolved, quantitatively transfer the solution to a 250 cm³ volumetric flask and dilute to the mark.
4. Transfer three 25 cm³ aliquots of the standard Ca²⁺ solution to three Erlenmeyer flasks.
5. Proceed to titrate each sample according to steps 7 - 11, following each step in sequence.

Tasks:

- 1.1 Calculate the solubility of calcium carbonate (expressed in mol dm⁻³) in a solution saturated with both CaCO₃ and CO₂ and in solution free of CO₂.
- 1.2 List all the ionic species that increase in concentration as a result of the dissolving of CaCO₃ in water.
- 1.3 Given below are brief descriptions of two solutions. Circle the one in which the concentration of CO₃²⁻ would be highest:
- a) a solution produced by dissolving CaCO₃(s) in CO₂-saturated water
 - b) a solution produced by dissolving CaCO₃(s) in CO₂-free water
- 1.4 Will the solubility of CaCO₃ increase or decrease in a solution from which the CO₂ has been removed?
-

SOLUTION

- 1.1 The results of the titration (volumes of titrants, mass of CaCO₃) and calculation of the concentration of the standardized EDTA solution were required to be written on the Answer Sheet.
- Moreover, it was necessary to measure and record *pH* values of the sample at steps 2, 4, and 14.
- It was expected to show the calculation of the solubility of CaCO₃ in its saturated solutions containing CO₂ and in those without CO₂.

The other tasks to be solved:

- 1.2 The ionic species mentioned above are as follows: Ca²⁺, HCO₃⁻, OH⁻.
- 1.3 Correct answer: (b) A solution produced by dissolving CaCO₃(s) in CO₂-free water.
- 1.4 The solubility of CaCO₃ will decrease.
-
-

25th



International Chemistry Olympiad

**5 theoretical problems
2 practical problems**

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

THEORETICAL PROBLEMS

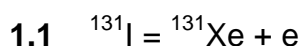
PROBLEM 1

^{131}I is a radioactive isotope of iodine (e^- emitter) used in nuclear medicine for analytical procedures to determine thyroid endocrine disorders by scintigraphy. The decay rate constant, k , of ^{131}I is $9.93 \times 10^{-7} \text{ s}^{-1}$.

Questions:

- 1.1 Write the decay reaction of ^{131}I .
- 1.2 Calculate the half-life of ^{131}I expressed in days.
- 1.3 Calculate the time necessary (expressed in days) for a sample of ^{131}I to reduce its activity to 30 % of the original value.
- 1.4 Knowing that a Geiger counter detects activities of the order of $10^{-4} \mu\text{c}$, calculate the minimum amount of ^{131}I (in grams) which could be detected by this counter.
1 Curie (c) is the amount of a radioisotope that produces 3.7×10^{10} disintegrations s^{-1} .

SOLUTION



1.2 Decay reactions are first order reactions. Then:

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

$$t_{1/2} = \frac{0.693}{9.93 \times 10^{-7} \times 86400 \text{ s d}^{-1}} = 8.08 \text{ d}$$

1.3 For a first order reaction:

$$\ln \frac{C_0}{C} = k t$$

where c_0 and c are the concentrations at time 0 and time t , respectively. Then:

$$\ln \frac{100}{30} = 9.93 \times 10^{-7} \times t$$

$$t = \frac{1.212 \times 10^6}{8.64 \times 10^4} = 14.03 \text{ d}$$

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

$$1 \text{ mc} = 3.7 \times 10^7 \text{ dis s}^{-1}$$

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

Then:

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

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

$$m = - \frac{dN}{dt} \times \frac{t_{1/2} \times A_r(\text{I})}{\ln 2 \times N_A} = \frac{3.7 \times 6.98 \times 10^5 \times 131}{0.693 \times 6.02 \times 10^{23}} = 8.11 \times 10^{-16} \text{ g}$$

PROBLEM 2

The reflux of bile duodenal matter is suspected to be the major cause of gastritis and medical therapy is based on the treatment with antiacida that buffer the *pH* of gastric juices by binding bile acids and lysolecithin. Two bile acids, i. e. cholic acid (CA) and glycocholic acid (GCA), were chosen to study the properties of some antiacida commercial formulations. Separation and determination of the two acids in artificial and natural gastric juices were required and high performance liquid chromatography (HPLC) was used as analytical technique.

Two chromatographic columns (A and B, respectively) were selected on the base of published literature data and preliminary tests were carried out to choose the column (between A and B) which would yield the best separation of the aforementioned compounds. The retention times (*t*) of the two acids, of a substance not retained by the chromatographic columns and of a compound used as internal standard (i.s.) are shown in the first two columns of the Table. Both chromatographic columns are 25 cm long and show the efficiency of 2.56×10^4 theoretical plates per meter ($N\ m^{-1}$).

In actual analysis, an artificial gastric juice was extracted with an appropriate solvents mixture and then final solution ($1\ cm^3$) contained 100 % of the two acids present in the original mixture. $100\ \mu cm^3$ of the extract with $2.7\ \mu moles$ of the internal standard were analysed by HPLC using the selected column. The response factors (F) of CA and GCA with respect to the i.s. and the chromatographic peak areas of the two compounds are reported in the Table.

	Column A <i>t</i> (s)	Column B <i>t</i> (s)	F	Area
Unretained compound	120	130	-	-
Cholic Acid (CA)	380	350	0.5	2200
Glycocholic Acid (GCA)	399	395	0.2	3520
Internal standard	442	430	-	2304

In answering to the questions remember that:

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

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

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

Questions:

- 2.1** Using R , α and K' values, demonstrate which of the two chromatographic columns would you use, considering that an accurate determination requires the best possible (baseline) separation of all compounds (do not take into account the unretained compound)?
- 2.2** Calculate the amounts of each acid in the extract solution.

SOLUTION

Nowadays, chromatography is the most powerful technique for the separation and quantification of organic compounds from volatiles to high molecular weight substances. In conjunction with a mass-spectrometer, it can lead to the undoubted identification of compounds even in extremely complex mixtures. Liquid chromatography (HPLC) is becoming a routine analytical technique in a large variety of fields and in particular in biochemistry and in medicine where compounds are unsuitable for gas chromatographic analysis.

- 2.1** Baseline separation requires $R \geq 1.5$ for each pair of peaks (GCA/CA, i.s./GCA). N can be calculated from $N \text{ m}^{-1}$ value taking into account that the column length is 25 cm:

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

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

For column A:

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

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

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

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

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

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

For column B:

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

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

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

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

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

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

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

2.2 The amount of acid in the extract solution (1 cm³) can be calculated from the relationship:

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

where F is the response factor.

Therefore:

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

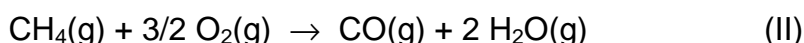
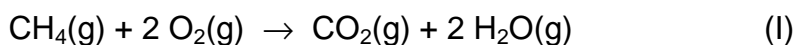
$$n(\text{CA}) = \frac{2200}{2304} \times \frac{1}{0.5} \times 2.7 \times 10 = 51.6 \mu\text{mol}$$

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

PROBLEM 3

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The student may be aware that the acceptable concentration of CO in air is ≤ 5 ppm and the maximum tolerable level is 50 ppm.

The following reactions occur in methane burner:



Compound	CH ₄	O ₂	CO ₂	CO	H ₂ O
ΔH_f° (kJ mol ⁻¹)	-74.9	0	-393.5	-110.5	-241.8
S° (J K ⁻¹ mol ⁻¹)	186.2	205.0	213.6	197.6	188.7

Questions:

- 3.1** Calculate the equilibrium constants for both reactions at $T = 1500$ K assuming that the values ΔH° and ΔS° are independent of the temperature.
- 3.2** Find the relationship between the mole numbers of oxygen and carbon monoxide at equilibrium ($T = 1500$ K, $p = 1$ atm) when air is admitted into the burner in such amount that the mole ratio CH₄ : O₂ is 1 : 2.

Assume the following volume composition of air: 80 % N₂ and 20 % O₂.

Make the approximation that $n(\text{CH}_4) \cong 0$ at equilibrium and justify it on the bases of the answers to the question 3.1.

- 3.3** Calculate the equilibrium mole fraction x of CO in the conditions given in the question 3.2. Assume that the mole fraction of CO is very small in comparison with that of CO₂ and consequently, the total number of moles does not appreciably vary during the combustion. Justify this assumption.

- 3.4** Repeat the calculations of items 3.2 and 3.3 assuming that twice the amount of air (compared to the conditions in question 3.2) is admitted into the burner (4 mol O₂ : 1 mol CH₄).
- 3.5** Calculate the concentrations of CO (expressed as ppm by volume) in the fumes after condensation of water vapour under the conditions of question 3.2 and 3.4, assuming that the composition does not change appreciably during the cooling from 1500 K to room temperature and neglecting the contribution of water vapour to the composition of the gas phase.

SOLUTION

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The problem involves the calculation of equilibrium constants, consideration of simultaneous equilibria and simple stoichiometric calculations.

$$\mathbf{3.1} \quad \Delta_1 H^0 = 74.9 - 393.5 - (2 \times 241.8) = -802.2 \text{ kJ mol}^{-1}$$

$$\Delta_1 S^0 = -186.2 - (2 \times 205.0) + 213.6 + (2 \times 188.7) = -5.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_1 = \exp - \frac{\Delta_1 H^0 - T \Delta_1 S^0}{R T} = \exp \frac{802.2 - 1.5 \times 5.2}{8.314 \times 1.5} = 4.62 \times 10^{27}$$

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

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

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

- 3.2** Since K_1 and K_{II} are very large, both equilibria are completely shifted to the right so that $n_{\text{CH}_4} = 0$.

$$\text{At equilibrium: } n_{\text{CH}_4} = 0; \quad n_{\text{H}_2\text{O}} = 2; \quad n_{\text{N}_2} = 8; \quad n_{\text{CO}_2} + n_{\text{CO}} = 1;$$

$$n_{\text{O}_2} = 2 - (2 n_{\text{CO}_2} + 1.5 n_{\text{CO}}) = 0.5 n_{\text{CO}}$$

- 3.3** In reaction I the total number of moles does not vary; in reaction II it changes from 8.5 to 9 (taking into account the presence of N₂), but this change affects the total number of moles only negligibly since $K_{II} \ll K_1$.

Before reaction: $n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{O}_2} + n_{\text{N}_2} = 1 + 2 + 8 = 11$

$$\frac{K_{\text{II}}}{K_{\text{I}}} = \frac{p_{\text{CO}} p_{\text{O}_2}^{1/2}}{p_{\text{CO}_2}} = \frac{x_{\text{CO}} (x_{\text{O}_2} p)^{1/2}}{x_{\text{CO}_2}}$$

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{tot}}} = \frac{1 - n_{\text{CO}}}{n_{\text{tot}}} = \frac{1}{11} \quad \text{since } n_{\text{CO}} \ll n_{\text{CO}_2} \text{ as a consequence of } K_{\text{II}} \ll K_{\text{I}}$$

$$x_{\text{CO}}^{3/2} = \frac{K_{\text{II}} (2/p)^{1/2}}{K_{\text{I}} \cdot 11} = \frac{2.13 \times 10^{22} \times 1.414}{4.62 \times 10^{27} \times 11} = 5.93 \times 10^{-7}$$

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

3.4 $n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{O}_2} + n_{\text{N}_2} = 1 + 4 + 16 = 21$

At equilibrium: $n_{\text{O}_2} = 4 - (2 n_{\text{CO}_2} + 1.5 n_{\text{CO}}) = 2 + 0.5 n_{\text{CO}} = 2$

$$n_{\text{CO}_2} = 1 - n_{\text{CO}}$$

$$\frac{K_{\text{II}}}{K_{\text{I}}} = \frac{x_{\text{CO}} (x_{\text{O}_2} p)^{1/2}}{x_{\text{CO}_2}} = x_{\text{CO}} (2/21)^{1/2} \times 21 = (42)^{1/2} x_{\text{CO}}$$

$$x_{\text{CO}} = 42^{-1/2} \frac{K_{\text{II}}}{K_{\text{I}}} = 42^{-1/2} \times \frac{2.13 \times 10^{22}}{4.62 \times 10^{27}} = 7.11 \times 10^{-7}$$

3.5 As a consequence of the condensation of water vapour, the number of moles in the gaseous phase changes from 11 to 9 in case c), and from 21 to 19 in case d).

Therefore the mole fraction of CO changes to:

$$x_{\text{CO}} = 7.06 \times 10^{-5} \times \frac{11}{9} = 8.63 \times 10^{-5} \quad \text{and to:}$$

$$x_{\text{CO}} = 7.11 \times 10^{-7} \times \frac{21}{19} = 7.86 \times 10^{-7} \quad \text{in case 3.4}$$

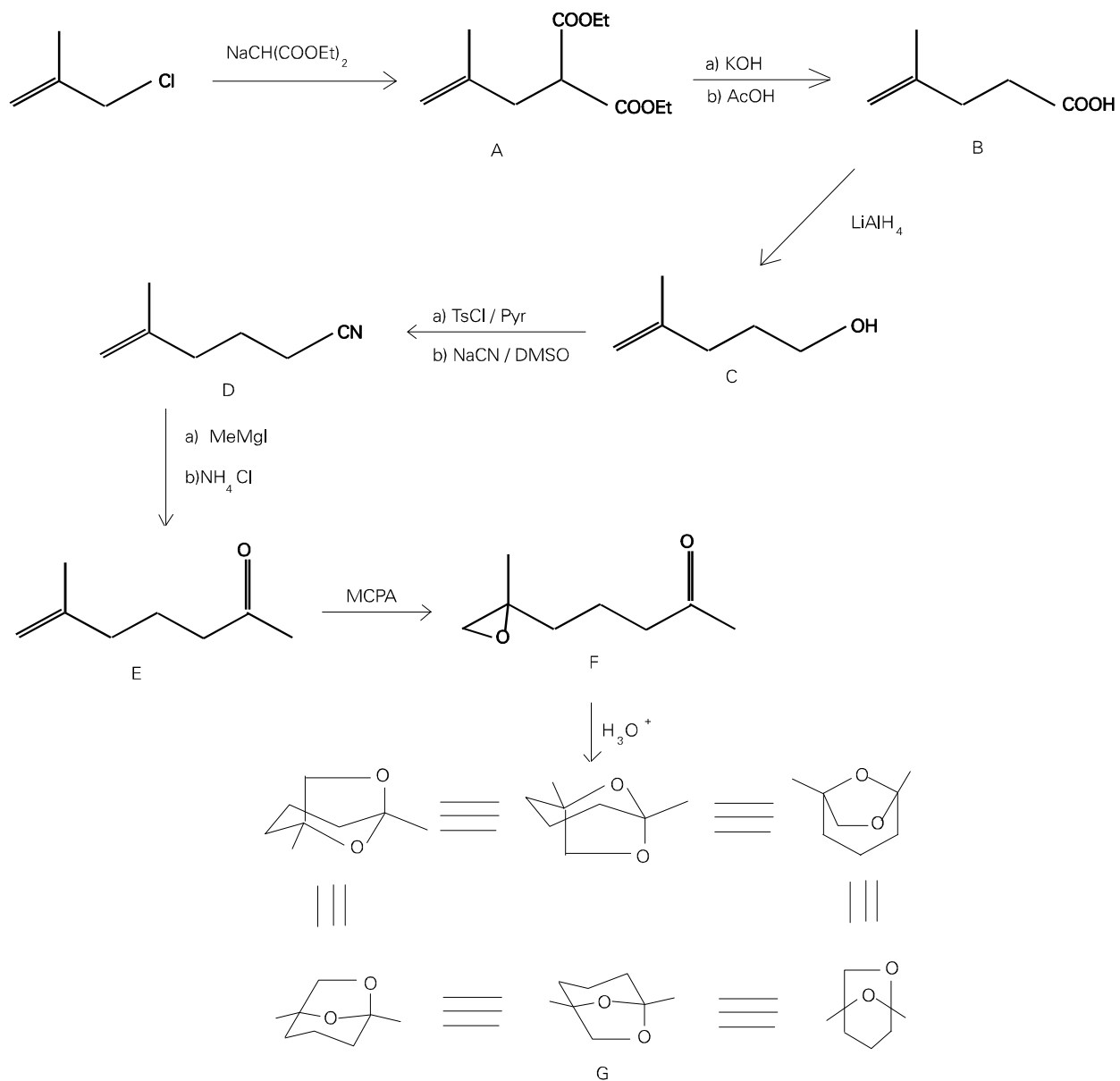
These values correspond to 86 and 0.8 ppm, respectively.

PROBLEM 4

- i) Frontalin is a pheromone of the western pine beetle with composition C 67.58 %, H 9.92 %, O 22.50 %. It is an acetal that can be prepared through a rather long synthesis starting from sodium diethylmalonate (sodium salt of propanedioic acid, diethyl ester) and 3-chloro-2-methylpropene.
- ii) The product **A** resulting from this first step is subsequently hydrolyzed by conc. potassium hydroxide and then decarboxylated by treatment with hot acetic acid to give a compound **B**. The latter reacts with aq NaHCO₃ (gas evolution is observed) as well as with cold aq KMnO₄ which turns to a brown colour.
- iii) The compound **B** is then converted by LiAlH₄ into a new compound **C** (C₆H₁₂O).
- iv) Treatment of **C** with p-toluenesulfonyl chloride in pyridine and then sodium cyanide in dimethylsulfoxide, affords **D** (C₇H₁₁N).
- v) The subsequent reaction of **D** with methylmagnesium iodide, followed by hydrolysis, yield **E** (C₈H₁₄O). **E** shows IR absorption at ca 1700 cm⁻¹.
- vi) The epoxidation of **E** with metachloroperbenzoic acid then affords **F** (C₈H₁₄O₂) which, by treatment with diluted acids is converted to frontalin acetal **G**.

Questions:

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

SOLUTION**4.1**

PROBLEM 5

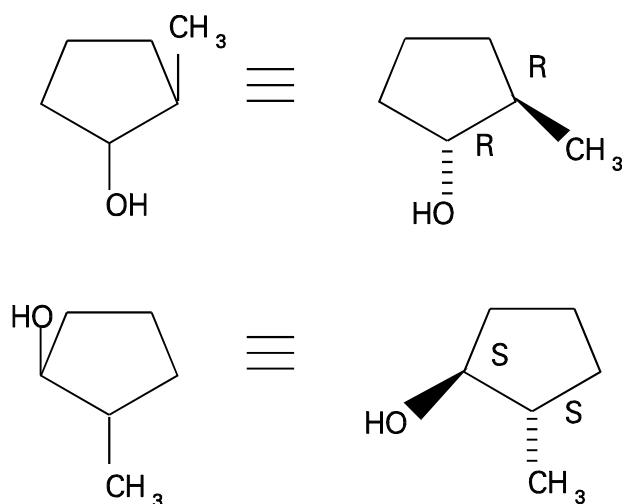
By treatment with a chiral optically active hydroborating agent (R_2^*BH) and subsequent oxidative work-up, 1-methylcyclopentene affords a mixture of alcohols that rotates the plane of the polarized light.

Questions:

- 5.1 Write the structures of the alcohols.
- 5.2 Assign the configurations (R , S) to the chiral centres.
- 5.3 Explain in a sentence why the obtained mixture of alcohols exhibits optical activity.

SOLUTION

5.1, 5.2



- 5.3 Due to the chirality of the hydroborating agent, one enantiomer prevails against the other.

In alternative: $R,R > S,S$ or $S,S > R,R$

PRACTICAL PROBLEMS

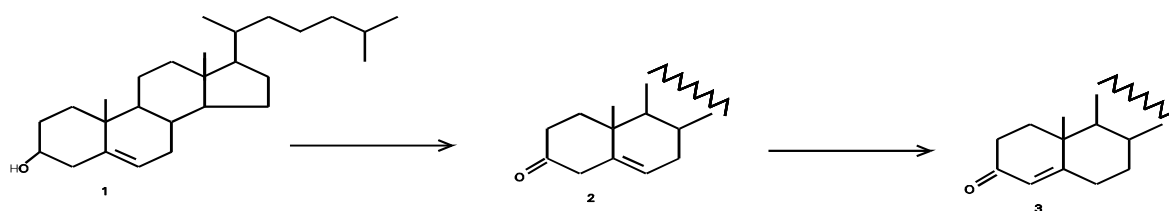
PROBLEM 1 (Practical)

Synthesis

Cholesterol (1) is a natural sterol metabolite present in animal and vegetal organisms. This compound can be oxidized by Jones' reagent into its corresponding 3-ketoderivative (2). The latter, when treated with bases, undergoes isomerization of the carbon-carbon double bond leading to α,β -unsaturated ketone (3).

The conversion of Δ^5 -3 β -hydroxy steroids into their corresponding Δ^4 -3-ketones is an important reaction in steroid chemistry and represents the last step of the synthesis of a variety of commercial hormones.

You will be marked for the purity of the product (3).



Procedure:

- Dissolve your pre-weighed sample of cholesterol (386 mg, 1 mmol) contained in a 50 cm³ flask A with acetone (20 cm³) warming gently the flask in a bath tub of hot water. When the sample is completely dissolved, cool the flask containing the solution to the temperature by cold water.
- Add dropwise 0.40 cm³ of Jones' reagent to the solution, gently swirling the flask in a bath of cold water. The formation of a green precipitate [Cr₂(SO₄)₃] is observed during the addition of Jones' reagent.
- Remove the green precipitate by filtration with paper filter.
- Add slowly water (10 cm³) to the clean filtrate. The ketone (2) begins to precipitate.
- Filter the precipitate over the Büchner funnel under reduced pressure, washing the crystals with small portions of a 2 : 1 acetone/water mixture.
- Dissolve the ketone (2) in methanol (15 cm³). Add to the solution just one drop of 5 % methanolic NaOH solution and warm the mixture in a bath of hot water for 10 min.

- g) The Δ^4 -3-ketosteroid (3) precipitates spontaneously, upon addition of water (ca. 2 cm³) to the cooled reaction mixture. Filter the crystals over the Büchner funnel under reduced pressure and recrystallize the product by methanol. If you do not get the crystals, add a few drops of water. *Remember! You are getting a mark for the purity, not the yield.*
- h) Dry carefully the crystals on a porous plate. Determine the melting point of the ketone (3) and write its value on your student's report. Taking into account the correction reported on the top of the thermometer (see example at the end).
- i) Put the crystals in the plastic vial B, write on it your personal identification number (see the left corner of your badge), and deliver it to one of the supervisors.

The melting point of the ketone (3) will be checked by the lab supervisors.

SOLUTION

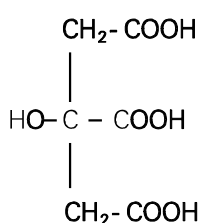
Points were given accordingly to the amount of product.

Some additional points were given for melting point measurements.

PROBLEM 2 (Practical)Analysis

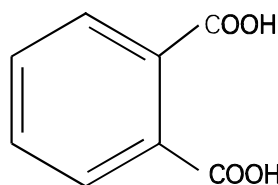
Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is widely distributed in plants and in animal tissues. Lemon juice contains from 5 to 8% of this acid. It is produced by mycological fermentation on an industrial scale using crude sugar solutions, such as molasses, and stains of *Aspergillus niger*.

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



MM = 192.12 g/mol

$\text{pK}_1 = 3.06$; $\text{pK}_2 = 4.74$; $\text{pK}_3 = 5.40$



MM = 204.23 g/mol

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

Procedure:

A preweighed quantity (2.050 g) of potassium hydrogen phthalate is in the 100 cm³ volumetric flask B. Dilute this sample with water to the mark. Phenolphthalein indicator (2 - 3 drops) is added to an aliquot of 25.0 cm³ of the resulting solution and the solution is then titrated with the NaOH solution that has to be standardized.

Give the concentration of the NaOH solution.

- b) Titrimetric determination of citric acid

Procedure:

The unknown sample of citric acid is in the 100 cm³ volumetric flask C. Dilute the sample with water to the mark. Transfer 25.0 cm³ of the resulting solution into a 250 cm³ Erlenmeyer flask and dilute with water. Add 2 – 3 drops of phenolphthalein indicator and titrate with the previously standardized NaOH solution.

Give the mass of citric acid.

SOLUTION

Marks were given accordingly to determined mass of citric acid.

Some additional points were given for correct calculations.
