

17th



International Chemistry Olympiad

**8 theoretical problems
1 practical problem**

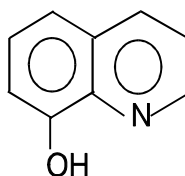
THE SEVENTEENTH INTERNATIONAL CHEMISTRY OLYMPIAD 1–8 JULY 1985, BRATISLAVA, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A solution was formed from 0.5284 g of a sample of an alloy containing aluminium. The aluminium was then precipitated as aluminium 8-hydroxyquinolate. The precipitate was separated, dissolved in hydrochloric acid and the 8-hydroxyquinoline formed was titrated with a standard solution of potassium bromate containing potassium bromide. The concentration of the standard potassium bromate solution was 0.0200 M and 17.40 cm³ of it were required. The resultant product is a dibromo derivative of 8-hydroxyquinoline.

The structural formula of 8-hydroxyquinoline is:



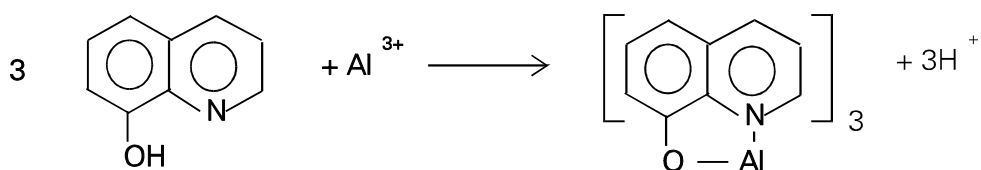
The relative atomic mass of aluminium is 26.98.

Problems:

- 1.1 Write the balanced equation for the reaction of the aluminium (III) ion with 8-hydroxyquinoline, showing clearly the structure of the products.
- 1.2 Give the name of the type of compound which is formed during the precipitation.
- 1.3 Write the balanced equation for the reaction in which bromine is produced.
- 1.4 Write the balanced equation for the reaction of bromine with 8-hydroxyquinoline.
- 1.5 Calculate the molar ratio of aluminium ions to bromate ions.
- 1.6 Calculate the percentage by weight of aluminium in the alloy.

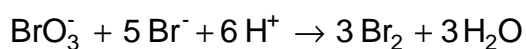
SOLUTION

1.1



1.2 Chelate

1.3



1.4



1.5 As $\text{Al} \triangleq \text{Al}(\text{oxine})_3 \triangleq 3 \text{ oxine} \triangleq 12 \text{ Br} \triangleq 12 \text{ e}$,
the chemical equivalent of Al equals $26.98/12 = 2.248$.

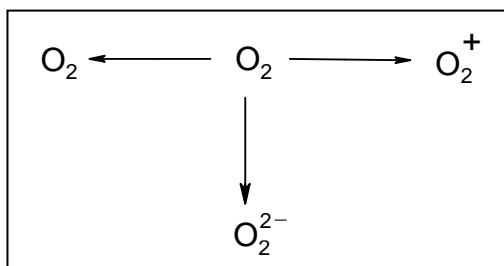
1.6 The percentage of the aluminium in the sample is

$$\% \text{Al} = \frac{17.40 \times 0.1000 \times 2.248 \times 100}{528.4} = 0.74$$

The alloy contains 0.74% of aluminium.

PROBLEM 2

It is possible to prepare compounds containing ions O_2^- , O_2^{2-} or even O_2^+ . These ions are usually formed from molecules of oxygen during various reactions, as indicated in the scheme below:



- 2.1** Indicate clearly which of the above reactions correspond to the oxidation and which to the reduction of the oxygen molecule.
- 2.2** For each of the ions in the scheme give the formula of a compound containing that particular ion.
- 2.3** It has been found that one of the species in the scheme is diamagnetic. Which one is it?
- 2.4** Copy out the following table:

Species	Bond order	Interatomic distance	Bonding energy
O_2			
O_2^+			
O_2^-			
O_2^{2-}			

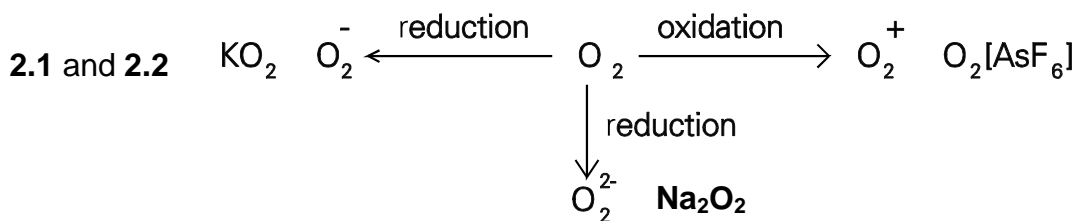
The interatomic distances, O-O, in the above species have the values 112, 121, 132 and about 149 pm. Write these values in the appropriate column in the table.

$$1 \text{ pm} = 10^{-12} \text{ m.}$$

- 2.5** Three of the bond energies, $E_{\text{O-O}}$, have the values approximately 200, 490 and 625 kJ mol^{-1} . The value for one of the species is uncertain and, therefore, not given. Write the values in the appropriate spaces in the table.

- 2.6 Determine the bond order for the individual species and write the answers in the table.
- 2.7 Is it possible to prepare compounds containing the F_2^{2-} ion? Give reasons for your answer.

SOLUTION



2.4 - 2.6

Species	Bond order	Interatomic distance (pm)	Bonding energy (kJ mol^{-1})
O_2	2	121	490
O_2^+	2.5	112	625
O_2^-	1.5	132	–
O_2^{2-}	1	149	200

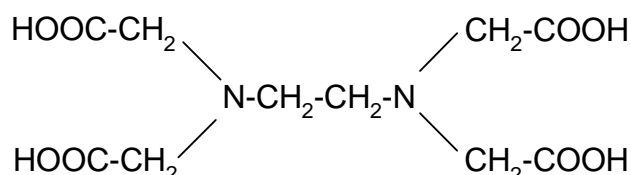
- 2.7 Ion F_2^{2-} does not exist. The number of electrons in the bonding and antibonding orbitals would be the same and thus, the bonding F–F cannot be formed. Therefore, there exists no compound containing ion F_2^{2-} .

PROBLEM 3

Calcium sulphate is a sparingly soluble compound. Its solubility product is given by:

$$K_s(\text{CaSO}_4) = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 6.1 \times 10^{-5}$$

Ethylenediaminetetraacetic acid (EDTA) has the formula $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$ and the structure:



The anion of this acid, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$, forms a stable complex $\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{2-}$ with calcium ions. The stability constant of this complex ion is given by:

$$K = \frac{[\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{2-}]}{[\text{Ca}^{2+}][\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}]} = 1.0 \times 10^{11}$$

EDTA is completely dissociated in strongly alkaline solution. The equation for this dissociation is:

Problems:

- 3.1** Calculate the concentration of calcium ions in a saturated solution of calcium sulphate.
- 3.2** Calculate the concentration of free Ca^{2+} cations in a solution of 0.1 M $\text{Na}_2(\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$. You should ignore any protonation of the ligand.
- 3.3** How many moles of calcium sulphate will dissolve in 1 litre of a strongly alkaline solution of 0.1 M $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$?
What would be the concentrations of the calcium and sulphate ions in the resulting solution?
- 3.4** Suggest a structure for the complex ion $[\text{CaC}_{10}\text{H}_{12}\text{N}_2\text{O}_8]^{2-}$ assuming that it is approximately octahedral.
- 3.5** Is the structure you have suggested in 4) optically active?
If your answer is "yes" then draw the structure of the other optical isomer enantiomer).
- 3.6** Explain why the complexes formed by the anion $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8^{4-}$ are exceptionally stable.

SOLUTION

3.1 $[\text{Ca}^{2+}] = 7.8 \times 10^{-3} \text{ mol dm}^{-3}$

3.2 $[\text{Ca}^{2+}] = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$

3.3 The CaSO_4 amount dissolved is 0.1 mol.

$[\text{SO}_4^{2-}] = 0.10 \text{ mol dm}^{-3}$.

$[\text{Ca}^{2+}] = 6.1 \times 10^{-4} \text{ mol dm}^{-3}$

3.4 + 3.5

The complex is optically active. The structures of both enantiomers are

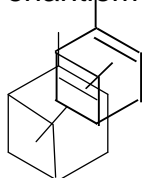


3.6 The high number of the chelate rings. Other factors also contribute to the complex ability, e.g. the character of the donor atoms, the magnitude and distribution of the charges in the anion, etc.

PROBLEM 4

At a temperature around 200 °C the racemisation of pinene can be followed in the gaseous phase by measuring the optical rotation.

If, for example, you take the (+)-enantiomer of α -pinene



an equilibrium is gradually established between the two enantiomers (optical isomers). The two opposing reactions are both of the first order.

In 1927 D. F. Smith obtained the following data in his study of racemisation of α -pinene:

T/K	α_1	α_2	t/min
490.9	32.75	18.01	579
490.9	29.51	15.59	587
503.9	30.64	8.74	371
505.4	12.95	8.05	120
510.1	23.22	6.15	216

α_1 and α_2 are the values for optical rotation in terms of the dimensions of the polarimeter scale; t is the time which has elapsed between the two measurements.

Problems:

4.1 What is the value for the equilibrium constant for the racemisation?

What is the corresponding value of $\Delta_r G^\circ$ (racemisation)?

What is the relationship between the forward and backward rate constants, k_1 and k_{-1} , in a state of dynamic equilibrium?

4.2 State the rate equation for the racemisation of pinene.

Derive a relationship which could be used to calculate the rate constant for the conversion of the (+)-enantiomer into the (-)-enantiomer using the data given in the table.

- 4.3 Calculate the rate constant for this reaction at the four temperatures given in the table.
- 4.4 Calculate the average value of the activation energy for this reaction. You should take the average of the values at a minimum of three temperatures or use a graphical method.

HINT:

If the loss of concentration of a substance obeys the rate equation:

$$-\frac{dc}{dt} = k(2c - \text{constant})$$

Then the dependence of concentration on time is given by:

$$\ln \frac{2c_0 - \text{constant}}{2c - \text{constant}} = 2kt$$

where c_0 is the initial concentration at time $t = 0$.

SOLUTION

- 4.1 The racemisation equilibrium constant equals unity at all temperatures and $\Delta_r G^\circ = 0$.
- 4.2 If the concentration of one enantiomer is c and that of the other is c' , then it holds for the rate of the loss of c that

$$-\frac{dc}{dt} = k_1c - k_{-1}c' = k(c - c') \text{ for } k_1 = k_{-1} = k$$

If the initial concentrations are c_0 and c_0' , then

$$c' = c_0 - c + c_0'$$

can be substituted for c' in the rate equation, obtaining

$$-\frac{dc}{dt} = k(2c - c_0 - c_0')$$

It then holds for concentrations c_1 and c_2 measured at times t_1 and t_2 , respectively, that

$$\ln \frac{2c_1 - c_0 - c_0'}{2c_2 - c_0 - c_0'} = 2k(t_2 - t_1)$$

and since $c_0 + c_0' = c_1 + c_1' = c_2 + c_2'$

$$\ln \frac{c_1 - c_1'}{c_2 - c_2'} = 2k(t_2 - t_1)$$

The measured optical rotation α is proportional to $c - c'$; hence $\ln \frac{\alpha_1}{\alpha_2} = 2k(t_2 - t_1)$

4.3

T/K	490.9	503.9	505.4	510.1
$10^4 k \text{ min}^{-1}$	5.3	16.9	19.8	30.7

$$4.4 \quad \ln \frac{k_2}{k_1} = \frac{E_A}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad E_A = \ln \frac{k_2}{k_1} \times \frac{R T_1 T_2}{T_2 - T_1}$$

If e.g. the value of k for 490.9 K (the average of two measurements) is combined with each of the remaining three values, three values of activation energy are obtained: 183400 J mol⁻¹, 177500 J mol⁻¹, 190500 J mol⁻¹. The average value equals 187100 J mol⁻¹.

PROBLEM 5

The equilibrium voltage of the cell,

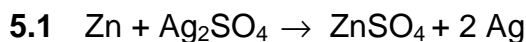


was measured at several temperatures and the results of the measurements are given in the following table:

t / °C	10	20	30
E / V	1.5784	1.5675	1.5566

Problems:

- 5.1 Give the equation for the reaction occurring in this galvanic cell.
- 5.2 Determine the value of the cell voltage at the temperature $T = 298 \text{ K}$.
- 5.3 Determine $\Delta_r G_{298}$ of the cell reaction.
- 5.4 Determine $\Delta_r H_{298}$ of the cell reaction.

SOLUTION

5.2 The temperature dependence is described by the equation,

$$E_T = E_{T_0} + \frac{dE}{dT} \cdot (T - T_0)$$

It follows from the plot for the slope,

$$\frac{dE}{dT} = -1.09 \times 10^{-3} \text{ V K}^{-1}$$

Hence,

$$E_{298} = 1.5675 - 1.09 \times 10^{-3} \times 5 = 1.562 \text{ V}$$

5.3 The relationship,

$$\Delta_r G = -nFE$$

holds for $\Delta_r G$. Then

$$\Delta_r G_{298} = -2 \times 96484.6 \times 1.563 = -301417.9 \text{ J mol}^{-1}$$

5.4 The equation,

$$\Delta G = \Delta H - T \Delta S,$$

is employed to calculate $\Delta_r H_{298}$, substituting

$$\Delta S = -\frac{dG}{dT}$$

Rearrangement yields the relationship

$$\Delta H = \Delta G - T \frac{dG}{dT}$$

As it holds that

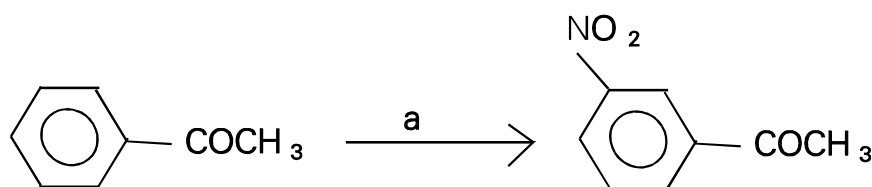
$$\frac{dG}{dT} = -nF \frac{dE}{dT}$$

the final expression is:

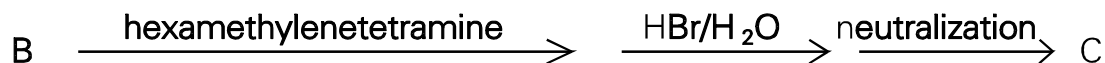
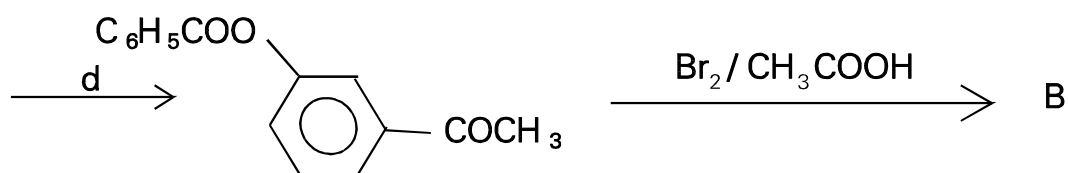
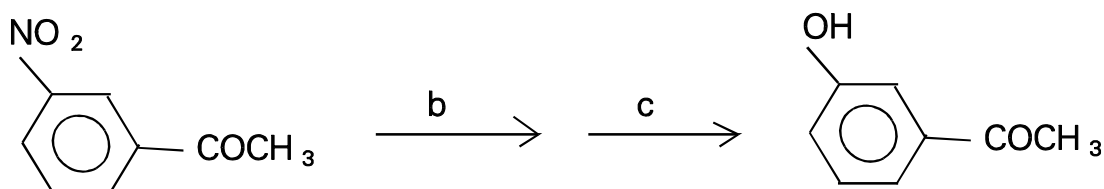
$$\begin{aligned}\Delta_r H_{298} &= \Delta G_{298} + nFT \frac{dE}{dT} \\ &= -301417.9 + [2 \times 96\,484.6 \times 298 \times (-1.09 \times 10^{-3})] = 364098.1 \text{ J mol}^{-1}\end{aligned}$$

PROBLEM 6

The following scheme describes the synthesis of a compound **D** (with sympathomimetic effects) whose skeleton consists of 2-phenylethylamine.



A Acetophenone



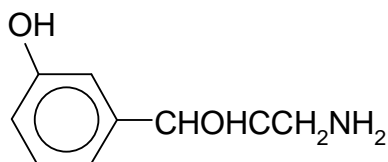
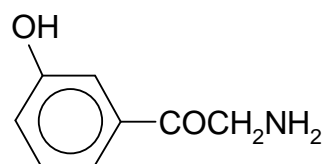
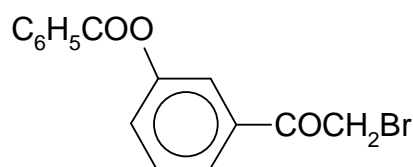
Problems:

- 6.1 What reagents were used in steps **a**, **b**, **c**, and **d**?
- 6.2 Give the structural formulae of compounds **B**, **C** and **D**.
- 6.3 Is it possible to prepare 3-hydroxyacetophenone from the reaction between phenol, acetylchloride and AlCl_3 ? Give reasons for your answer.
- 6.4 Give the formulae of the compounds that are formed by the reaction of compound **C** with a) 10% HCl and b) 10% NaOH .
- 6.5 By the asterisk denote the chirality centre in the formula of compound **D**.
- 6.6 Give the spatial formula of enantiomer (R) of compound **D**.

SOLUTION

- 6.1 a) $\text{HNO}_3/\text{H}_2\text{SO}_4$
 b) Fe/H^+
 c) NaNO_2/HCl
 d) benzoylchloride

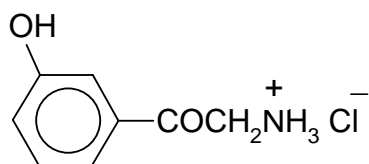
6.2



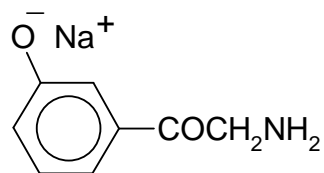
6.3 No

6.4

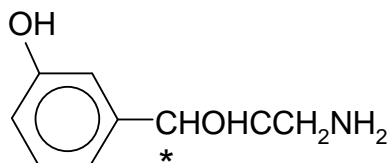
a)



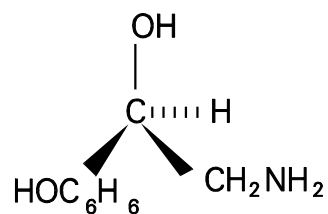
b)



6.5



6.6

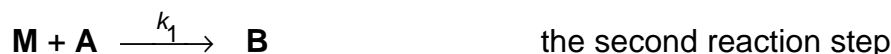
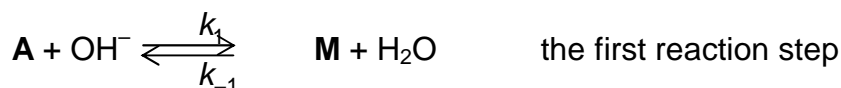


PROBLEM 7

Propanal, **A**, reacts in an aqueous-ethanolic solution of sodium hydroxide to yield compound **B** that is readily dehydrated to give compound **C** (C₆H₁₀O).

Problems:

- 7.1** Give the structural formulae of substances **B** and **C**.
- 7.2** Give the formula of intermediate **M** that is formed from propanal **A** by the action of hydroxide ions.
- 7.3** Give the formulae of the two most important mesomeric structures of intermediate **M** and denote the nonbonding electron pairs and the charge distribution.
- 7.4** The reaction of propanal **A** with sodium hydroxide, producing substance **B**, can be described by the scheme:



The rate of the formation of substance **B** is given by the equation:

$$v = k_2 [\text{M}] [\text{A}] \quad (1)$$

The above values of k are the rate constants for the individual reaction steps.

Assume that the concentration of intermediate **M** is small and constant during the reaction and express this fact by an equation involving terms with constants k_1 , k_{-1} and k_2 .

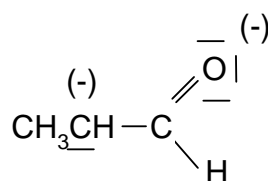
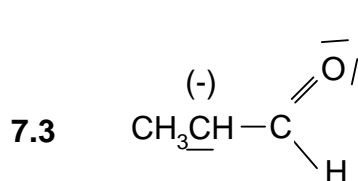
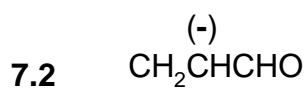
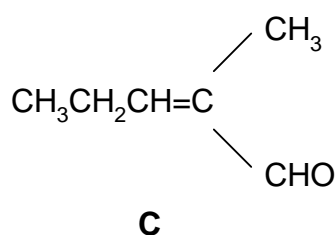
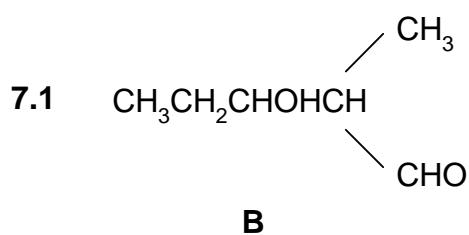
$$\frac{d[\text{M}]}{dt} = 0 \quad (2)$$

Derive an expression for the concentration of **M** from equation 2 and then substitute for **[M]** in equation 1. This gives equation 3 which is the complete rate equation for the formation of substance **B**.

If it is assumed that the second reaction step is rate determining, then the rearrangement of equation 3 gives equation 4, the rate equation.

Give equations 2, 3, and 4.

- 7.5** Determine the overall order of the reaction described by equation 4.

SOLUTION

7.4

$$\frac{d[\mathbf{M}]}{dt} = 0 = k_1[\mathbf{A}][\text{OH}^-] - k_{-1}[\mathbf{M}] - k_2[\mathbf{A}][\mathbf{M}] \quad (2)$$

$$[\mathbf{M}] = \frac{k_1[\mathbf{A}][\text{OH}^-]}{k_{-1} + k_2[\mathbf{A}]} \quad v = \frac{k_1 k_2 [\mathbf{A}]^2 [\text{OH}^-]}{k_{-1} + k_2[\mathbf{A}]} \quad (3)$$

for $k_2[\mathbf{A}][\mathbf{M}] \ll k_{-1}[\mathbf{M}]$ it holds, that

$$v = \frac{k_1 k_2 [\mathbf{A}]^2 [\text{OH}^-]}{k_{-1}} \quad (4)$$

7.5 Rate equation (4) corresponds to the overall reaction order of (3).

PROBLEM 8

The following reaction scheme represents part of anaerobic degradation of saccharides, i.e. the glycolysis, involving equilibrium constants K_1 and K_2 :



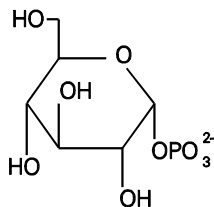
Problems:

- 8.1** Give the structural formulae for all the three reactants (compounds) that are mutually interconverted, i.e. α -D-glucose-1-phosphate, α -D-glucose-6-phosphate and α -D-fructose-6-phosphate.
- 8.2** In the beginning of the reaction the reaction mixture contained 1 mmol of glucose-6-phosphate. Calculate the amounts of glucose-6-phosphate, glucose-1-phosphate and fructose-6-phosphate in the mixture at equilibrium. (As the reaction take place in a constant volume, the ratio of the amounts of substances equals that of their concentrations.)

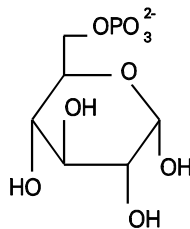
SOLUTION

8.1

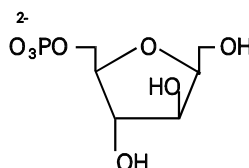
α -D-glucose-1-phosphate



α -D-glucose-6-phosphate



α -D-fructose-6-phosphate



8.2 It holds for the equilibrium constant of the successive reactions, that

$$\frac{\text{Fru-6-P}}{\text{Glc-1-P}} = 19 \times 0.5 = 9.5 \quad (\text{i})$$

If y mmoles of Glc-6-phosphate are converted into the same number of Glc-1-phosphate and another x mmoles of Glc-6-phosphate are converted into the same number of mmoles of Fru-6-phosphate, then $(1 - x - y)$ mmoles of Glc-6-phosphate remain in the reaction mixture at equilibrium. It follows from relationship (i) that

$$\text{Glc-1-phosphate} = y \quad x/y = 9.5$$

$$\text{Fru-6-phosphate} = x \quad x = 9.5 y$$

After substituting,

$$\text{Glc-6-phosphate} = 1 - x - y = 1 - 10.5y,$$

it is possible to write for the reaction mixture at equilibrium that

$$\frac{\text{Glc-6-P}}{\text{Glc-1-P}} = \frac{1 - 10.5y}{y} = 19 \quad 1 - 10.5y = 19 y$$

$$y = 1/29.5 = 0.034 \text{ mmoles Glc-1-phosphate}$$

It is further calculated that

$$x = 9.5y = 9.5 \times 0.034 \text{ or } 9.5/29.5 = 0.322 \text{ mmoles of Fru-6-phosphate}$$

$$1 - x - y = 1 - 0.322 - 0.034 = 0.644 \text{ mmoles of Glc-6-phosphate}$$

At equilibrium the reaction mixture contains 0.034 mmoles Glc-1-phosphate, 0.644 mmoles Glc-6-phosphate and 0.322 mmoles Fru-6-phosphate.

PRACTICAL PROBLEMS**PROBLEM 1 (practical)**

Determination of the relative molecular mass of a weak acid by acid-base titration in a non-aqueous solvent

Weak acid whose dissociation constants, K_a , are smaller than 1×10^{-7} can be satisfactorily titrated in ethanol or in a mixture of ethanol and benzene, using a standard ethanolic solution of potassium hydroxide or potassium alkoxide in the presence of phenolphthalein or thymolphthalein as an indicator.

Task:

Determine the molecular weight (chemical equivalent) of a weak monobasic acid by titration with potassium ethoxide in ethanolic solution using phenolphthalein as an indicator (the acid has the general formula $C_xH_yO_z$).

Chemicals and equipment:

Standard solution of potassium ethoxide in ethanol of concentration $c = 0.1000 \text{ mol dm}^{-3}$

Indicator: 0.1% solution of phenolphthalein in ethanol

Solvent: A mixture of ethanol and benzene

1.000 g of sample, accurately weighed,

3 titration flasks of volume 200 or 500 cm³, one 25 cm³ burette, one 50 cm³ pipette, one 250 cm³ volumetric flask, one 100 cm³ measuring cylinder, small funnels, beakers, filter paper.

Procedure:

You are provided with 1.000 g of the monobasic acid $C_xH_yO_z$. This sample is labelled with a number. This should be written clearly at the top of your answer paper.

Carefully transfer all the acid into the graduated (volumetric) flask and fill the solution in the flask with ethanol up to 250 ml. A portion of 50.00 ml of this solution should be titrated with the 0.1000 M alcoholic solution of potassium ethoxide using 5 drops of phenolphthalein as indicator. The first titration should be a rough titration for estimating the

approximate volume necessary to determine the endpoint. Subsequent titrations should be carried out with precision, using the same quantity of indicator each time.

Record all titration values. An extra titration should be carried out to eliminate any error that might be due to the action of the potassium hydroxide on the solvent, indicator or ethanol. This type of titration is known as a blank titration, its value should be recorded and used to correct the results of previous titrations. Care should be taken to use the same quantity of indicator as in previous titrations.

The correct titration values should be used to calculate the relative molecular mass (molecular weight) of the sample.

Note: The waste material containing organic solvents must not be discharged in a sink. Use labelled containers for this purpose.

Questions:

- 1) Suggest the name and formula of a common, monobasic acid which corresponds to the value you determined experimentally for your sample.
- 2) Write a general equation for the neutralisation of a monocarboxylic acid with:
 - i) potassium ethoxide,
 - ii) potassium hydroxide.
- 3) During the titration of some weak carboxylic (fatty) acids, similar to the titration that you have carried out, turbidity or cloudiness is observed. Suggest an explanation for this turbidity.
- 4) How would you produce 1 dm³ of a standard solution of 0.1 M potassium ethoxide? Which compound would you use, as a standard solution?
- 5) Why are the titrations of weak acids carried out in non-aqueous media?
- 6) Name another solvent which is suitable for use in the titration of weak acids.
- 7) How would you recover the organic solvent used in your experiment?
- 8) Sketch a schematic titration curve (pH as a function of volume) for the titration of 20 ml of a 0.1 M aqueous solution of a weak monobasic acid with a standard aqueous solution of 0.1 M potassium hydroxide.
- 9) Calculate the pH of 0.1 M aqueous solution of an acid which has a dissociation constant of 1×10^{-7} .