Our country, our future

525/1

S6 CHEMISTRY

Exam 1

PAPER 1

DURATION: 2 HOUR 45 MINUTES

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Instructions

- This paper consists of two sections A and B
- Section A is compulsory
- Attempt only six questions in section B
- Answers must be written in the spaces provided only.

Where necessary use the following:

Molar gas constant, R	= $8.31JK^{-1}mol^{-1}$
Molar volume of a gas at s.t.p	= 22.4litres
Standard temperarue	= 273K
Standard pressure	= $10125Nm^{-2}$

For Examiner's Use Only																
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

SECTION A

1. Write a balanced overall ionic equation for the following reactions:

   (a) $MnO_2(s) + HCl\ (aq) \longrightarrow MnCl_2\ (aq) + H_2O(l) + Cl_2(g)$

   $MnO_2(s) + 4HCl\ (aq) \longrightarrow MnCl_2\ (aq) + 2H_2O(l) + Cl_2(g)$

   (b) $KIO_3(aq) + HCl(aq) + KI(aq) \longrightarrow I_2(aq) + H_2O(l)$

   $KIO_3(aq) + 6HCl(aq) + 5KI(aq) \longrightarrow 3I_2(aq) + H_2O(l) + 6KCl\ (aq)$

   (c) $K_2Cr_2O_7(aq) + H^+(aq) + SO_2(g) \longrightarrow SO_4^{2-}(aq) + H_2O(l) + Cr^{3+}(aq)$

   $K_2Cr_2O_7(aq) + 2H^+(aq) + 3SO_2(g) \longrightarrow 3SO_4^{2-}(aq) + H_2O(l) + 2Cr^{3+}(aq) + 2K^+(aq)$

2. The osmotic pressure of an aqueous solution of a non- electrolyte containing 5.43 gdm^{-3} of solution is 7.093 x $10^4 Nm^{-2}$ at 25^0C. Calculate the freezing point of solution. (Kf for water = 18.6^0C per $100gmol^{-1}$)

   Solution

   First we find the formula mass of the solute

   From PV = nRT

   $7.093 \times 10^4 \times 1 \times 10^{-3} = \frac{5.43}{mr} \times 8.31 \times (273+ 25)$

   Mr = 190

Then find freezing point depression

190g cause a freezing point depression of 1.86^0 per mole per 1000g of solvent

5.43g of solute will cause $\frac{1.86\ x\ 5.43}{190} = 0.05^0$

Freezing point of solution = freezing point of water – freezing point depression

= 0 – 0.05

= -0.05^0

3. (a) Define the term "disproportionation."

Disproportionation, is a redox reaction in which one compound of intermediate oxidation state converts to two compounds, one of higher and one of lower oxidation states.

(b) Write the ionic equation for the disproportionation of the following species.

(i) MnO_4^{2-} in acidic media.

$3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(aq)$

(ii) Copper (I) in aqueous solution.

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

(iii) Chlorine in hot concentrated sodium hydroxide solution

$3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

4. The following data was obtained for the reaction between hydrogen peroxide and iodine ions and hydrogen ions

Expt. No.	Concentration ($moldm^{-3}$)			Rate of reaction ($moldm^{-3}s^{-1}$)
	I-(aq) ion	H_2O_2(aq)	H^+(aq) ions	
1	0.010	0.010	0.010	1.76×10^{-6}
2	0.010	0.030	0.010	5.25×10^{-6}
3	0.020	0.030	0.010	1.05×10^{-5}
4	0.020	0.030	0.020	1.05×10^{-5}

(i) State the order of reaction with respect to

H_2O_2

*It is **first order** because when the concentration of I- and H+ are kept constant while the concentration of H_2O_2 is multiplied by 3 in experiments 1 and 2, the rate multiplies by 3*

I^-

Experiments 2 and 3 show that it *is **first order** because when the concentration of H_2O_2 and H^+ are kept constant while the concentration of I^- is multiplied by 2 the rate multiplies by 2*

H^+

Experiments 3 and 4 show that it *is **zero order** because when the concentration of H_2O_2 and I^- are kept constant while the concentration of H^+ is multiplied by 2 the rate remain unchanged; therefore the rate is independent of the concentration of H^+.*

(ii) Write the rate equation for the reaction:

Rate = $K[H_2O_2][I^-]$

(iii) Calculate the rate constant (K) for the reaction and indicate its units.

Substituting terms of experiment 1 in rate equation

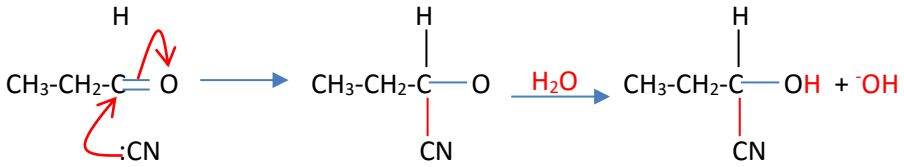
$1.76 \times 10^{-6} = K \times 0.01 \times 0.01$

$K = 1.76 \times 10^{-2} mol^{-1} dm^3 s^{-1}$

5. Complete each of the following equations and write the accepted mechanism.

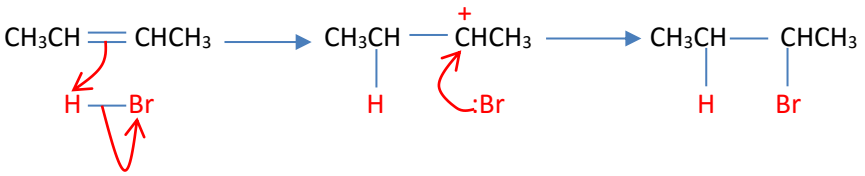
(i) $CH_3\text{-}CH_2\text{-}CHO \xrightarrow[10\text{-}20^0C]{KCN/\ dil\ H_2SO_4} CH_3CH_2CH(OH)\text{-}CN$

Mechanism



(ii) $CH_3CH{=}CHCH_3 + HBr\ (g) \longrightarrow CH_3CH(H)\text{-}CH(Br)CH_3$ (2 ½ marks)

Mechanism



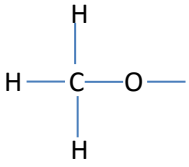
6. (a) Define the term "standard enthalpy of atomization"

Standard enthalpy of atomization is enthalpy change when 1 mole of gaseous atoms are formed from an element at 298K and 1 atmosphere.

(b) Bond energies for some bonds are given below.

Bond	Bond energy
C-O	358
C-H	413
O-H	464

Calculate the standard enthalpy of atomization of methanol

Bond in methanol  H are 3C-H + C – O + O - H

Bond energies = 3 x 413 + 358 + 464 = 2061

(d) Explain why ammonium nitrate is readily soluble in water even though the standard enthalpy of solution has a positive value.

Because increase in entropy offsets the positive enthalpy of solution to make Gibb's free energy negative

7. Name the reagent that can be used to distinguish between Co^{2+} and Mn^{2+} ions. State what is observed when the aqueous solution of each ion is separately treated with the reagent.

Reagent: Sodium hydroxide

Observations:

Co^{2+} (aq): forms a blue precipitate insoluble in excess which turns pink on standing

Mn^{2+}(aq): form a white precipitate insoluble in excess which rapidly turns brown

(b) Cobalt forms a complex of formula $Co(NH_3)_n^{3+}3Cl^-$.

5×10^{-3} moles of a complex were heated in excess alkali and the ammonia liberated was absorbed in 50 cm^3 of dilute sulphuric acid of concentration 0.5M. The excess acid remaining after the absorption required 20.00cm^3 of 1M sodium hydroxide for complete neutralization. Calculate the value of **n** in the formula of the complex.

Solution

Moles sodium hydroxide that reacted with excess sulphric acid.

1000cm^3 of sodium hydroxide solution contain 1 mole

20.0cm^3 of sodium hydroxide contain $\frac{1\ x\ 20}{1000} = 0.02\ moles$

Moles of excess sulphuric acid = ½ the moles sodium hydroxide that reacted = ½ x 0.02 =0.01moles.

Total moles of sulphuric acid

1000cm^3 of sulphuric acid contain 0.5moles

50 cm^3 of the acid contains $\frac{0.5\ x\ 50}{1000} = 0.025\ moles$

Moles of sulphuric acid that reacted with ammonia = total moles – excess moles of the acid

= 0.025 – 0.01

= 0.015

Moles of ammonia that reacted = twice the moles of sulphuric acid reacted = 0.015 x 2 = 0.03 moles

$$n = \frac{moles\ of\ a\ mmonia}{moles\ of\ comples} = \frac{0.03}{0.005} = 6$$

8(a) Explain what is meant by the term "**condensation polymerization?"**

A condensation polymerization is a form of step-growth polymerization in which monomers and/or oligomers react with each other to form larger structural units while releasing smaller molecules as a byproduct such as water or methanol.

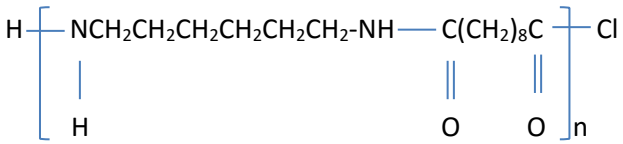
(b) Nylon 6, 10 can be made by reacting 1, 6-diaminohexanewith decanedoiyl chloride $ClOC(CH_2)_8COCl$.

Write the structural formula of:

(i) 1.6-diaminohexane

$H_2N\text{-}\ CH_2CH_2CH_2CH_2CH_2CH_2\text{-}NH_2$

(ii) Nylon 6,10



(c) State one use of nylon 6, 10.

Packing material, clothes, water pipes

9. Ammonium carbamate (NH_4CONH_2) decomposes according to the following equation:

$NH_4CONH_2\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2(g)\ \ +\Delta H^0\ (kJmol^{-1})$

(a) Write the expression for the equilibrium constant (Kp)

$K_p = P^2_{NH_3} \times P_{CO_2}$

(b) At equilibrium, the total pressure of the system is 0.36 atm. at 40^0C. Calculate the value of Kp for the reaction at 40^0C (indicate units).

Solution

$P_{NH_3} = \frac{2}{3}\ x\ 0.36 = 0.24$ atm

$P_{CO_2} = \frac{1}{3}\ x\ 0.36 = 0.12$ atm

$K_p = P_{NH_3}^2$ x P_{CO_2} = 0.24^2 x 0.12 = 0.006912atm^3

(c) State what happens to the Kp calculated in (a)(i) if

(i) More solid ammonium carbamate is added to the equilibrium mixture.

The concentration of the carbamate has no effect on the value of Kp

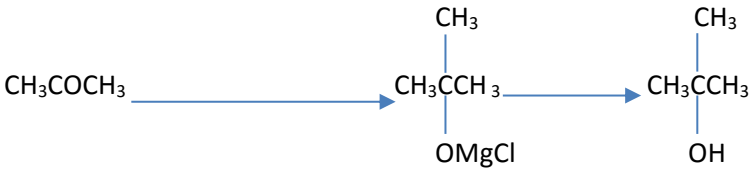
(ii) The temperature is increased to 80^0C.

Increasing temperature increases the value of Kp because the reaction is endothermic.

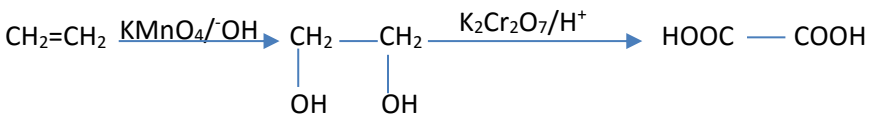
SECTION B

10 Show how the following organic conversions can be effected. (Indicate suitable reagents and conditions of reaction's n each). (3marks each)

(a) $(CH_3)_3COH$ from CH_3COCH_3



(b) $H_2C_2O_4$ from $CH_2=CH_2$



(c) CH_3NH_2 from CH_3COOH

$CH_3COOH \longrightarrow CH_3C0Cl \longrightarrow CH_3CONH_2 \longrightarrow CH_3NH_2$

11. Explain the following observations

(a) Silicon and phosphorus are both covalent substances, but the melting of silicon is much higher than that of phosphorus. (3marks)

Silicon forms big molecules of 3 dimensional array of silicon atoms in which each silicon atom is bonded to 4 silicon atoms by strong covalent bonds whereas phosphorus molecules (P_4) are bonded by weak Van der Waal forces.

(b) Magnesium oxide (MgO) has the same crystalline structure as sodium chloride (NaCl) but the lattice energy of MgO is more exothermic than that of NaCl. (3marks)

Magnesium ion have a valence of +2 while sodium ion has a valence of +1. The force of attraction between Mg^{2+} and O^{2-} are thus stronger that those between Na^{+} and O^{2-}.

(c) A concentrated solution of calcium chloride forms a precipitate with sodium hydroxide but no precipitate form with aqueous ammonia. (3marks)

Sodium hydroxide is a strong base while ammonia solution is a weak base. Therefor ammonia does not produce enough hydroxide ion to exceed Ksp of calcium hydroxide.

12.(a) Phenylamine was mixed with concentrated hydrochloric acid and sodium nitrite at 0-5^{0}C. The resultant solution Y was then treated with a mixture of phenol in aqueous sodium hydroxide. State what is observed and write the equation of reaction that takes place between:

(i) Phenylamine and a mixture of concentrated hydrochloric acid and sodium nitrite.

Observation (½ mark)

No observable change

Equation: (1½ marks)

(ii) Y and phenol in aqueous sodium hydroxide

Observation (½ mark)

Orange solution

Equation: (1 ½ marks)

(b) 20 cm^3 of 0.05M aqueous phenylamine was mixed with 50cm^3 of 1M sodium bromide and electrolyzed at current of 0.2A. The first permanent bromine color was observed after 49.93 minutes; then electrolysis was stopped. (Faradays constant =96500$Cmol^{-1}$).

(i) Calculate the moles of bromine that reacted with 1 mole of phenylamine (3 ½ marks)

Solution

Charge Q = It = 0.2 x 49.93 x 60 =599C

Mole of bromine

96500C x 2 liberate 1mole od Br2

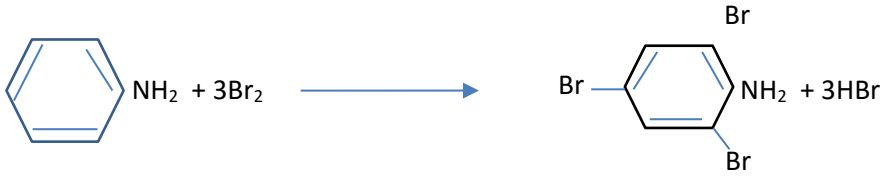
599C will liberate $\frac{1\ x\ 599}{2\ x\ 96500} = 0.003\ moles$

Moles of phenylamine = $\frac{20\ x\ 0.05}{1000} = 0.001 moles$

Moles of bromine that react with 1 mole of phenylamine = $\frac{0.003}{0.001} = 3$

(iii) Hence write equation of the reaction between bromine and phenylamine. Name the product

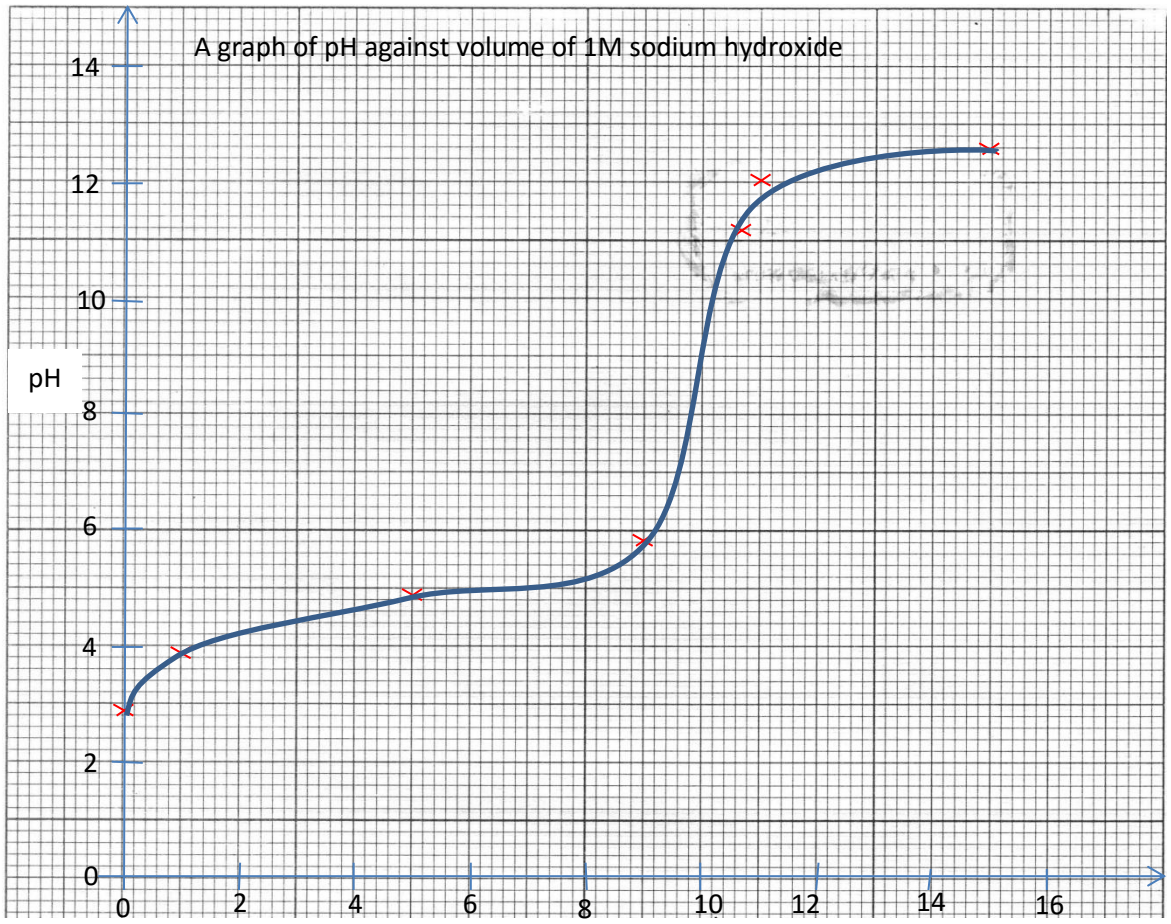
(1 ½ marks)



13. The table below gives data obtained when 100cm^3 of propanoic acid was titrated with 1.0M sodium hydroxide solution.

Volume of 1M NaOH added/ cm^3	0.0	1.0	5.0	9.0	10.5	11.0	15.0
pH of solution	2.94	3.92	4.87	5.82	11.70	12.00	12.70

(a) (i) Plot a graph of pH against volume of 1M sodium hydroxide (3marks)



(ii) Using the graph determine the pH and volume 1.0M sodium hydroxide used at equivalent point (1mark)

10cm^3

(iii) Name the suitable indicator that can be used for the titration (½ mark)

Phenolphthalein with pH range 8- 10

(b) Explain the shape of the graph.

- Initially the pH is relatively high because propanoic acid is a weak acid that partially ionize to liberate few hydrogen ions.

- pH increase as the volume of sodium hydroxide added due to removal of hydrogen ions by hydroxyl ions.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

- The end point occurs at PH above 7 due to hydrolysis of propanoate ions at a volume of sodium hydroxide = $10cm^3$ to produce hydroxyl ions.

$CH_3CH_2COO^- + H_2O \leftrightarrow CH_3CH_2COOH + OH^-$

- After the end point pH increases due to excess hydroxyl ions.

14. The table below shows formulae of oxides of silicon, Aluminium and phosphorus. (Indicate the chemical nature, bonding type and the structure adopted by the oxide)

Oxide	Chemical nature	Bonding	Structure
SiO_2	acidic	Covalent bond	3-dimension covalent solid
Al_2O_3	amphoteric	Ionic bond	Ionic solid
P_4O_{10}	acidic	covalent	molecular

(c) Write equations of reaction to illustrate the chemical nature of

(i) P_4O_{10}

Equation

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

(ii) Al_2O_3

Equation

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H2O(l)$

Or

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$

15 (a) Define the term "Phase" (1mark)

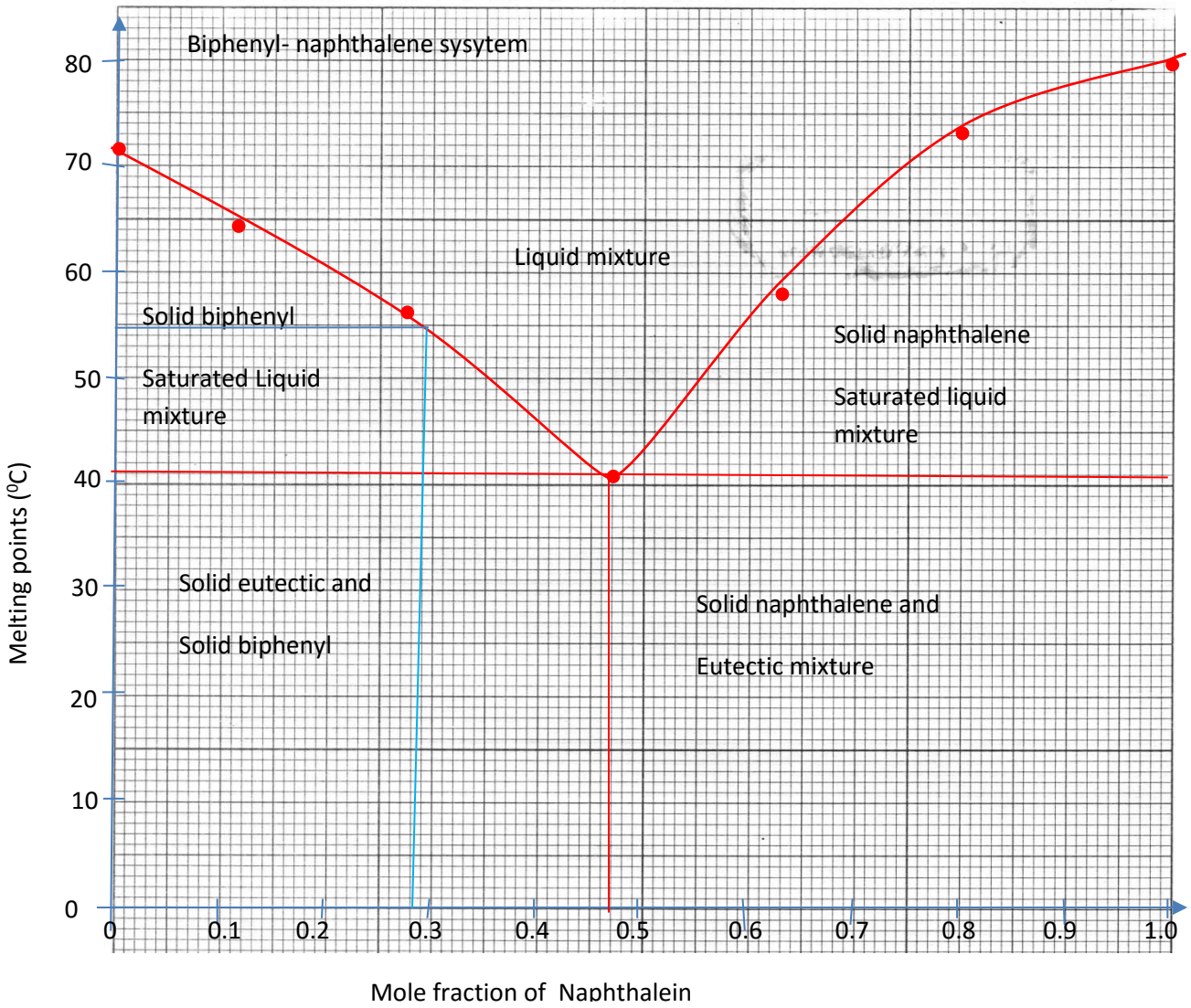
A phase is a homogeneous state into which a substance can exist i.e. solid, liquid or gas.

(b) The melting points of various composition of Naphthalene-biphenyl system are given below:

Mole fraction of Naphthaleine	0.800	0.625	0.275	0.125
Melting points/^{0}C	72.6	58.0	56.0	64.5

Naphthalene-biphenyl system form a eutectic mixture of composition of 0.47 mole fraction of naphthalene at temperature of 41.0^{0}C

(i) Plot a phase diagram for naphthalene-biphenyl system and label all regions. Melting point pure Naphthalene = 80^{0}C and mpt. Of biphenyl = 71^{0}C) (5marks)



(ii) Describe what happens when a mixture containing 0.70 mole fraction of biphenyl is Cooled. (2marks)

- Solution freezes at 55^0C.
- Solid biphenyl separates out
- The concentration of biphenyl decreases to 0.59 mole fraction by 41^0
- At 41^0, temperature remains constant as both biphenyl and naphthalene freeze together to form a solid of constant composition.

- After all the liquid has solidified at 410, the temperature of the solid falls to that f room temperature.

(c) State one application of eutectic mixture (½ mark)

To make alloys.

16. 3.70g of an organic compound Q containing carbon, hydrogen and oxygen was exploded in excess oxygen, 4.50g of water and 6.48dm^3 of gaseous substance were passed through sodium hydroxide solution, 2.0dm^3 of oxygen was found unreacted. (All volumes of gaseous substances were measured at stp).

(a) (i) Determine the empirical formula of Q: (4marks)

Mass of hydrogen atoms in the compound

18g of water contain 2g of hydrogen

4.50g of water contain $\frac{4.5\ x\ 2}{16} = 0.5g\ of\ hydrogen$

Volume of carbon dioxide = 6.48 – 2 = 4.48dm^3 at stp

Mass of carbon in the compound

22.4dm^3 of carbon dioxide contain 12g of carbon

4.48dm^3 of carbon dioxide contain $\frac{12\ x\ 4.48}{22.4}$ =2.4g

Mass of oxygen = 3.70 – 0.5 – 2.4 =0.8

Elements	hydrogen	Carbon	hysrogen
Symbols	H	C	O
Mass	0.5	2.4	0.8
Atomic mass	1	12	16
Mole	0.5	0.2	0.05
Mole ratio	10	4	1

Empirical formula: $C_4H_{10}O$

(iii) If the vapor density of Q is 37, determine the molecular formula of Q (1½ marks)

Molecular formula = 2 x 37 = 74

$[C_4H_{10}O]n = 74$

$[12 \times 4 + 1 \times 10 + 16]n = 74$

$n = 1$

molecular formula = $C_4H_{10}O$

(d) Q reacts with a mixture of sodium hydroxide and iodine solution to give a yellow precipitate

(i) Identify Q (1mark)

Butan-2-ol

(ii) Name the reagent(s) used to confirm the functional group in Q. (½ marks)

Sodium gives effervescence of hydrogen gas

17. (a) Explain what is meant by the term "salt hydrolysis" (1½ marks)

Hydrolysis is the reaction of a salt with water to give either alkaline or acidic solution

(b) Sodium sulphide undergoes hydrolysis. Write the

(i) Equation for hydrolysis of sodium sulphide

$S^{2-}(aq) + H_2O \leftrightarrow HS^-(aq) + OH^-(aq)$.

(iii) expression for hydrolysis constant (K_h), for sodium sulphide.

Kh = $\frac{[HS^-][OH^-]}{[S^{2-}]}$

(c)(i) Calculate the pH of solution containing 3.9gdm^{-3} of sodium sulphide (Hydrolysis constant at 25^{0}C of sodium sulphide = 1.25 x 10^{-10} moldm^{-3}) (4marks)

Formula mass of NaS = 23 + 32= 55

Molarity of sodium sulphide = $\frac{3.9}{55}$ $0.071 moldm^3$

Let the concentration of OH^- be x

$\frac{x^2}{0.071} = 1.25\ x\ 10^{-10}$ => x= 3 x 10^{-6}

Concentration of hydrogen ion = $\frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{3\ x\ 10^{-6}}$ 3.3 x 10^{-9} moldm^3

pH = -log[H^+] =8.47

(iv) State whether the resultant solution in (a)(i) is basic, neutral or acid (Give a reason for your answer) (1marks)

It is alkaline because it has pH above 7