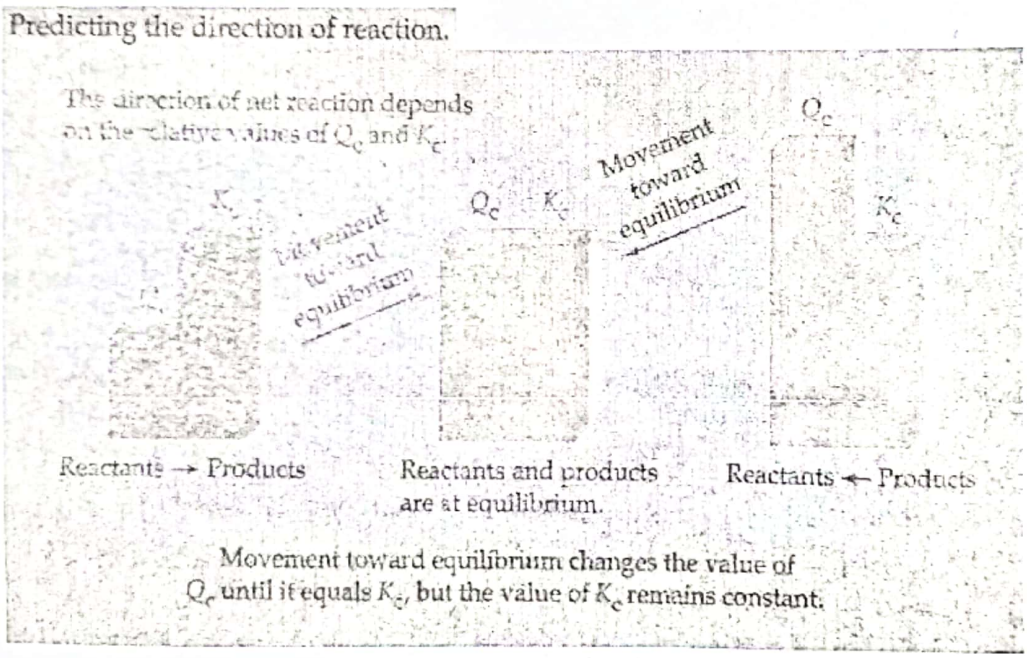
Department of Examinations - Sri Lanka

G.C.E. (A/L) Examination - 2022 (2023)

02 - Chemistry

Marking Scheme



This has been prepared for the use of marking examiners. Changes would be made according to the views presented at the Chief/Assistant Examiners' meeting.

Amendments to be included.

General Certificate of Education (Adv. Level) Examination –2022(2023)
(02) - Chemistry

Marking Scheme

Distribution of Marks

Paper I	:	1 X 50	=	50
Paper II	:			
Part A	:	100 X 4	=	400
Part B	:	150 X 2	=	300
Part C	:	150 X 2	=	300
Total			=	1000
Paper II – Final Marks			=	100

ශ්‍රී ලංකා විභාග දෙපාර්තමේන්තුව
இலங்கைப் பரீட்சைத் திணைக்களம்
අ.පො.ස.(උ.පෙළ)විභාගය/க.பொ.த. (உயர் தர)ப் பரீட்சை - 2022 (2023)

විෂයඅංකය பாட இலக்கம் 02 විෂය பாடம் Chemistry

ලකුණු දීමේපටිපාටිය/புள்ளிவழங்கும் திட்டம்

I පත්‍රය/பத்திரம் I

ප්‍රශ්නඅංකය வினா இல.	පිළිතුරු අංකය விடை இல.	ප්‍රශ්නඅංකය வினா இல.	පිළිතුරු අංකය விடை இல.	ප්‍රශ්නඅංකය வினா இல.	පිළිතුරු අංකය விடை இல.	ප්‍රශ්නඅංකය வினா இல.	පිළිතුරු අංකය விடை இல.	ප්‍රශ්නඅංකය வினா இல.	පිළිතුරු අංකය விடை இல.
01.	2	11.	5	21.	2	31.	1	41.	1
02.	4	12.	4	22.	1	32.	4	42.	1
03.	1	13.	3	23.	5	33.	5	43.	3
04.	5	14.	3	24.	5	34.	5	44.	4
05.	3	15.	5	25.	3	35.	1	45.	2
06.	5	16.	3	26.	3	36.	1	46.	1
07.	4	17.	2	27.	4	37.	2	47.	5
08.	1	18.	5	28.	4	38.	4	48.	2
09.	3	19.	3	29.	5	39.	5	49.	5
10.	3	20.	2	30.	3	40.	2	50.	4

✪විශේෂඋපදෙස්/விசேடஅறிவுறுத்தல் /Special Instructions:

එක් පිළිතුරකට ලකුණු 01 බැගින් /ஒருசரியானவிடைக்கு 01 /புள்ளிவீதம்
01 Mark for each question
මුළු ලකුණු/மொத்தப் புள்ளிகள் / Total Marks 1× 50= 50

PART A

Answer all four questions on this paper itself. (Each question carries ten marks.)

1. (a) State whether the following statements are true or false on the dotted lines. Reasons are not required.

(i) The Lyman series observed in the emission spectrum of atomic hydrogen lies in the ultra-violet region of the electromagnetic spectrum. ..... True .....

(ii) There are only 10 electrons in a calcium atom with the azimuthal quantum number $l = 0$. ..... False .....

(iii) The number of Lewis dot-dash structures (resonance structures) that can be drawn for the N_2O molecule is 3. ..... True .....

(iv) Among the second row elements of the Periodic Table, fluorine has the largest negative value of electron gain energy. ..... True .....

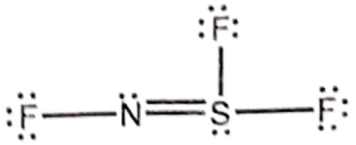
(v) The boiling point of argon (Ar) is higher than that of chlorine (Cl_2). ..... False .....

(vi) Ne has the highest first ionization energy, among the noble gases He, Ne and Ar. ..... False .....

(04 marks x 6=24 marks)

1(a): 24 marks

(b) (i) The skeleton of a molecule containing only the elements N, F and S is given below. Draw the most acceptable Lewis dot-dash structure for this molecule.



(05)

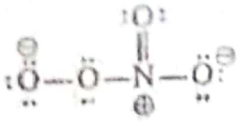
(ii) Give, (I) shapes around the N and S atoms and (II) oxidation numbers of the atoms in the structure drawn in (i) above.

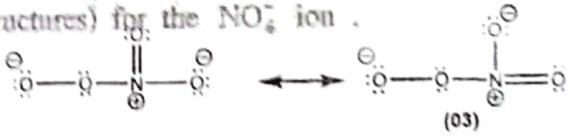
(I) N ...Angular..... , S ..... trigonal pyramidal or pyramidal ..... (shape) (01)+(01)

(II) N .....-1..... , S .....+4..... (oxidation number) (01)+ (01)

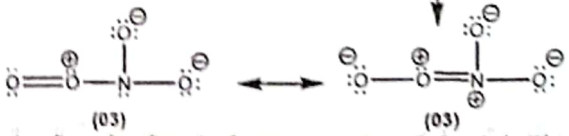
sign must

(iii) A Lewis dot-dash structure for the NO_4^- ion is given below. Draw three more Lewis dot-dash structures (resonance structures) for the NO_4^- ion .



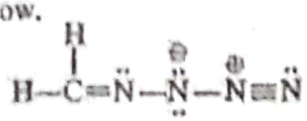


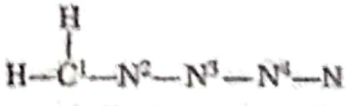
(03)



(03) (03)

(iv) Complete the given table based on the Lewis dot-dash structure and its labelled skeleton given below.





		C^1	N^2	N^3	N^4
I.	the number of VSEPR pairs around the atom	3	3	4	2
II.	electron pair geometry around the atom	trigonal planar	trigonal planar	tetrahedral	linear
III.	shape around the atom	trigonal planar	angular/ V	angular/ V	linear
IV.	hybridization of the atom	sp^2	sp^2	sp^3	sp

(01 mark X 16 = 16 marks)

Do not write in this column.

- Parts (v) to (viii) are based on the Lewis dot-dash structure given in part (iv) above. Labelling of atoms is as in part (iv).

(v) Identify the atomic/hybrid orbitals involved in the formation of σ bonds between the two atoms given below.

no mark for SP_2 SP_3..

I.	$H—C^1$	H ..1s..	C^1 ..sp^2..
II.	$C^1—N^2$	C^1 ..sp^2..	N^2 ..sp^2..
III.	$N^2—N^3$	N^2 ..sp^2..	N^3 ..sp^3..
IV.	$N^3—N^4$	N^3 ..sp^3..	N^4 ..sp..
V.	$N^4—N$	N^4 ..sp..	N ..2p..or..sp..

(01 mark X 10 = 10 marks)

(vi) Identify the atomic orbitals involved in the formation of π bonds between the atoms given below.

I.	$C^1—N^2$	C^1 ..2p..	N^2 ..2p..
II.	$N^4—N$	N^4 ..2p..	N ..2p..
		N^4 ..2p..	N ..2p..

(01 mark X 6 = 06 marks)

(vii) State the approximate bond angles around C^1, N^2, N^3 and N^4 atoms.

C^1 ..$(120° \pm 1)$.., N^2 ..$(118° \pm 1)$.., N^3 ..$(104° \pm 1)$.. $N^4(180° \pm 1)$

(01 mark X 4 = 04 marks)

(viii) Arrange the atoms N^2, N^3 and N^4 in the increasing order of their electronegativity.

..N^3.. < ..N^2.. < ..N^4..

(02 marks)

1(b): 56 marks

(c) Arrange the following species in the increasing order of the property indicated in parentheses. Reasons are not required.

(i) (i) CaF_2, $CaCl_2$, $CaBr_2$, CaI_2 (ionic character)

...CaI_2.. < ..$CaBr_2$. < $CaCl_2$.... < CaF_2....

(ii) ClF_5, ClF_2^+, ClF_2^- (bond angle)

....ClF_5.. < .ClF_2^+... < ...ClF_2^-..

(iii) Na^+, S^{2-}, Cl^-, K^+ (ionic radius)

...Na^+... < ..K^+..... < ...Cl^-..... < .....S^{2-}....

(iv) CO, CO_3^{2-}, HCO_2^-, H_2CO, CH_3OH (C—O bond length)

...CO.... < ...H_2CO. < ..HCO_2^-. < ...CO_3^{2-}... < CH_3OH.

(v) Li, N, F, Mg, P (first ionization energy)

...Li..... < ...Mg.... < ....P..... < .....N..... < .....F.....

(04 marks x 5 = 20 marks)

100

1(c): 20 marks

[see page four

Do not write in this column.

2. (*a*) The questions (i), (ii) and (iii) are based on the following reactions.

A is an ionic compound composed of three elements in the ratio 1:4:1 (Not in order of the chemical formula). One of these is a *d*-block element that belongs to the fourth period of the Periodic Table. When **A** is subjected to the flame test, a lilac (purple) flame is observed. On dissolving **A** in water, a purple coloured solution is obtained.

B is also an ionic compound composed of the same three elements as in **A**. **B** dissolves in water to give a green coloured solution.

C is a viscous colourless liquid composed of two elements. It disproportionates to give another colourless liquid **D** as one of the products. **C** can act as an oxidizing agent as well as a reducing agent. When **C** is added to a solution of **B**, the brown precipitate **E** is obtained.

F is a compound composed of three elements. One of these elements is a 3*d* element found in hematite. When $BaCl_2(aq)$ is added to an aqueous solution of **F**, the white precipitate **G** that is insoluble in dil. H_2SO_4 is formed.

H is composed of three elements. When an aqueous solution of **H** in a test tube is treated with a saturated solution of **F**, followed by addition of a small volume of conc. H_2SO_4 slowly, along the wall of the test tube, a brown colouration is seen on the surface where the liquids meet. The species responsible for the brown colouration is **I**. Brown fumes are not evolved when dil. H_2SO_4 is added to **H**. When **H** is subjected to the flame test, a yellow flame is observed.

J is the sodium salt of a weak dibasic acid. On treatment of a solution of **J** with $CaCl_2(aq)$, the white precipitate **K** is formed. **K** reacts with dil. H_2SO_4 to give the weak dibasic acid **L** as one of the products. A warm solution of **J** acidified with dil. H_2SO_4 decolourizes an aqueous solution of **A**.

(i) Identify **A** to **L**. Note: Write the chemical formulae.

A	$KMnO_4$	**G**	$BaSO_4$
B	K_2MnO_4	**H**	$NaNO_3$
C	H_2O_2	**I**	$[Fe(NO)]^{2+}$ or $[Fe(NO)]SO_4$
D	H_2O	**J**	$Na_2C_2O_4$
E	MnO_2	**K**	CaC_2O_4
F	$FeSO_4$	**L**	$H_2C_2O_4$

(04 marks x 12 = 48 marks)

(2a(i): 48 marks)

(ii) Give balanced chemical equations for the following (physical states not required).

I. Formation of **D** from **C**.

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$ (04)

II. Formation of **I**.

$$NO_3^- + 2H_2SO_4 + 3Fe^{2+} \rightarrow 3Fe^{3+} + NO + 2SO_4^{2-} + 2H_2O$$ (04)

or

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$$ (04)

or

$$NO_3^- + 4H^+ + 3e \rightarrow 2NO + 2H_2O$$ (01)

$$3(Fe^{2+} \rightarrow Fe^{3+} + e)$$ (01)

and

$$Fe^{2+} + NO \rightarrow [Fe(NO)]^{2+}$$ (01)

or

$$FeSO_4 + NO \rightarrow [Fe(NO)]SO_4$$ (01)

III. Formation of **K**.

$$Na_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4\downarrow + 2NaCl$$ (05)

(2a(ii): 14 marks)

(iii) Give balanced ionic equations for the reactions that take place when A is added to the following solutions (physical states not required). Do not write in this column.

I. an acidified solution of C

$2(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O)$ (02)
$5(H_2O_2 \rightarrow 2H^+ + O_2 + 2e)$ (02)
$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ (06)

II. an aqueous solution of F acidified with dil. H_2SO_4

$(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O)$ (02)
$5(Fe^{2+} \rightarrow Fe^{3+} + e)$ (02)
$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (06)

III. an acidified solution of J

$2(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O)$ (02)
$5(C_2O_4^{2-} \rightarrow 2CO_2 + 2e)$ (02)
$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ (06)

Note: For complete reaction 06 marks For only half reaction 02 marks each

(2a(iii): 18 marks)

(b) Give balanced chemical equations for the reactions that take place between the following (physical states not required). State the function (oxidizing agent/reducing agent) of H_2S and SO_2 in reactions (i)–(iii).

(i) Mg(s) and H_2S(g)

$Mg(s) + H_2S(g) \rightarrow MgS(s) + H_2(g)$ (04)

H_2S: Oxidizing agent (01)

(ii) Mg(s) and SO_2(g)

$2Mg(s) + SO_2(g) \rightarrow 2MgO(s) + S(s)$ or $3Mg(s) + SO_2(g) \rightarrow 2MgO(s) + MgS(s)$ (04)

SO_2: Oxidizing agent (01)

(iii) H_2S(g) and SO_2(g)

$2\,H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$ (03)

H_2S: Reducing agent, SO_2: Oxidizing agent (01+01)

(iv) S(s) and conc. HNO_3(aq) $S(s) + 6HNO_3(aq) \rightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$ (05)

Note: Physical states are not required

2(b): 20 marks

If reaction is incorrect, no mark for the function. If reaction is correct but unbalanced, can be awarded for function.

$SO_3 + H_2O$ not accepted

3. (a) (i) A closed container equipped with a piston contains a given mass of an ideal gas at a constant temperature T. Give the relationship between pressure P and volume V of the gas using a mathematical expression.

$P \propto \frac{1}{V}$ or $PV = K\ (constant)$ (10)

(ii) Show that the density d of the ideal gas in (i) above, at a constant temperature T is directly proportional to the pressure P.

$PV = K$ (02)
$d = \frac{m}{V}$ $(m = mass\ of\ gas)$ (02)
$Hence, P \times \frac{m}{d} = K$ (02)
$P = \frac{Kd}{m}$ (02)
$d = \frac{m}{K} P$ $(\frac{m}{K} = constant)$ (02)
$Hence, d \propto P$ (02)

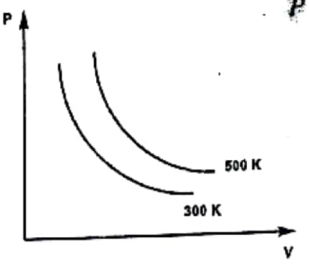
10

OR

$PV = nRT$ (02)
$P = \frac{n}{V} RT$
$P = \frac{m}{M} \times \frac{1}{V} \times RT$ $(m = mass\ of\ gas)$ $(M = relative\ molecular\ mass\ of\ gas)$ (02)
$d = \frac{m}{V}$ (02)
$Hence, P = \frac{d}{M} \times RT$ (02)
$d = \frac{M}{RT} \times P$ $(\frac{M}{RT} = constant)$ (02)
Hence $d \propto P$

(3a(ii): 10 marks)

(iii) Show the variation of P with V of the system in (i) above at the two different temperatures of 300 K and 500 K, by drawing two graphs in the figure given below. Indicate clearly the temperature corresponding to each graph.



(10)

3(a): 30 marks

(b) Depletion of $O_3(g)$ occurs according to the mechanism given below in the presence of Cl(g) and O(g) atoms.

Step 1: $O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$

Step 2: $ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$

(i) Write the overall reaction for the mechanism given above.

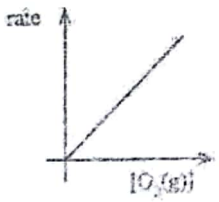
(1) + (2) $O_3(g) + O(g) \rightarrow 2O_2(g)$ **(05)**

(ii) Giving reasons, identify the catalyst and the intermediate product of the above mechanism.

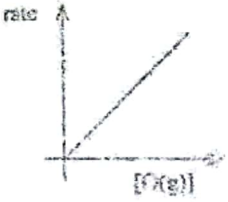
Cl(g) is the catalyst. **(05)**
Reason: consumed in step (1) and regenerated in step (2) **(05)**

ClO(g) is the intermediate. **(05)**
Reason: Generated in step (1) and consumed in step (2) **(05)**

(iii) The following graphs were obtained from an experiment carried out in relation to the overall reaction in (i) above at temperature T. Rates and concentrations are measured in units of mol dm^{-3} s^{-1} and mol dm^{-3} respectively.



Graph 1



Graph 2

Graph 1 was obtained by keeping [O(g)] constant.
Graph 2 was obtained by keeping $[O_3(g)]$ constant.

I. With the help of graphs 1 and 2, deduce orders of the reaction with respect to $O_3(g)$ and O(g). What is the overall order of the reaction?

Graph 1 is a straight line going through the origin. **(05)**

Hence, order with respect to $O_3(g)$ = 1 **(05)**

Graph 2 is a straight line going through the origin. **(05)**

Hence, order with respect to O(g) = 1 **(05)**

Hence, overall order of the reaction = 2 **(05)**

II. If the rate constant of the reaction is k at temperature T, write the rate law of the reaction.

$Rate = k[O_3(g)][O(g)]$ **(05)**

iii. Derive the units of k.

$$k = \frac{Rate}{[O_3(g)][O(g)]} = \frac{mol\ dm^{-3}\ s^{-1}}{(mol\ dm^{-3})(mol\ dm^{-3})} = mol^{-1}dm^3\ s^{-1}$$ **(05)**

iv. In an experiment carried out at temperature T, the concentrations of $O_3(g)$ and $O(g)$ were 1.0×10^{-3} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3} respectively. The rate of the reaction was found to be 1.0×10^{-3} mol dm^{-3} s^{-1}. Calculate the value of k.

$Rate = k[O_3(g)][O(g)]$

$1.0 \times 10^{-3}\ (mol\ dm^{-3}s^{-1}) = k[1.0 \times 10^{-3}](mol\ dm^{-3})[1.0 \times 10^{-4}](mol\ dm^{-3})$ **(04 + 01)**

$\boldsymbol{Hence, k = 1.0 \times 10^4\ mol^{-1}\ dm^3\ s^{-1}}$ **(04 +01)**

3(b): 70 marks

Do not write in this column.

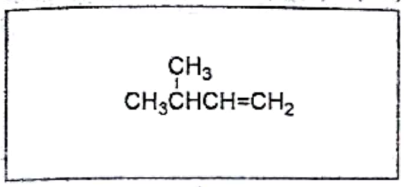
100

units should be substituted inside eqn no mark for only write the final unit.

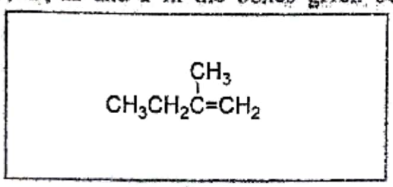
4. (a) **A**, **B** and **C** are hydrocarbons having the molecular formula C_5H_{10}. None of them show geometric isomerism. Both **A** and **B** are chain isomers of **C**. When **A** and **B** are separately treated with cold concentrated H_2SO_4 and the products obtained are diluted with water and heated, **D** and **E** are formed respectively. Of the two compounds **D** and **E**, only **D** shows optical isomerism. On catalytic hydrogenation, both compounds **A** and **B** give the same compound **F**, while compound **C** gives **G**. When **B** reacts with HBr in the presence of peroxide, **H** which is a primary alkyl halide is formed. Compound **H** when treated with aqueous NaOH gives **I**.

(i) Draw the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G**, **H** and **I** in the boxes given below.

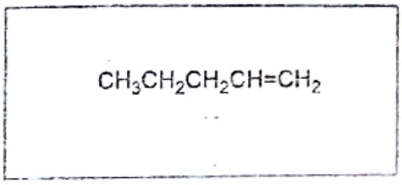
A



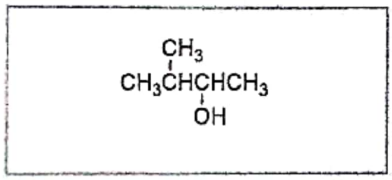
B



C



D



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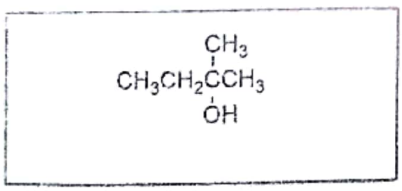

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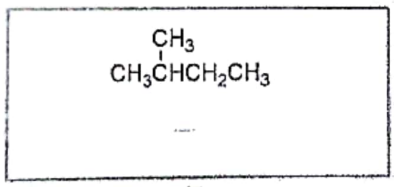

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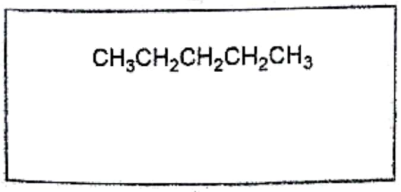

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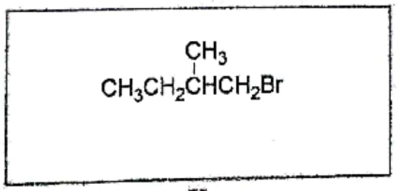
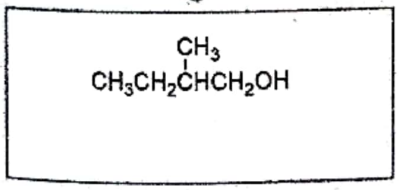


I



(06 marks x 9 = 54 marks)

(4a(i): 54 marks)

For the test, instead of HCl/$ZnCl_2$, if Lucas test or Lucas reagent is given, award only 01 mark

All three structures D, E & F have to be correct for this part

(ii) Describe a chemical test to distinguish **D**, **E** and **I** from one another.

Lucas test

Add conc. $HCl/ZnCl_2$ to each compound. **(03)**

E – Gives a turbidity in a very short time. **(01)**

D – Gives a turbidity in a few minutes **(01)**

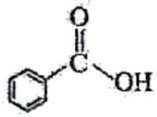
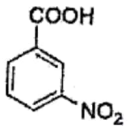
I – Does not give a turbidity / Gives a turbidity after a long time. **(01)**

(4a(ii): 06 marks

4(a): 60 marks

(b) (i) Draw the structures of the products **J**, **K**, **L**, **M** and **N** of the following reactions (I–V) in the given boxes.

(I) $CH_3CH(CH_3)CH_2CH_2Br$ —alcoholic KOH→ **J**: $CH_3CH(CH_3)CH=CH_2$

(II)  —conc. HNO_3/conc. H_2SO_4→ **K**: 

(III) $CH_3C(CH_3)=CH_2$ —HBr→ **L**: $CH_3C(CH_3)(Br)CH_3$

(IV) $CH_3COCH_2CH_3$ —HCN→ **M**: $CH_3C(OH)(CN)CH_2CH_3$

(V) $CH_3CH_2CH(CH_3)CH_2Br$ —KCN→ **N**: $CH_3CH_2CH(CH_3)CH_2CN$

(05 marks x 5 = 25 marks

(4b(i): 25 marks

Products must be correct for award marks

(ii) Selecting from the reactions I–V, give **one** example each, for each type of reaction given below.

Nucleophilic addition reaction	Reaction IV
Electrophilic addition reaction	Reaction III
Elimination reaction	Reaction I

(05 marks x 3 = 15 marks

(4b(ii): 15 marks

4(b): 40 marks

PART B — ESSAY

Answer two questions only. (Each question carries 150 marks.)

5. (a) Consider the reaction (1) given below at a temperature of 800 °C.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ ---------- (1)}$$

Initially, 0.45 mol of HI(g) was introduced into a 1.0 dm^3 evacuated rigid closed container at 800 °C, and allowed to reach the equilibrium given above. It was found that 0.05 mol of $H_2(g)$ was present at equilibrium.

(i) Calculate the equilibrium constant K_{C_1}, for the above equilibrium at a temperature of 800 °C.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \text{-----Rxn-1}$$

Initial con.	*0*	*0*	*0.45*	*mol dm^{-3}*
Change	*0.05*	*0.05*	*0.45 – 2 × 0.05*	*mol dm^{-3}*
Eqm con.	*0.05*	*0.05*	*0.35*	*mol dm^{-3}*

(03+01)

Note: All three concentrations need to be correct for award of 03 marks.

$$K_{C_1} = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \quad \textbf{(04)}$$

Note: Physical states are required for award of marks.

$$K_{C_1} = \frac{[0.35]^2}{[0.05][0.05]}$$

Note: If concentrations are not stated but have been substituted into K_{C_1} expression with units award (03+01) marks.

$$K_{C_1} = 49 \quad \textbf{(03+01)}$$

(5a(i): 12 marks)

(ii) In a separate similar evacuated container at a temperature of 800 °C, reaction (2) takes place with an equilibrium constant $K_{C_2} = 1.2 \times 10^8$ mol^{-1} dm^3.

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g) \text{ ---------- (2)}$$

When the two containers are connected together, the following reaction (3) takes place at a temperature of 800 °C.

$$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g) \text{ ---------- (3)}$$

Calculate the equilibrium constant K_{C_3} for the reaction (3) at a temperature of 800 °C.

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g) \quad \text{-----}\boldsymbol{Rxn-2} \qquad K_{C_2} = 1.2 \times 10^8 mol^{-1}\, dm^3$$

$$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g) \text{-----} \boldsymbol{Rxn-3} \qquad K_{C_3} = ?$$

Rxn-3 = 2 × Rxn-1 – Rxn-2

$$\therefore K_{C_3} = \frac{K_{C_1}{}^2}{K_{C_2}} \quad \textbf{(04)}$$

$$K_{C_3} = \frac{(49)^2}{1.2 \times 10^8} \quad \textbf{(04)}$$

$$K_{C_3} = 2.0 \times 10^{-5} mol\ dm^{-3} \quad \textbf{(03+01)}$$

Note: For correct concentration of K_{C_3} using $1/K_{C_3}$ award full marks.

(5a(ii): 12 marks)

(iii) A 1.0 dm^3 rigid closed container at a temperature of 800 °C contains an equilibrium mixture of (3) in (ii) above with 5.00×10^{-5} mol HI(g), 1.25×10^{-6} mol $S_2(g)$ and 2.50×10^{-5} mol $H_2S(g)$. Calculate the number of moles of $I_2(g)$ in the above mixture.

$$For\ \boldsymbol{Rxn-3}:\ K_{C_3} = \frac{[S_2(g)][HI(g)]^4}{[H_2S(g)]^2[I_2(g)]^2}$$

$$K_{C_3} = 2.0 \times 10^{-5}\ mol\ \ dm^{-3} = \frac{[1.25 \times 10^{-6}][5.0 \times 10^{-5}]^4}{[2.5 \times 10^{-5}]^2[I_2(g)]^2} \quad \textbf{(04)}$$

Note: If only K_{C_3} expression is given award (02) marks.

$$\therefore [I_2(g)] = 2.5 \times 10^{-5}\ mol\ \ dm^{-3}$$

$$nI_2 = 2.5 \times 10^{-5}\ mol\ \ dm^{-3} \times 1.0\ dm^3 = 2.5 \times 10^{-5}\ mol \quad \textbf{(03+01)}$$

(5a(iii): 08 marks)

(iv) An extra 2.50×10^{-5} mol $I_2(g)$ was added to the equilibrium mixture in (iii) above at a temperature of 800 °C.

I. Calculate the reaction quotient (Q_c) at the moment the extra $I_2(g)$ is added.

II. Explain the change in the equilibrium that takes place upon the addition of extra $I_2(g)$.

III. Sketch the variation in the concentrations of each constituent in the mixture, with time, upon the addition of extra $I_2(g)$.

I. When an extra $2.5 \times 10^{-5}\ mol$ of $I_2(g)$ was added:

New $[I_2(g)] = 5.0 \times 10^{-5}\ mol\ \ dm^{-3}$ **(04)**

At this point:

$$Q_{C_3} = \frac{[S_2(g)][HI(g)]^4}{[H_2S(g)]^2[I_2(g)]^2}$$

$$Q_{C_3} = \frac{[1.25 \times 10^{-6}][5.0 \times 10^{-5}]^4}{[5.0 \times 10^{-5}]^2[5.0 \times 10^{-5}]^2} \quad \textbf{(04)}$$

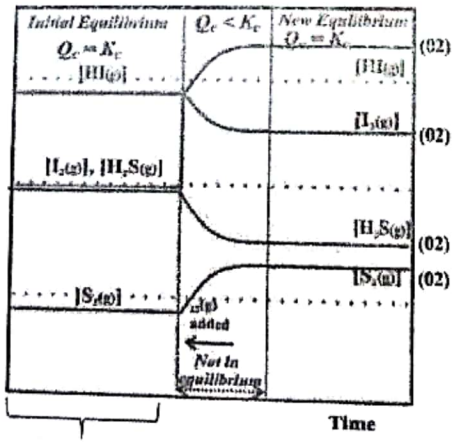
$$Q_{C_3} = 5.0 \times 10^{-6}\ mol\ \ dm^{-3} \quad 1.25 \times 10^{-6}\ mol\,dm^{-3} \quad \textbf{(04)}$$

Note: If only Q_{C_3} expression is given award (02) marks.

II. Since, $Q_{C_3} < K_{C_3}$ **(04)**

$\therefore$ Reaction will proceed to the right until $Q_{C_3} = K_{C_3}$ **(04)**

III.



not required **(08)**

Note: Variations can be given in individual plots.

(5a(iv): 28 marks)

5(a): 60 marks

(b) (i) Using the data given below, calculate ΔH°, ΔS° and ΔG° for the reaction (4) at 27 °C.

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$ ---------- (4)

At 27 °C : $H_2(g) + I_2(s) \longrightarrow 2HI(g)$; $\Delta H^\circ = 53$ kJ mol^{-1}, $\Delta S^\circ = 410$ J K^{-1} mol^{-1}

$I_2(s) \longrightarrow I_2(g)$; $\Delta H^\circ = 63$ kJ mol^{-1}, $\Delta S^\circ = 260$ J K^{-1} mol^{-1}

If standard state of ΔH ΔS, ΔG are not given deduct only 04 mark

$H_2(g) + I_2(s) \rightarrow 2HI(g)$ **Rxn-1** ; $\Delta H_1^\theta = 53\ kJ\ mol^{-1}, \Delta S_1^\theta = 410\ J\ K^{-1}mol^{-1}$

$I_2(s) \rightarrow I_2(g)$ **Rxn-2** ; $\Delta H_2^\theta = 63\ kJ\ mol^{-1}, \Delta S_2^\theta = 260\ J\ K^{-1}mol^{-1}$

Rxn-4=Rxn-1 – Rxn-2 **(04)**

$H_2(g) + I_2(g) \rightarrow 2HI(g)$ **-----Rxn-4**

$\Delta H_4^\theta = \Delta H_1^\theta - \Delta H_2^\theta$ **(02)**

$= 53 - 63 = -10\ kJ\ mol^{-1}$ **(01+ 01)**

$\Delta S_4^\theta = \Delta S_1^\theta - \Delta S_2^\theta$ **(02)**

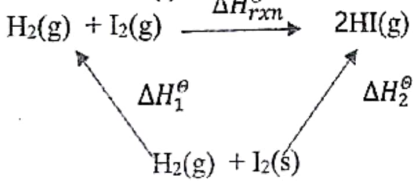
$= 410 - 260 = 150\ J\ K^{-1}mol^{-1}$ **(01 + 01)**

$\Delta G_4^\theta = \Delta H_4^\theta - T\Delta S_4^\theta$ **(04)**

$= -10 - 300 \times 0.150 = -55 kJ\ mol^{-1}$ **(03 +01)**

(5b(i): 20 marks)

Alternative answer for b (i)



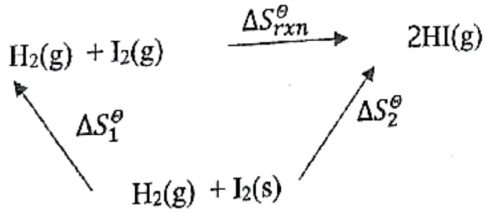
(02)

Note :Physical states are required for award of marks.

From Hess's Law **(02)**

$\therefore \Delta H_1^\theta + \Delta H_{rxn}^\theta = \Delta H_2^\theta$

$\Delta H_{rxn}^\theta = 53kJ\ mol^{-1} - 63kJ\ mol^{-1} = -10\ kJ\ mol^{-1}$ **(01 + 01)**



(02)

Note : Physical states are required for award of marks.

(02)

$\Delta S_{rn}^\theta = \Delta S_2^\theta - \Delta S_1^\theta$ **(01 + 01)**

$= 410\ J\ K^{-1}mol^{-1} - 260\ J\ K^{-1}mol^{-1} = 150\ J\ K^{-1}mol^{-1}$

(04)

$\Delta G_4^\theta = \Delta H_1^\theta - T\Delta S_1^\theta$ **(03 +01)**

$= -10 - 300 \times 0.150 = -55\ kJ\ mol^{-1}$ **(5b(i): 20 marks)**

(ii) Using the data given below, calculate ΔH°, ΔS° and ΔG° for the reaction (5) at 27 °C.

$2H_2S(g) \rightarrow 2H_2(g) + S_2(g)$ ---------- (5)

At 27 °C:		ΔH_f° / kJ mol^{-1}	ΔS_f° / J K^{-1} mol^{-1}
$H_2(g)$	:	0	130
$S_2(g)$	:	127	230
$H_2S(g)$	:	-20	200

$$\Delta H_5^{\theta} = 2\Delta H^{\theta}_{f(H_{2(g)})} + \Delta H^{\theta}_{f(S_{2(g)})} - 2\Delta H^{\theta}_{f(H_2S(g))} \quad \textbf{(04)}$$

$$= 0 + 127 - (2 \times -20) = 167\ kJ\ mol^{-1} \quad \textbf{(03 + 01)}$$

$$\Delta S_5^{\theta} = 2\Delta S^{\theta}_{f(H_{2(g)})} + \Delta S^{\theta}_{f(S_{2(g)})} - 2\Delta S^{\theta}_{f(H_2S(g))} \quad \textbf{(04)}$$

$$= 2 \times 130 + 230 - (2 \times 200)$$

$$= 90\ J\ K^{-1}mol^{-1} \quad \textbf{(03 + 01)}$$

$$\Delta G_5^{\theta} = \Delta H_5^{\theta} - T\Delta S_5^{\theta} = 167 - 300 \times 0.090$$

$$= 140\ kJ\ mol^{-1} \quad \textbf{(03 + 01)}$$

(5b(ii): 20 marks)

(iii) Using the answers obtained in (b)(i) and (b)(ii) above, predict giving reasons whether the reaction (6) below is spontaneous or not at 27 °C.

$2I_2(g) + 2H_2S(g) \rightarrow S_2(g) + 4HI(g)$ ---------- (6)

Rxn-6 = 2 × Rxn-4 + Rxn-5

or

$$\therefore \Delta G_6^{\theta} = 2\Delta G_4^{\theta} + \Delta G_5^{\theta} \quad \textbf{(04)}$$

$$\Delta G_6^{\theta} = 2(-55) + 140 \quad \textbf{(04)}$$

$$= 30\ kJ\ mol^{-1} \quad \textbf{(03 + 01)}$$

ΔG_6^{θ} *is positive* **(04)**

∴ **Reaction is non-spontaneous** **(04)**

Note: For correct prediction based on incorrect value for ΔG_6^{θ}, award marks.

(5b(iii): 20 marks)

5(b): 60 marks

(c) An aqueous solution of volume 1.0 dm^3 in a beaker at a temperature of 25 °C contains 2.0×10^{-2} mol of $Cl^-(aq)$ ions and 2.0×10^{-2} mol of $CrO_4^{2-}(aq)$ ions. Small portions of concentrated aqueous $AgNO_3$ solution were added **slowly** to the above solution. At 25 °C, K_{sp} $(AgCl(s)) = 1.60 \times 10^{-10}$ $mol^2\ dm^{-6}$ and K_{sp} $(Ag_2CrO_4(s)) = 8.0 \times 10^{-12}$ $mol^3\ dm^{-9}$. Assume that there was no significant change in solution volume upon the addition of $AgNO_3(aq)$ solution.

(i) Show that AgCl precipitates first by a suitable calculation.

For AgCl

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ **(02)**

$K_{sp} = [Ag^+(aq)]\,[Cl^-(aq)]$ **(02)**

$[Ag^+(aq)] = K_{sp} / [Cl^-(aq)]$

$= (1.60 \times 10^{-10} / 2.00 \times 10^{-2})$ **(02)**

$= \mathbf{8.0 \times 10^{-9}\ mol\ dm^{-3}}$ **(01+01)**

For Ag_2CrO_4

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$ **(02)**

$K_{sp} = [Ag^+(aq)]^2\,[CrO_4^{2-}(aq)]$ **(02)**

$[Ag^+(aq)]^2 = K_{sp} / [CrO_4^{2-}(aq)]$

$= (8.0 \times 10^{-12} / 2.00 \times 10^{-2})$ **(02)**

$[Ag^+(aq)] = \mathbf{2.0 \times 10^{-5}\ mol\ dm^{-3}}$ **(01+01)**

physical states are required for award of marks

$[Ag^+(aq)]$ needed to precipitate $AgCl(s) < [Ag^+(aq)]$ needed to precipitate $Ag_2CrO_4(s)$ **(02)**

∴ **AgCl(s) precipitates first** **(02)**

(5c(i): 20 marks)

(ii) Calculate the concentration of $Cl^-(aq)$ ions present in the solution at the time Ag_2CrO_4 starts to precipitate.

$[Cl^-(aq)]$ present in the solution at the time Ag_2CrO_4 starts to precipitate **(04)**

$= (K_{sp} / 2.0 \times 10^{-5})$ **(02)**

$= (1.60 \times 10^{-10} / 2.0 \times 10^{-5})\ mol\ dm^{-3}$ **(04)**

$= \mathbf{8.0 \times 10^{-6}\ mol\ dm^{-3}}$

(5c(ii): 10 marks)

5(c): 30 marks

6. (a) You are provided with an aqueous solution of sodium acetate (CH_3COONa) at 25 °C.

(i) Write the equilibrium reaction for the hydrolysis of sodium acetate in aqueous medium.

$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NaOH(aq)$ (08)

or

$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$ (04)

$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ (04)

(6a(i): 08 marks)

(ii) Write the expression for the equilibrium constant K_h of the equilibrium in (i) above.

Equilibrium constant for the above hydrolysis

$$K_h = \frac{[CH_3COOH(aq)][OH^-(aq)]}{[CH_3COO^-(aq)]} \text{: Eqn-1}$$ (04)

Note: Physical states are required for award of marks.

(6a(ii): 04 marks)

(iii) If the dissociation constants for $CH_3COOH(aq)$, and $H_2O(l)$ are K_a and K_w respectively at 25 °C, show that $K_h = \frac{K_w}{K_a}$.

physical states important

$$K_h = \frac{[CH_3COOH(aq)][OH^-(aq)][H^+(aq)]}{[CH_3COO^-(aq)][H^+(aq)]}$$ (04)

physical states

$$\because \frac{1}{K_a} = \frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)][H^+(aq)]}$$ (04)

$$K_w = [H^+(aq)][OH^-(aq)]$$ (04)

$$\therefore K_h = \frac{K_w}{K_a}$$

(6a(iii): 12 marks)

(iv) Given that, $K_a = 1.8 \times 10^{-5}$ mol dm^{-3} and $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C, calculate the value of K_h at 25 °C.

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$ (04)

$$= 5.6 \times 10^{-10}\ mol\ dm^{-3} \text{ or } 5.56 \times 10^{-10}\ mol\ dm^{-3}$$ (03 + 01) (04)

(6a(iv): 08 marks)

(v) A portion of 25.00 cm^3 of 0.10 mol dm^{-3} CH_3COONa solution is titrated with a solution of 0.10 mol dm^{-3} HCl. What is the volume of 0.10 mol dm^{-3} HCl required to reach the equivalence point? Calculate the pH of the solution at the equivalence point.

Titration of 25.00 cm^3 of 0.10 mol dm^{-3} $CH_3COONa(aq)$ with 0.10 mol dm^{-3} $HCl(aq)$

$CH_3COONa(aq) + HCl(aq) \rightarrow CH_3COOH(aq) + NaCl(aq)$ or

$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH + Cl^-(aq)$ or

$CH_3COONa(aq) : HCl(aq) = 1 : 1$

∴ Volume of HCl(aq) needed for the equivalence point = 25.00 cm^3 (04)

(04)

Calculation of pH at the equivalence point

NaCl(aq) is a neutral salt and therefore pH is determined by the dissociation/hydrolysis of $CH_3COOH(aq)$

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$ (02)

Concentration of $CH_3COOH(aq)$ = 0.05 mol dm^{-3} (volume is doubled) (02)

	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons$	$CH_3COO^-(aq)$	$+ H_3O^+(aq)$
Initial con.	0.05	0	0 mol dm^{-3}
Eqm con	0.05-x	x	x mol dm^{-3}

(04)

$$K_a = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH(aq)]} = \frac{x^2}{0.05-x}$$

$1.8 \times 10^{-5}\ mol\ dm^{-3} \sim \frac{x^2}{0.05}$ $(0.05 - x \sim 0.05)$ (04)

$x^2 = 90 \times 10^{-8}$ or 9×10^{-7}

$x = 9.49 \times 10^{-4}\ mol\ dm^{-3}$ (04)

$pH = -\log [H_3O^+(aq)] = 3.02$ or $pH = -\log [H^+(aq)] = 3.02$ ≃3 (04)

(6a(v): 28 marks)

(vi) Sketch the titration curve (pH vs. volume of HCl) for the above titration in (v).

pH curve

Initial pH is due to the hydrolysis of $CH_3COONa(aq)$

$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

∴ the solution is basic (weak)

Final pH is just above 1 (0.10 mol dm^{-3} HCl(aq))

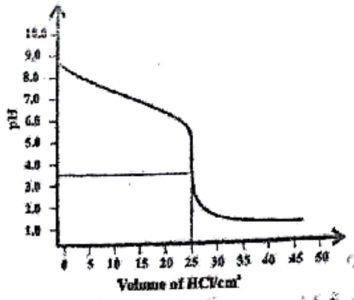
Calculation of initial pH – optional

$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

Initial con.	0.10	0	0 mol dm^{-3}
Eqm con	0.10-x	x	x mol dm^{-3}

$K_b = K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = \frac{x^2}{0.05-x}$

$pOH = 5.13$ $pH = 8.87$



y axis with relevant pH (01)

x axis with relevant volumes of HCl (01)

starting pH > 8 (02)

equivalence point pH =3.02 and volume=25.00 cm^3 (02)

pH at completion (02)

shape (02)

(6a(vi): 10 marks)

(vii) State an indicator which can be used for the titration in (v) above.

Methyl orange (04)

(6a(vii): 04 marks)

(viii) Explain why it is not possible to titrate a 0.10 mol dm^{-3} CH_3COOH solution with a solution of 0.10 mol dm^{-3} aqueous ammonia.

Difficult to detect end-point (02)

Due to smaller vertical portion/rapid pH change near end point (04)

(6a(viii): 06 marks)

6(a): 80 marks

(b) An ideal binary liquid mixture was prepared by mixing two volatile liquids A and B at a given temperature. When the composition of the liquid phase was $X_A = 0.2$ and $X_B = 0.8$, the pressure of the vapour phase was P (X_A and X_B are mole fractions of A and B respectively in the liquid phase). When the composition of the liquid phase was changed to $X_A = 0.5$, $X_B = 0.5$, the pressure of the vapour phase becomes $\frac{5}{3}P$. At this temperature, saturated vapour pressures of A and B are P_A^0 and P_B^0 respectively.

(i) Show that $P_A^0 = 5P_B^0$.

(i) For an ideal gas mixture: Total pressure P_T is given by

$$P_T = X_i \, P_i^0 \qquad (03)$$

For the initial condition $P_A = 0.2 \, P_A^0$ (03)

$P_B = 0.8 \, P_B^0$ (03)

Total pressure; $P = P_A + P_B = 0.2 \, P_A^0 + 0.8 \, P_B^0$ ..... **Eqn 1** (03 + 03)

After the change $P_A = 0.5 \, P_A^0$ (03)

$P_B = 0.5 \, P_B^0$ (03)

And total pressure $= \frac{5}{3}$P (03)

$\frac{5}{3}$ P = $0.5 \, P_A^0 + 0.5 \, P_B^0$ .....**Eqn 2** (03)

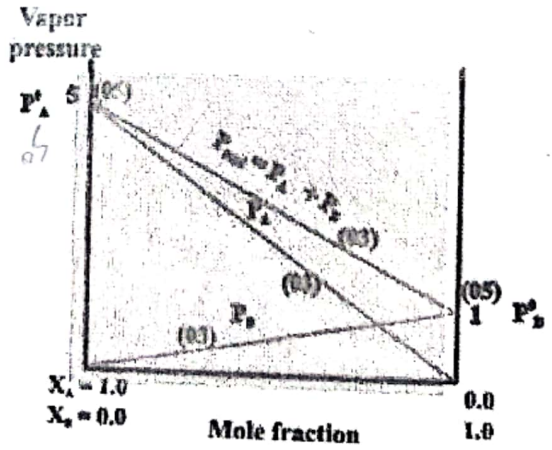
$\frac{Eqn\ 1}{Eqn\ 2} = \frac{0.2 \, P_A^0 + 0.8 \, P_B^0}{0.5 \, P_A^0 + 0.5 \, P_B^0} = \frac{3}{5}$ (03)

$1.5 \, P_A^0 + 1.5 \, P_B^0 = 1.0 \, P_A^0 + 4.0 \, P_B^0$ (03)

$\therefore P_A^0 = 5 \, P_B^0$ (03)

(6b(i): 36 marks)

(ii) Draw the corresponding temperature – vapour pressure diagram for the mixture of A and B by showing the variation of P_A, P_B and P_{Total} and label the diagram.



(6b(ii): 19 marks)

(iii) Calculate the composition of the liquid phase at the point where $P_A = P_B$.

When $P_A = P_B$

$$P_A = X_A \, P_A^0$$

And $P_B = (1 - X_A) \, P_B^0$ **(03)**

As $P_A = P_B$ **(03)**

$$1 = \frac{P_A}{P_B} = \frac{X_A \, P_A^0}{(1-X_A) \, P_B^0} = \frac{5X_A}{(1-X_A)}$$ **(03)**

$$(1 - X_A) = 5X_A$$

$$X_A = \frac{1}{6}$$ **(03)**

$$X_B = \frac{5}{6}$$ **(03)**

(6b(iii): 15 marks)

6(b): 70 marks

7. (a) A galvanic electrochemical cell was constructed at 25 °C based on the following half - reactions (1) and (2).

$2H_2O(l) + O_2(g) + 4e \longrightarrow 4OH^-(aq)$ ---------- (1); $E^\circ = 0.40\ V$

$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-(aq)$ ---------- (2); $E^\circ = -0.83\ V$

(i) Identify the anodic and cathodic half reactions of the cell.

$2H_2O(l) + O_2(g) + 4e \rightarrow 4OH^-(aq)$ **Rxn-1**

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ **Rxn-2**

Rxn-1 represents the cathodic half reaction (05)

Rxn-2 represents the anodic half reaction (05)

Note: Identifying the anodic half reaction as $2OH^-(aq) + H_2(g) \rightarrow 2H_2O(l) + 2e$ can be accepted.

(7a(i): 10 marks)

(ii) Write the overall balanced cell reaction of the cell.

Rxn-1 $- 2 \times$ **Rxn-2** (05)

Overall reaction

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (05)

Note: Physical states are required for award of marks. **(7a(ii): 10 marks)**

(iii) Calculate E°_{cell} of the cell at 25 °C.

$E^\theta_{cell} = E^\theta_{cathode} - E^\theta_{anode}$ or $E^\theta_{cell} = E^\theta_R - E^\theta_L$ (05)

$E^\theta_{cell} = 0.40\ V - (-0.83\ V) = 1.23\ V$ **(04 + 01)**

(7a(iii): 10 marks)

(iv) The cell was operated for a duration of 600 s. During this period, 1.0 mol $H_2(g)$ was consumed.

I. Calculate the number of moles of electrons which passed through the cell.

II. Calculate the amount of electricity (in coulombs) generated in the cell during its operation ($1\ F = 96500\ C\ mol^{-1}$).

III. Assuming that the current drawn from the cell is constant during the operation, calculate its value.

I. $1.0\ mol \times \frac{2\ mol\ e}{1\ mol\ H_2} = 2.0\ mol\ e$ (05)

II. Amount of electricity passed during the operation is

$2.0\ mol\ e \times \frac{96500\ C}{1\ mol\ e} = 1.93 \times 10^5\ C$ (05)

III. Current passed through the cell is;

$I = \frac{q}{t} = \frac{1.93 \times 10^5\ C}{600\ s}$

$= 321.67\ A$ or $322\ A$ (05)

(04 + 01)

(7a(iv): 20 marks)

(v) In the above galvanic electrochemical cell propane ($C_3H_8(g)$) is used instead of $H_2(g)$.

I. Write the half-cell reaction for the propane electrode assuming propane is converted to $CO_2(g)$ and $H_2O(l)$.

II. Derive the balanced equation for the overall cell reaction by using propane instead of $H_2(g)$ in the answer given in (ii) above.

III. Giving reasons, state one environmental advantage of the cell which uses $H_2(g)$ over the cell that uses propane.

I. $C_3H_8(g) + 20\ OH^-(g) \rightarrow 14H_2O(l) + 3CO_2(g) + 20e$ **(10)**

II. $C_3H_8(g) + 5O_2(g) \rightarrow 4H_2O(l) + 3CO_2(g)$ **(05)**

III. Cell with C_3H_8 produces $CO_2(g)$ **(04)**

$CO_2(g)$ contributes to global warming **(04)**

With $H_2(g)$ product is only the $H_2O(l)$ **(02)**

(7a(v): 25 marks)

7(a): 75 marks

(b) (i) X is a *d*-block element that belongs to the fourth period of the Periodic Table. On reacting X with dil. HCl, the colourless solution X_1 and the gas X_2 are obtained. When X_1 is treated with dil. NH_4OH/NH_4Cl and H_2S is bubbled through the solution thereafter, the white precipitate X_3 is obtained. X_3 is soluble in dil. HCl. On addition of dil. NaOH to X_1, the gelatinous white precipitate X_4 is formed. X_4 dissolves in excess dil. NaOH and in excess dil. NH_4OH to give X_5 and X_6 respectively. Both X_5 and X_6 are colourless.

I. Identify the species X and X_1 to X_6. (Give chemical formulae) Note: Reasons are not required.

II. Write the electronic configuration of X.

III. Explain why X_1 is colourless.

IV. Write the IUPAC name of X_6.

I. **X:** Zn (04)

X_1: $ZnCl_2$ or Zn^{2+} or $[Zn(H_2O)_6]^{2+}$ (04)

X_2: H_2 (04)

X_3: ZnS (04)

X_4: $Zn(OH)_2$ (04)

X_5: Na_2ZnO_2 or $Na_2[Zn(OH)_4]$ or $[Zn(OH)_4]^{2-}$ or ZnO_2^{2-} (04)

X_6: $[Zn(NH_3)_4]^{2+}$ (04)

II. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ (02)

III. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ($X_1 = Zn^{2+}$) (02)

All *d*-orbitals are filled (i.e. no partially filled *d*-orbitals are available) (03)

IV. tetraamminezinc(II) ion (02)

(7b(i): 37 marks)

(ii) Y is also a *d*-block element that belongs to the same row as X in the Periodic Table. Y has two common oxidation numbers n and m. m is greater than n. Y^{n+} forms the pink coloured species Y_1 in aqueous solution. On treatment of the solution containing Y_1 with dil. NaOH the pink precipitate Y_2 is formed. When H_2S is bubbled through a slightly basic solution containing Y_1, the black precipitate Y_3 is obtained. The yellowish-brown species Y_4 is formed on addition of excess conc. ammonia to a solution containing Y_1. On treatment of a solution containing Y_1 with conc. HCl, the blue coloured species Y_5 is obtained. On exposure of Y_4 to air, the brownish-red species Y_6 is formed.

I. Give the values of n and m.

II. Identify the species Y and Y_1 to Y_6. (Give chemical formulae) Note: Reasons are not required.

III. Write the electronic configurations of Y^{n+} and Y^{m+}.

IV. Write the IUPAC name of Y_5.

(75 marks)

I. n = 2 m = 3 **Note: n = +2 and m = +3 can be accepted.** (02 + 02)

II. **Y:** Co (04)

Y_1: $[Co(H_2O)_6]^{2+}$ (04)

Y_2: $Co(OH)_2$ (04)

Y_3: CoS (04)

Y_4: $[Co(NH_3)_6]^{2+}$ (04)

Y_5: $[CoCl_4]^{2-}$ (04)

Y_6: $[Co(NH_3)_6]^{3+}$ (04)

III. **Y^{2+}:** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ (02)

Y^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ (02)

IV. tetrachloridocobaltate(II) ion (02)

(7b(ii): 38 marks)

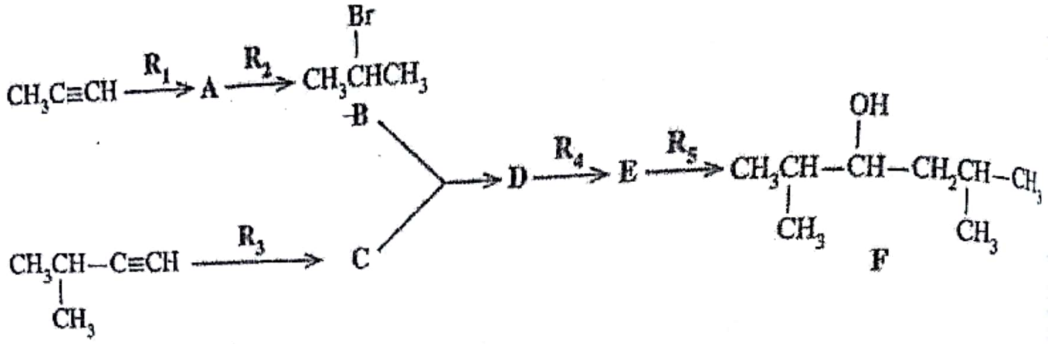
7(b): 75 marks

no marks for capital letter
no marks for (II) simple roman

PART C — ESSAY

Answer two questions only. (Each question carries 150 marks.)

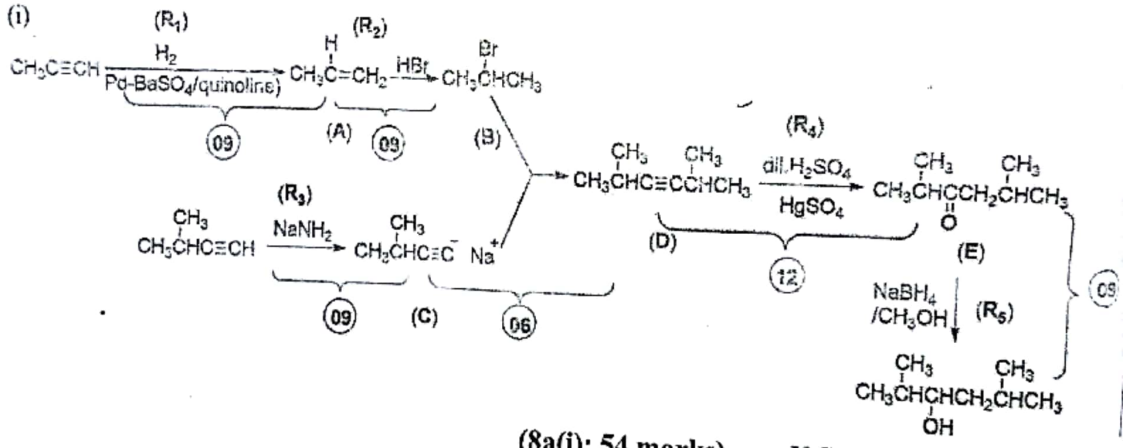
8. (*a*) Preparation of the compound **F** has been carried out using $CH_3C{\equiv}CH$ and $(CH_3)_2CHC{\equiv}CH$ according to the reaction scheme given below.



(i) Give the structures of the compounds **A**, **C**, **D** and **E** and the reagents R_1, R_2, R_3, R_4 and R_5.
Only the chemical substances given below should be used either **singly or as combinations** as reagents.

Chemical substances:
H_2, $NaNH_2$, $NaBH_4$, $HgSO_4$, HBr, dil. H_2SO_4, Pd-$BaSO_4$/Quinoline catalyst, CH_3OH

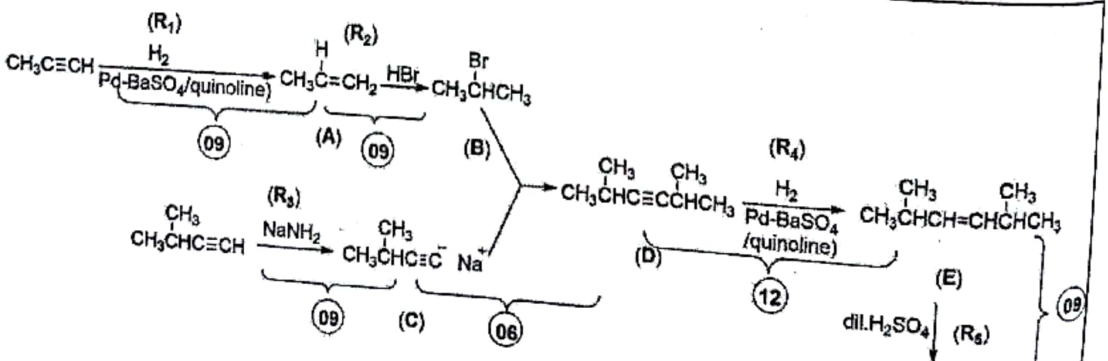
If the starting material and the product are correct award marks for reagent



(8a(i): 54 marks)

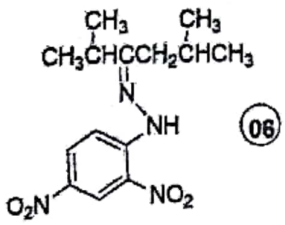
If CH_3OH is not given for R_5 Deduct **03 marks**

Alternative answer for (i)



(ii) Compound F was reacted with $H^+/K_2Cr_2O_7$. When the product obtained from this reaction is reacted with 2,4-dinitrophenylhydrazine (2,4-DNP), compound G is formed. Give the structure of G.

(ii)



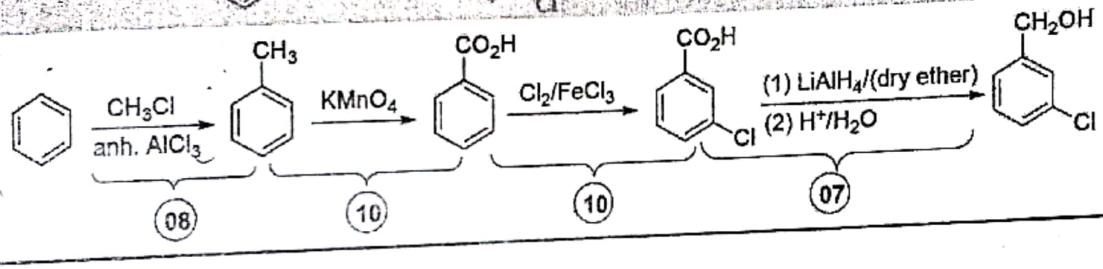
(G) (06)

(8a(ii): 06 marks)

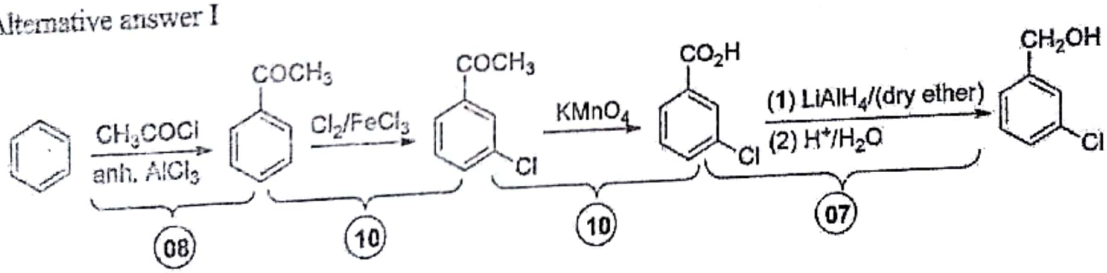
8(a): 60 marks

(b) (i) Show how the transformation given below can be carried out using not more than four (04) steps.

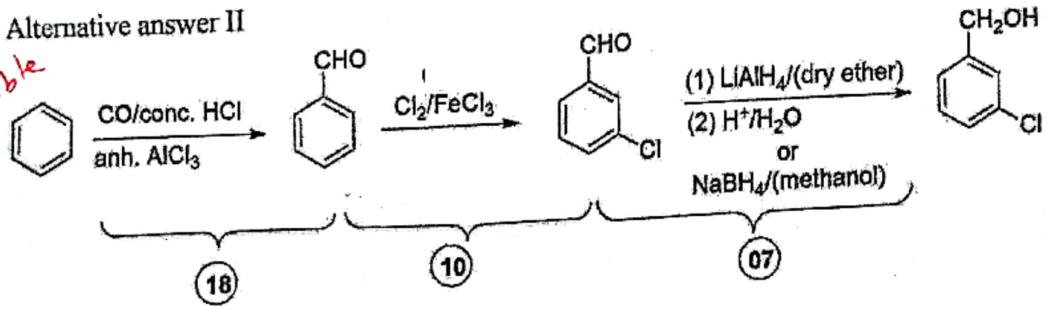
(i)



Alternative answer I



Alternative answer II



Alternative answer II.

The first reaction in this answer is not in the syllabus. However, marks are allocated for correct chemistry.

(8b(i): 35 marks)

(ii) Show how the transformation given below can be carried out using not more than three steps.

$$CH_3CH_2OH \longrightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2OH$$

(ii) $CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow{\text{aq. NaOH}} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO \xrightarrow[\text{(methanol)}]{NaBH_4} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2OH$

(08) (10) (07)

Alternative answer

$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow{\text{aq. NaOH}} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO \xrightarrow[(2)\ H^+/H_2O]{(1)\ LiAlH_4/\text{(dry ether)}} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2OH$

(08) (10) (07)

(8b(ii): 25 marks)

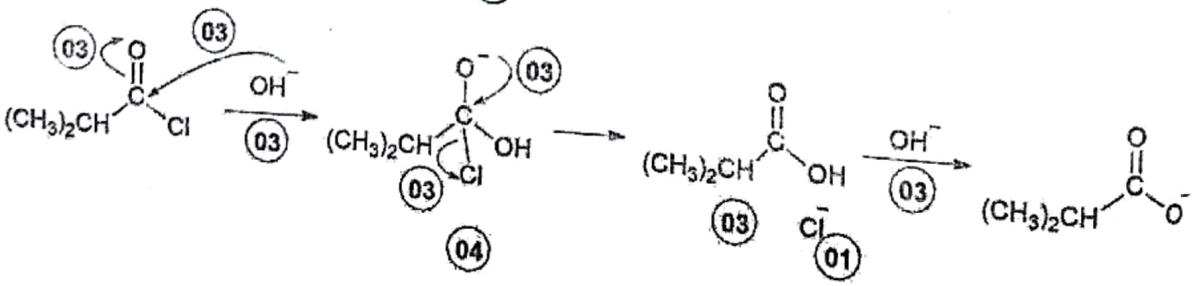
8(b): 60 marks

(c) Give the structure of the product **H** of the following reaction. Write the mechanism of this reaction.

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCl \xrightarrow{\text{aqueous NaOH}} H$$

H = $(CH_3)_2CH-C(=O)-O^- Na^+$ (03 + 01 = 04)

(04)



8(c): 30 marks

9. (a) A and B are water soluble inorganic compounds. A is coloured while B is colourless. When aqueous solutions of A and B are mixed together, the white precipitate C and the water soluble compound D are formed. C dissolves in dil. HCl to give the gas E with a pungent smell as one of the products. When E is passed through a solution of acidified $K_2Cr_2O_7$, the solution turns green. Addition of dil. NH_4OH to an aqueous solution of A gives a green precipitate F. F dissolves in excess dil. NH_4OH to give a dark blue solution G. A black precipitate is formed when H_2S is bubbled through an aqueous solution of A to which NH_4OH/NH_4Cl has been added. On addition of $AgNO_3(aq)$ to an aqueous solution of B, a white precipitate H that is soluble in dil. NH_4OH is formed. Addition of $Pb(NO_3)_2(aq)$ to an aqueous solution of B gives a white precipitate I that is soluble in hot water. When dil. H_2SO_4 is added to an aqueous solution of B, a white precipitate J that is insoluble in dil. HCl is formed. B gives a green coloured flame in the flame test.

(i) Identify the species A to J. (Give chemical formulae) Note: Reasons are not required.

A: $NiSO_3$ **(06)**

B: $BaCl_2$ **(06)**

C: $BaSO_3$ **(06)**

D: $NiCl_2$ or $[Ni(H_2O)_6]Cl_2$ **(06)**

E: SO_2 **(06)**

F: $Ni(OH)_2$ **(06)**

G: $[Ni(NH_3)_6]^{2+}$ **(06)**

H: $AgCl$ **(06)**

I: $PbCl_2$ **(06)**

J: $BaSO_4$ **(06)**

(9a(i): 60 marks)

(ii) Write balanced chemical equations for the following.

I. Formation of C and D

II. Dissolution of C in dil. HCl

I. $BaCl_2 + NiSO_3 \rightarrow BaSO_3 + NiCl_2$ **(07)**

II. $BaSO_3 + 2HCl \rightarrow BaCl_2 + SO_2 + H_2O$ **(08)**

(9a(ii): 15 marks)

9(a): 75 marks

(b) An iron ore, X, contains FeO, Fe_2O_3 and inert substances. The following experimental procedure was used to determine the mass percentages of FeO and Fe_2O_3 in X.

A mass of 0.4800 g of X was dissolved in 10 cm^3 of concentrated acid. This solution was filtered to remove insoluble matter, and thereafter diluted to 50.00 cm^3 using distilled water. This entire diluted solution was titrated with 0.020 mol dm^{-3} $KMnO_4$ solution. The titration reading at the end point was 20.00 cm^3. The pH of the entire solution, obtained after the titration, was raised to 12. At this stage, the metal ions in solution were precipitated as their hydroxides. The precipitate was filtered and dried until a constant mass was obtained. The mass of the precipitate obtained was 0.5706 g.

(i) Write balanced chemical equations for titration and precipitation reactions.

half reaction not accepted

$8H^+ + 5Fe^{2+} + MnO_4^- \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (06)

$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$ (03)

$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$ (03)

(9b(i): 12 marks)

(ii) Calculate the mass percentages of FeO and Fe_2O_3 in X.
Note: Assume that the composition does not change during drying of metal hydroxides and there is no effect from dissolved oxygen in solution.
(H = 1, O = 16, Mn = 55, Fe = 56)

Moles of MnO_4^- = 0.02 moldm^{-3} x 20 x 10^{-3} dm^{-3} = 4.0 x 10^{-4} mol (03)

As $\frac{n_{Fe^{2+}}}{n_{MnO_4^-}} = \frac{5}{1}$ (03)

Moles of Fe^{2+} = 5 x 0.02 x 20 x 10^{-3} mol = 2.0 x 10^{-3} mol (03)

Molar mass of FeO = 56.0 + 16.0 = 72 g mol^{-1} (02)

Mass of FeO = 2 x 10^{-3} mol x 72 g mol^{-1} (03)

= 0.144 g (03)

$$\% \text{ FeO} = \frac{0.144}{0.480} \times 100\%$$ (03)

= 30%

Precipitate contains $Fe(OH)_3$ and $Mn(OH)_2$ (03)

Molar mass of $Fe(OH)_3$ = 56.0 + (16.0 x 3) + (1 x 3) = 107.0 g mol^{-1} (04)

Mass of $Fe(OH)_3$ precipitated from FeO = 2 x 10^{-3} mol x 107.0 g mol^{-1} = 0.214 g (02)

Molar mass of $Mn(OH)_2$ = 55.0 + (16 x 2) + (1 x 2) = 89.0 g mol^{-1} (03)

Mass of $Mn(OH)_2$ precipitated from $KMnO_4$ titration = $\frac{0.02}{1000} \times 20\ mol \times 89\ g\ mol^{-1} = 0.0356\ g$ (02)

Mass of $Fe(OH)_3$ that resulted due to Fe_2O_3 = 0.5706 g - 0.214 g - 0.0356 g (03)

= 0.321 g (02+02+02 = 06)

No marks after this if the mass of $Fe(OH)_3$ is wrong

Moles of $Fe(OH)_3$ that resulted due to Fe_2O_3 = $\frac{0.321g}{107g\ mol^{-1}} = 3.0 \times 10^{-3}\ mol$ (03)

Moles of Fe_2O_3 = $\frac{1}{2} \times 3.0 \times 10^{-3}\ mol = 1.5 \times 10^{-3}\ mol$ (03)

Molar mass of Fe_2O_3 = (56 x 2) + (16 x 3) = 160 g mol^{-1} (03)

The mass of Fe_2O_3 = 1.5 x 10^{-3} mol x 160 g mol^{-1} = 0.240 g (02)

% Fe_2O_3 = $\frac{0.240\ g}{0.480\ g} \times 100\%$ (03)

= 50% (03)

(9b(ii): 63 marks)

10.(a) The following questions [(i) – (v)] are based on the manufacture of sulphuric acid by the Contact Process.

(i) State the three raw materials used.

Sulfur (S) / ores containing S / S obtained as a byproduct during petroleum refining / S extracted from earth / metal sulfides **(03)**

Air **(03)**

H_2O **(03)**

(10a(i): 09 marks)

(ii) Write balanced chemical equations for the reactions taking place. State proper conditions where necessary.

$S(s) + O_2(g) \rightarrow SO_2(g)$ **(03)**

(marks may also be allocated for metal sulfide + $O_2 \rightarrow SO_2$ + metal oxide if balanced equation is given)

$$2\,SO_2(g) + O_2(g) \underset{V_2O_5 \text{ catalyst } \mathbf{(01)}}{\overset{1 \text{ atm } \mathbf{(01)},\ 450\ ^\circ C\ \mathbf{(01)}}{\rightleftharpoons}} 2\,SO_3(g)$$ **(03)**

$SO_3(g) + \text{conc } H_2SO_4(l) \rightarrow H_2S_2O_7(aq)$ **(03)**

$H_2S_2O_7(aq) + H_2O(l) \rightarrow 2\,H_2SO_4(aq)$ **(03)**

Note : Physical states not required.

(10a(ii): 15 marks)

(iii) State two strategies used to increase the efficiency of the Contact Process.

Using several steps to convert entire amount of SO_2 to SO_3 via catalytic surfaces/chambers **(03)**

Using atmospheric air to increase O_2 concentration to maintain O_2:SO_2 ratio as 1:1 **(03)**

(10a(iii): 06 marks)

(iv) State two principles used in the determination of the optimum conditions for the Contact Process and briefly explain each principle using a reaction you specified in part (ii) above.

Le Chatelier Principle **(03)**

Counter Current Principle **(03)**

Le Chatelier Principle

$$2\,SO_2(g) + O_2(g) \underset{V_2O_5 \text{ catalyst}}{\overset{1 \text{ atm},\ 450\ ^\circ C}{\rightleftharpoons}} 2\,SO_3(g)$$

Because this reaction is highly exothermic, decreasing the temperature is expected to favour the forward reaction. But low temperatures will decrease rate of reaction. Therefore an optimum temperature of 450 °C will be used. **(01+01+01+01)**

Or

Increasing O_2 concentration favours the forward reaction. Therefore although a ratio of 2:1 is suggested by stoichiometry, actually a 1:1 ratio of SO_2 : O_2 is used. **(01+01+01+01)**

Counter Current Principle

$SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(aq)$

SO_3 gas moves in an upward direction while H_2SO_4 trickles downward enabling the more efficient absorption of SO_3 into H_2SO_4. **(01+01+01+01)**

Note : Reaction must be indicated or specified to award marks

(10a(iv): 14 marks)

(v) Name **two** industries which utilize sulphuric acid as a raw material.

phosphate fertilizer or ammonium sulphate fertilizer manufacturing industries

artificial fiber (rayon and plastics) industries

manufacture of detergents containing alkyl and aryl sulfonates

dyes / explosive / medicine manufacturing industry

battery acid manufacture

industries which dry gases

Any **two**

(03 marks x 2 = 06 marks)
(10a(v): 06 marks)

10(a): 50 marks

(b) Gaseous compounds of carbon, nitrogen and sulphur with various oxidation numbers directly contribute to global environment issues.

(i) Name two non-halogenated carbon compounds and one nitrogen compound that directly contribute to global warming and state the oxidation numbers of C and N in these compounds.

CO_2 +4

CH_4 -4

N_2O +1

(02 marks for compound and 01 mark for oxidation state)

(03 marks x 3 = 09 marks)
(10b(i): 09 marks)

(ii) State how the three compounds you named in (i) above are released to the atmosphere due to human activities.

CO_2 : Carbon compounds of fossil fuel and biomass are converted to CO_2 by combustion
or
Biomass grounded during deforestation is converted /oxidized to CO_2 by aerobic microorganisms /bacterial action.

CH_4 : Improper disposal of waste materials produce CH_4 due to the action of anaerobic microorganisms on organic matter.
or
Extensive rearing of ruminant animals in animal farming releases CH_4 due to conversion of organic matter by gut bacteria.
or
CH_4 is released to the atmosphere by fossil fuel retrieval and refinery process.

N_2O : Soil bacterial action on nitrogen fertilizer produces N_2O

(03 marks x 3 = 09 marks)
(10b(ii): 09 marks)

(iii) Explain how the compounds you mentioned in (i) above contribute to global warming.

The above three compounds are greenhouse gases (02)
These greenhouse gases absorb infrared radiation that are reradiated from planet surface. (02)
The infrared absorption retains thermal energy for a longer time and heats up the planet and maintains the temperature. (02)
Elevation of the composition these gases due to human activities (02)
Retention of more IR radiation energy and elevates the global temperature. (02)

(02 marks x 5 = 10 marks)
(10b(iii): 10 marks)

(iv) Name two nitrogen compounds with the oxidation numbers of N that directly contribute to photochemical smog.

NO +2
NO_2 +4

(**02** marks for compound and **01** mark for oxidation state)

(06 marks)
(10b(iv): 06 marks)

(v) Write balanced chemical equations for the formation of tropospheric ozone by a nitrogen compound you stated in (iv) above.

$NO_2 \rightarrow NO + O$

$O + O_2 \rightarrow O_3$

(03 marks x 2 = 06 marks)
(10b(v): 06 marks)

(vi) Explain why the tropospheric ozone level reaches its maximum level in the afternoon.

Solar radiation is the essential factor for photochemical smog (02)
Intensity of solar radiation reaches the maximum at noon (02)
and therefore photochemical smog reaches its maximum level in the afternoon.

(10b(vi): 04 marks)

(vii) State three water quality parameters that are affected as a result of the dissolution of oxides of nitrogen and sulphur in water bodies.

pH/ acidity

electrical conductivity

algal nutrient (NO_3^-/ PO_4^{3-} - any one)

heavy metal ($As_2O_3^{2-}$ / Cd^{2+} / Pb^{2+} / Hg^{2+} - any one) levels

water hardness/ Ca^{2+} , Mg^{2+} levels.

Any three

(02 marks x 3 =06 marks)
(10b(vii): 06 marks)

10(b): 50 marks

(c) The following questions are based on chemical products related to plant sources.

(i) Give relevant balanced equations to indicate the chemical changes that take place when ethanol in coconut toddy is produced by fermentation of sweet toddy.

If the balanced equation is correct award marks for the enzymes

$2C_6H_{12}O_6$ award mark

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Sucrase/ invertase (01)}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose — Glucose — Fructose (04)

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast (01)}} 2C_2H_5OH + 2CO_2$$ (04)

(10c(i): 10 marks)

(ii) Explain why it is necessary to remove free fatty acids from plant oils taken as raw materials in the production of bio-diesel.

02 02

To obtain biodiesel of high purity. (04)

To have high yield of biodiesel (04)

If plant oils contain free fatty acids (RCOOH), they may react with NaOH to give soap (RCOONa). 02 02 (04)

If soap is formed, foam is also formed, which inhibits (the catalytic action of NaOH used for) the transesterification reaction. 02 01 (03)

(10c(ii): 15 marks)

(iii) Explain briefly why essential oils can be extracted from plant materials by steam distillation at a temperature which is below the boiling points of both pure water and essential oil.

Essential oil and water are immiscible

Gaseous phase can be considered as a mixture of saturated vapours of water and essential oil. (04)

$P_T = P^0_{H2O} + P^0_{\text{essential oil}}$ (04)

The mixture boils when $P_T = P_{external}$ (04)

In the case of pure liquids (04)

$P_{external} = P^0_{liquid}$ at the boiling point.

In the mixture since both the liquids contribute, P_T becomes equal to $P_{external}$ at a temperature lower than the boiling points of either liquid. (04) (05)

(10c(iii): 25 marks)

10(c): 50 marks