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CH

Department of Examinations - Sri Lanka

G.C.E. (A/L) Examination - 2021 (2022)

02 - Chemistry

Marking Scheme

G.C.E. (A/L) Examination - 2021 (2022)

02 - Chemistry

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
Department of Examinations – Sri Lanka

අ.පො.ස.(උ.පෙළ)විභාගය/G.C.E. (A/L)- 2021 (2022)

විෂයය අංකය Subject No: 02
විෂයය Subject: Chemistry

ලකුණු දීමේ පටිපාටිය/Marking Scheme

I පත්‍රය/Paper I

ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.	ප්‍රශ්න අංකය Question No.	පිළිතුරු අංකය Answer No.
01.	4	11.	3	21.	4	31.	4	41.	1
02.	5	12.	2	22.	4	32.	4	42.	1
03.	2	13.	5	23.	5	33.	2	43.	2
04.	1	14.	4	24.	1	34.	3	44.	5
05.	2	15.	5	25.	1	35.	5	45.	1
06.	3	16.	2	26.	4	36.	4	46.	4
07.	4	17.	2	27.	3	37.	1	47.	1
08.	5	18.	5	28.	3	38.	5	48.	1
09.	3	19.	3	29.	3 OR 4	39.	5	49.	1
10.	5	20.	5	30.	2	40.	2	50.	3

✪විශේෂ උපදෙස්/Special Instructions:

එක් පිළිතුරකට ලකුණු 01 බැගින්/ 01 Mark for each question

මුළු ලකුණු/Total Marks 01 × 50 = 50

PART A — STRUCTURED ESSAY

Answer all four questions on this paper itself. (Each question carries 100 marks.)

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

(i) Rules related to polarizing power of cations and polarizability of anions predict that the melting point of KBr is higher than that of LiI. ......True......

(ii) The electron gain energy of Be is positive. ......True......

(iii) The spacing between two adjacent lines in a given series of the atomic spectrum of hydrogen decreases gradually in the direction of decreasing wavelengths. ......True......

(iv) The de Broglie wavelength associated with the N_2 molecule is shorter than the de Broglie wavelength of the O_2 molecule when travelling at the same velocity. ......False......

(v) The effective nuclear charge (Z_{eff}) felt by a valence electron of C is greater than the effective nuclear charge felt by a valence electron of N. ......False......

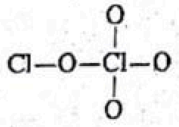
(vi) All C–O bonds in carbonic acid (H_2CO_3) are equal in length. ......False......

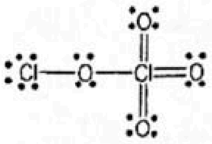
(04 marks x 6 = 24 marks)

Note: True ✓ or T, False - × or F accepted

1(a): 24 marks

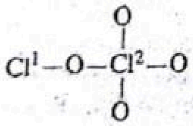
(*b*) (i) Draw the **most** acceptable Lewis dot-dash structure for the molecule Cl_2O_4. Its skeleton is given below.





(06)

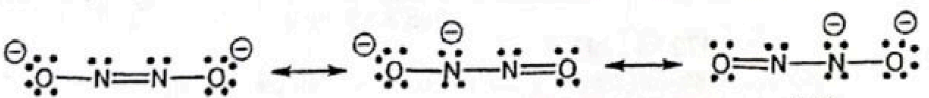
(ii) Give the oxidation states of the two chlorine atoms in the structure drawn in (i) above. The chlorine atoms are labelled as follows.



Cl^1 ...+I (+1)... , Cl^2 ...+VII (+7)...

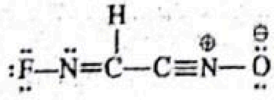
(01 + 01)

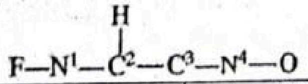
(iii) The **most** stable Lewis dot-dash structure for the ion $N_2O_2^{2-}$ is shown below. Draw **two** additional Lewis dot-dash structures (resonance structures) for this ion.



(02) (02)

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





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

(01 mark x 16 = 16 marks)

- 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.

I. $N^1—F$ N^1 sp^2 F $2p$ or sp^3

II. $N^1—C^2$ N^1 sp^2 C^2 sp^2

III. $C^2—H$ C^2 sp^2 H $1s$

IV. $C^2—C^3$ C^2 sp^2 C^3 sp

V. $C^3—N^4$ C^3 sp N^4 sp

VI. $N^4—O$ N^4 sp O $2p$ or sp^3

(01 mark x 12 = 12 marks)

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

I. $N^1—C^2$ N^1 $2p$ C^2 $2p$

II. $C^3—N^4$ C^3 $2p$ N^4 $2p$

C^3 $2p$ N^4 $2p$

(01 mark x 6 = 06 marks)

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

N^1 (118° ± 1), C^2 (120° ± 1) C^3 (180° ± 1) N^4 (180° ± 1)

(01 mark x 4 = 04 marks)

(viii) Arrange the atoms N^1, C^2, C^3 and N^4 in the increasing order of electronegativity.

C^2 < C^3 < N^1 < N^4 **(04)**

1(b): 54 marks

(c) (i) A laser emits photons of wavelength 695 nm.

I. To which region of the electromagnetic spectrum do these photons belong?

Visible region **(02)**

II. Calculate the energy of a mole of these photons in kJ mol^{-1}.
Velocity of light $c = 3.00 \times 10^8$ m s^{-1} Planck constant $h = 6.63 \times 10^{-34}$ J s

Energy of a photon (E) $= h\nu$

$= h\frac{c}{\lambda}$ **(01)**

Energy of a mole of photons $= h\frac{c}{\lambda} \times N_A$ **(01)**
(N_A = Avogadro constant)

Therefore, Energy of a mole of photons

$$= \frac{6.63 \times 10^{-34} \text{ (J s)} \times 3.00 \times 10^8 \text{ (m s}^{-1}) \times 6.022 \times 10^{23} \text{ (mol}^{-1})}{695 \times 10^{-9} \text{ (m)}}$$ **(03+01)**

$= 172$ kJ mol^{-1} **(02)**

Note: Marks can be awarded for combining steps.
$h = 6.626 \times 10^{-34}$ (J s) is accepted.

(ii) A molecule of formula AX_3 has three A–X σ bonds. Here, A and X represent symbols of elements and A is the central atom.
Name the molecular shape(s) possible for AX_3 in I and II given below.

I. if AX_3 is polar T shape, trigonal pyramidal or pyramidal **(02 + 02)**

II. if AX_3 is non-polar trigonal planar **(02)**

III. Give one example each, for the shapes stated by you in I and II above.
(Note: Molecular formulae are required.)

AX_3 is polar T shape – ClF_3, BrF_3, IF_3 (any one) **(02)**
trigonal pyramidal – NH_3, PH_3, NCl_3, PCl_3 (any one) **(02)**

AX_3 is non-polar BF_3, BCl_3, BBr_3, BI_3, $AlCl_3$ (any one) **(02)**

Note : If shape is wrong, do not award marks for examples.
For III shape needs to be indicated for award of marks for examples.

1(c): 22 marks

2. The questions [(*a*)–(*d*)] given below relate to elements/species designated as **A**, **B**, **C** and **D**.

(*a*) **A** is a *s*-block element. It has an atomic number less than 20. It reacts with water vigorously with ignition to give a strongly basic solution, with the evolution of a gas. **A** reacts with excess $O_2(g)$ to give the superoxide. The naturally occurring ore Sylvite contains a compound of **A**.

(i) Write the chemical symbol of **A**. ......K............ **(05)**

(ii) Write the complete electronic configuration of **A**. $1s^22s^22p^63s^23p^64s^1$ **(05)**

(iii) Name the gas evolved in the reaction of **A** with water. Hydrogen or H_2 **(05)**

(iv) What is the colour given by **A** in the flame test? ......Lilac (violet)......... **(05)**

(v) Write the balanced chemical equation for the reaction of **A** with excess $O_2(g)$.

$K + O_2 \rightarrow KO_2$ **(05)**

(vi) Is the first ionization energy of **A** higher or lower than that of the element in the same group and the period above it in the Periodic Table? Briefly explain your answer.

Lower **(02)**

When going down the group, change in effective nuclear charge (or Z_{eff}) for the outer most / last electron is negligible. **(01)**

However, atom size increases. **(01)**

Therefore, attraction of outer electron to nucleus decreases. **(01)**

(vii) Give the chemical formula of the compound of **A** in Sylvite. .....KCl............... **(05)**

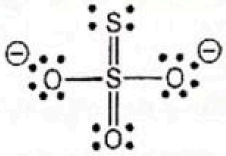
Note: (vi) Award marks for reasoning only if 'lower' is written.

2(a): 35 marks

(*b*) **B** is an anion containing only the two elements **X** and **Y**, in the ratio 2:3 respectively. Both **X** and **Y** are *p*-block elements that belong to the same group in the Periodic Table. The atomic number of each element is less than 20. The electronegativity of **X** is less than the electronegativity of **Y**. When **X** reacts with hot concentrated sulfuric acid, a colourless gas with a pungent smell is evolved as one of the products.

(i) Write the chemical formula, including the charge, of **B**. $S_2O_3^{2-}$ **(05)**

(ii) Draw the Lewis dot-dash structure of **B**.



(05)

(iii) Give the oxidation state of the central atom of **B**. ......+4......................... **(05)**

(iv) Give a chemical test to identify **B**. (**Note:** Observation(s) is/are also required.)

Test	Observation
1. Add dil. H_2SO_4 **(02)**	Colourless gas with a pungent smell **(01)** and colloidal sulfur precipitate (or milky solution) **(02)**
2. Add $Pb(OAc)_2$ **(02)**	White precipitate which turns black on heating **(03)**
3. Add $AgNO_3$ **(02)**	White precipitate which turns black on standing / heating **(03)**

Any one of the above.

Note: Test must be correct to award marks for observation.

(v) Write the chemical formula for the compound which has **A** as the cation and **B** as the anion.

$K_2S_2O_3$ **(05)**

2(b): 25 marks

(*c*) **C** is an oxidizing agent. It is composed of three elements in the ratio 1:1:3. One of the elements of **C** is **A**. The other two elements belong to the *p*-block of the Periodic Table. One of these two elements is also present in **B**. The salt formed between Ag^+ and the anion of one of these elements is yellow in colour, and insoluble in concentrated ammonia solution. Write the chemical formula of **C**. KIO_3 **(10)**

2(c): 10 marks

Note: Complete formulae are required for award of marks for (b)(v) and (c)

(*d*) **D** is a compound composed of two elements. Both these elements are also present in **C**.

(i) When **C**(aq) is mixed with an excess of **D**(aq) in acidic medium, a reddish-brown solution results.

I. Identify **D**. D = KI **(05)**

II. Write the balanced **ionic** equation for the reaction that takes place.

$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ or $IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O$ **(10)**

(ii) On addition of an excess of a solution containing **B**, to the reddish-brown solution obtained in (i) above, the reddish-brown solution becomes colourless. Write the balanced **ionic** equation for the reaction that takes place.

$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$ or $I_3^- + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 3I^-$ **(05)**

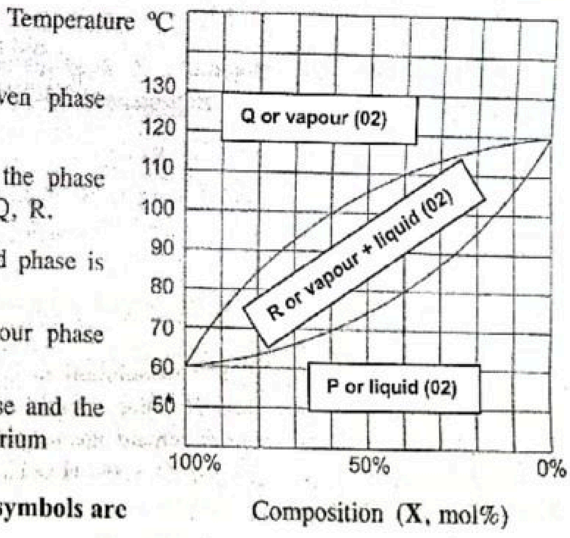
(iii) The concentration of a solution containing **B** can be determined by volumetric analysis utilizing the reactions in (i) and (ii) above. State an indicator which can be used and give the expected colour change at the end point.

Indicator : starch **(05)**

Colour change : blue / dark blue/ blue-violet to colourless **(05)**

2(d): 30 marks

3. (*a*) **X** and **Y** are two volatile liquids that form an ideal solution. The temperature-composition phase diagram (at a pressure of 1.0×10^5 Pa) for a system containing **X** and **Y** is given below.



- Parts (i) to (v) are based on the given phase diagram.

(i) Indicate the following regions on the phase diagram by writing the letters P, Q, R.

P – region where only the liquid phase is present

Q – region where only the vapour phase is present

R – region where the liquid phase and the vapour phase are in equilibrium

Note: Do not award marks if any other symbols are used without defining

(ii) Give the boiling points of pure **X** and pure **Y**.

X = 60 °C Y= 120 °C **(02+01)x2**

(iii) What is the temperature at which a liquid mixture of **X** and **Y** containing 40 mol% of **X** begins to boil?

80 °C **(02+01)**

(iv) What is the lowest temperature at which a mixture of **X** and **Y** containing 60 mol% of **X** is completely converted to vapour?

100 °C **(02+01)**

(v) Calculate the saturated vapour pressure of **X** at the temperature of 100 °C.

$P_X^g = P_X^0 x_X^l$ **(03)**

$P_X^g = P^{total} x_X^g$ **(03)**

Therefore, $P_X^0 = \frac{P^{total} x_X^g}{x_X^l}$ **(03)**

$P_X^0 = \frac{1\times10^5\ Pa \times 60}{15}$ **(05+01)**

$P_X^0 = 4.0\ \times 10^5\ Pa$ **(04+01)**

Note: Steps can be combined.

(vi) In a separate experiment, a mixture containing **X** and **Y** was allowed to reach equilibrium in a **closed rigid** container at temperature T. It was then found that the liquid phase in equilibrium with the vapour phase contained 0.10 mol of **X** and 0.10 mol of **Y**. Saturated vapour pressures of **X** and **Y** at this temperature are 4.0×10^5 Pa and 2.0×10^5 Pa, respectively. Using Raoult law, calculate the partial pressures of **X** and **Y**.

$P_X = \frac{0.1\ mol \times 4.0\times 10^5\ Pa}{0.1\ mol + 0.1\ mol}$ **(02+01)**

$P_X = 2.0\ \times 10^5 Pa$ **(02+01)**

$P_Y = \frac{0.1\ mol \times 2.0\times 10^5\ Pa}{0.1\ mol + 0.1\ mol}$ **(02+01)**

$P_Y = 1.0\ \times 10^5 Pa$ **(02+01)**

3(a): 50 marks

(*b*) The concentration of an aqueous solution of acetic acid (solution **Z**) was determined by titrating with an aqueous solution of NaOH. A volume of 12.50 cm^3 of solution **Z** required 25.00 cm^3 of NaOH solution of concentration 0.050 mol dm^{-3} to reach the end point.

(i) Calculate the concentration of acetic acid in solution **Z**.

$[CH_3COOH(aq)] = \frac{25.00\ cm^3 \times 0.05\ mol\ dm^{-3}}{12.50\ cm^3}$ **(02+01)**

$= 0.10\ mol\ dm^{-3}$ **(02+01)**

(ii) Calculate the pH value of solution **Z**. Acid dissociation constant of acetic acid (K_a) at the temperature at which the experiment was carried out is 1.80×10^{-5} mol dm^{-3}.

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ **(02)**

Or

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

Initial concentration of acetic acid = C

Fraction dissociated = α (or amount dissociated = *x*)

Note: Physical states are required for K_a

$K_a = \frac{[H^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$ or $K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$ **(02)**

$K_a = \frac{C\alpha\ C\alpha}{C(1-\alpha)}$ or $K_a = \frac{x^2}{C-x}$ **(02)**

[if the equation, $K_a = \frac{C\alpha\ C\alpha}{C(1-\alpha)}$ or $K_a = \frac{x^2}{C-x}$ is not written but the calculation is done correctly, award 02 marks for the calculation]

Since $\alpha \ll 1$ or $x \ll c$ **(02)**

pH calculation
(Do not deduct marks if physical states are not given)

$[H^+(aq)] = \sqrt{K_aC}$

$[H^+(aq)] = \sqrt{1.80 \times 10^{-5}\, mol\, dm^{-3} \times 0.1\, mol\, dm^{-3}}$ **(02)**

$[H^+(aq)] = 0.00134\, mol\, dm^{-3}$ **(02)**

$pH = -\log\left[\frac{H_3O^+(aq)}{1.0\, mol\, dm^{-3}}\right]$ or $pH = -\log\left[\frac{H^+(aq)}{1.0\, mol\, dm^{-3}}\right]$ **(02)**

or $pH = -log[H^+(aq)]$ or $pH = -log[H_3O^+(aq)]$

$pH = 2.87$ **(02)**

Alternate answer for pH calculation
Using Henderson equation,
(Do not deduct marks if physical states are not given)

$-\log[H^+(aq)] = 1/2(-\log(K_ac))$ **(02)**

$pH = 1/2(-\log\,(1.8 \times 10^{-5} \times 0.1)$ **(04)**

$pH = 2.87$ **(02)**

(iii) To another portion (100.00 cm^3) of solution **Z**, 0.200 g of pure solid NaOH was added and dissolved. Calculate the pH value of this solution assuming that the volume and the temperature of the solution remain unchanged.
[Relative atomic mass: Na = 23, O = 16, H = 1]

Amount of CH_3COOH in 100.00 cm^3 of solution = 1.0×10^{-2} mol **(02)**

Amount of NaOH added = 0.005 mol **(02)**

Amount of CH_3COOH left in the medium (after reacting with NaOH) = 5.00×10^{-3} mol **(02)**

Therefore, in solution,
(Do not deduct marks if physical states are not given)

$[CH_3COOH(aq)] = 0.05\ mol\ dm^{-3}$ **(02)**

$[CH_3COONa(aq)] = 0.05\ mol\ dm^{-3}$ **(02)**

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pH calculation
(Do not deduct marks if physical states are not given)

$[H^+(aq)] = \frac{K_a\,[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$ **(02)**

$[H^+(aq)] = \frac{1.80 \times 10^{5}\, mol\, dm^{-3} \times 0.050\, mol\, dm^{-3}}{0.050\, mol\, dm^{-3}}$ **(02)**

$[H^+(aq)] = 1.80 \times 10^{-5}\, mol\, dm^{-3}$

$pH = 4.74$ **(02)**

Alternate answer for pH calculation
(Do not deduct marks if physical states are not given)

$pH = pK_a + \log [\frac{[CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$ (02)

$pH = -\log (1.8 \times 10^{-5}) + \log [\frac{[0.05]}{[0.05]}$ (02)

$pH = 4.74$ (02)

(iv) Does the solution described in (iii) above behave as a buffer solution? Explain your answer.

The solution in (iii) above behaves as a buffer solution. (02)
The solution contains a weak acid and the sodium salt of its conjugate base (02+02)

(v) In a separate experiment, 0.800 g of pure solid NaOH was dissolved in a 100.00 cm^3 volume of solution **Z**. Does this solution behave as a buffer solution? Explain your answer using a suitable calculation. Assume that the volume and temperature of the solution remain unchanged.

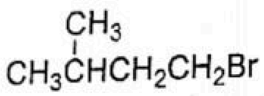
The amount of CH_3COOH in 100.00 cm^3 = 0.01 mol

The amount of NaOH added = 0.02 mol (02)
Solution does not contain CH_3COOH (or CH_3COOH has reacted completely) (02)
Solution does not behave as a buffer solution (02)

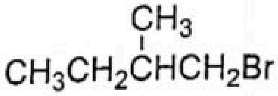
3(b): 50 marks

4. (*a*) **A**, **B** and **C** are structural isomers having the molecular formula $C_5H_{11}Br$. Of these three isomers, only **B** exhibits optical isomerism. **A** and **C** are positional isomers of each other. When **A**, **B** and **C** were reacted separately with aqueous NaOH, compounds **D**, **E** and **F** having the molecular formula $C_5H_{12}O$ were formed respectively. **D**, **E** and **F** were treated separately with PCC. **F** did not react with PCC. **D** and **E** reacted with PCC and gave **G** and **H** respectively. Both compounds **G** and **H** gave coloured precipitates with 2,4-dinitrophenylhydrazine (2,4-DNP) and silver mirrors with ammonical $AgNO_3$.

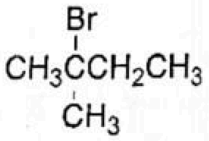
Draw the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G** and **H** in the boxes given below.


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2Br$

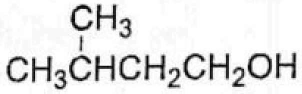
A


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2Br$

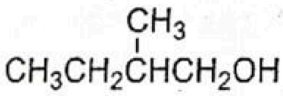
B


$CH_3\overset{Br}{\underset{CH_3}{C}}CH_2CH_3$

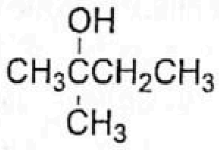
C


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2OH$

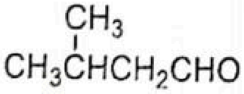
D


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$

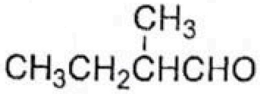
E


$CH_3\overset{OH}{\underset{CH_3}{C}}CH_2CH_3$

F


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CHO$

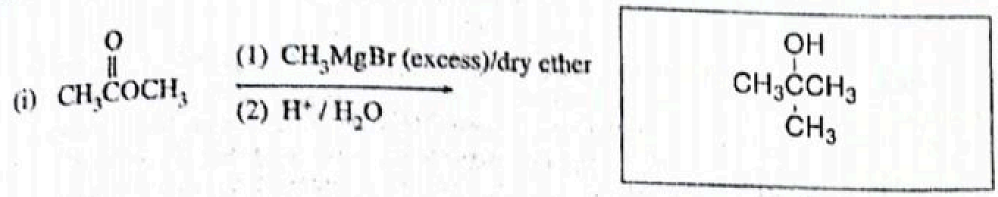
G


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCHO$

H

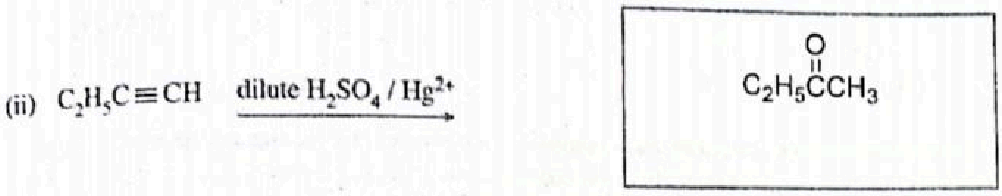
4(a): 07 marks × 8 = 5

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



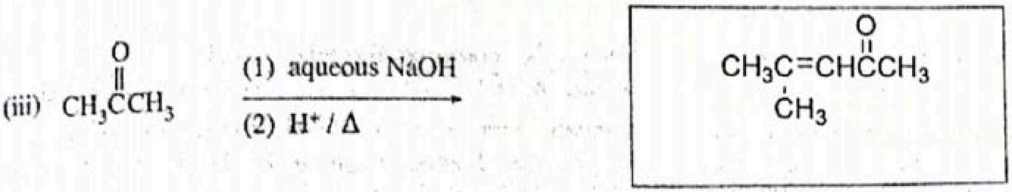
(i) $CH_3\overset{\overset{O}{\|}}{C}OCH_3 \xrightarrow[(2)\ H^+/H_2O]{(1)\ CH_3MgBr\ (excess)/dry\ ether} \boxed{CH_3\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3}$

I



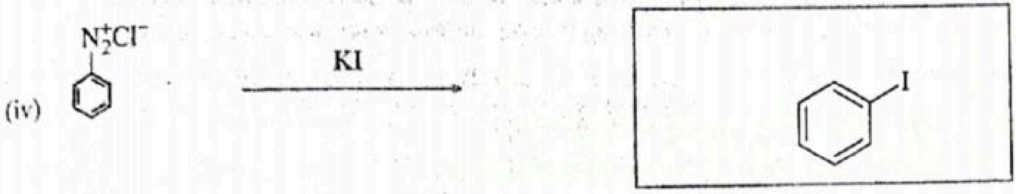
(ii) $C_2H_5C{\equiv}CH \xrightarrow{dilute\ H_2SO_4\ /\ Hg^{2+}} \boxed{C_2H_5\overset{\overset{O}{\|}}{C}CH_3}$

J



(iii) $CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[(2)\ H^+/\Delta]{(1)\ aqueous\ NaOH} \boxed{CH_3\underset{\underset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}CH_3}$

K

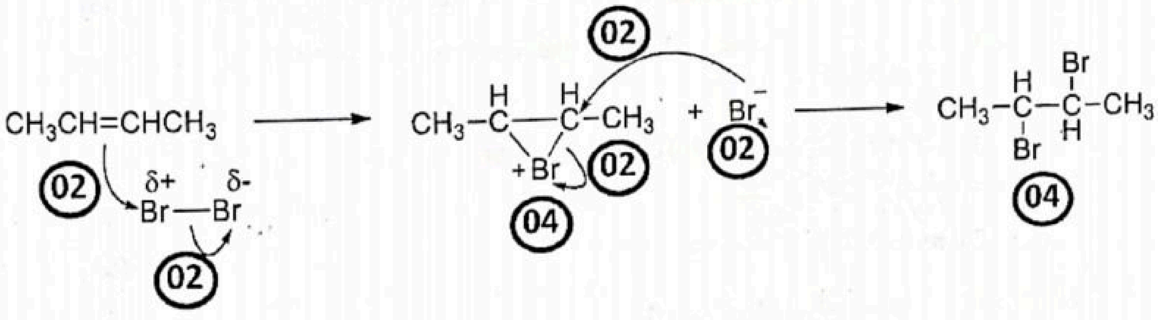


(iv) KI

L

4(b): 06 marks × 4 = 24

(c) Give the mechanism and the structure of the product formed for the reaction between $CH_3CH{=}CHCH_3$ and Br_2/CCl_4.



(02) For the polarization of Br_2

4(c): 20 marks

PART B — ESSAY

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

5. (*a*) (i) A gas mixture containing CH_4, C_2H_6 and excess O_2 was introduced into an evacuated closed rigid container. The volume of the container was 8.314×10^{-3} m^3. The pressure of the container at 400 K was 4.80×10^6 Pa. Calculate the total number of moles of gases in the container. Assume that all the gases behave ideally and that there is no reaction at this temperature.

Using pV=nRT, **(05)**

At 400K, $n_1 = \frac{4.8\times10^6 Pa\, 8.314\times10^{-3} m^3}{8.314\, J\, mol^{-1}K^{-1}\, 400K}$ **(04+01)**

$n_1 = 12.0\, mol\ or\ 12.0$ **(05)**

(ii) All the hydrocarbons in the container were completely combusted by increasing the temperature of the container to 800 K. The pressure of the container after the combustion reactions at 800 K was 1.00×10^7 Pa. Calculate the total number of moles of gases in the container after combustion. Assume that H_2O is present as a gas under these conditions.

At 800K, $n_2 = \frac{1.0\times10^7 Pa\, 8.314\times10^{-3} m^3}{8.314\, J\, mol^{-1}K^{-1}\, 800K}$ **(04+01)**

$n_2 = 12.5\, mol\ or\ 12.5$ **(05)**

(iii) Write balanced chemical equations (giving physical states, at 800 K) for the combustion reactions of the gases given below.

I. $CH_4(g)$

II. $C_2H_6(g)$

I. $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$ **(05)**

II. $2\,C_2H_6\,(g) + 7\,O_2(g) \rightarrow 4\,CO_2(g) + 6\,H_2O(g)$ **(05)**

(iv) Only one of the two hydrocarbons above contributes to the change in the number of moles of gases before and after combustion. Calculate the number of moles of this hydrocarbon initially introduced into the container.

Hydrocarbon that contributes to the change of the number of moles before and after the combustion is C_2H_6

No. of moles increased after combustion = 0.5 mol **(05)**

The amount of C_2H_6 introduced initially = 0.5 mol x 2 = 1.0 mol or 1.0 **(05)**

(v) The container was then cooled to 300 K and the water was removed. Then the pressure of the container was 2.10×10^6 Pa. Calculate the following.

Amount (moles) of gases after removing water,

$n_3 = \frac{2.1\times10^6\, Pa\, 8.314\times10^{-3} m^3}{8.314\, J\, mol^{-1}K^{-1}\, 300K}$ **(04+01)**

$n_3 = 7.0\, mol\ or\ 7.0$ **(05)**

I. Total number of moles of H_2O produced

The amount of water formed = (12.5 – 7.0) mol = 5.5 mol or 5.5 **(05)**

II. Number of moles of H_2O produced from the combustion of C_2H_6

The amount of water generated from the combustion of $C_2H_6 = \frac{6.0\, mol \times 1.0\, mol}{2.0\, mol}$

= 3.0 mol or 3.0 **(05)**

III. Number of moles of H_2O produced from the combustion of CH_4

The amount of water generated from the combustion of CH_4 = (5.5 – 3.0) mol
= 2.5 mol or 2.5 **(05)**

IV. Number of moles of O_2 introduced initially into the container

The amount of O_2 introduced initially = 12.0 mol – (1.0 mol + amount of CH_4 introduced)
= 12.0 mol – (1.0 + 2.5/2) mol
= 9.75 mol or 9.75 **(05)**

5(a) : 75 marks

Alternate answers for (iv) and (v)

(iv) Hydrocarbon that contributes to the change of the number of moles before and after the combustion is C_2H_6. **(05)**

Let the number of moles of the species as follows

Initially,

$CH_4 = n_1$ $C_2H_6 = n_2$ and $O_2 = 2n_1 + 7/2n_2 + n_{excess}$

After combustion,

$CO_2 = n_1 + 2n_2$, $H_2O = 2n_1 + 3n_2$ and $O_2 = n_{excess}$

Before combustion the number of moles in the container => 12.0 mol = $n_1 + n_2 + 2n_1 + 7/2n_2 + n_{excess}$ --(1)

After combustion the number of moles in the container => 12.5 mol = $n_1 + 2n_2 + 2n_1 + 3n_2 + n_{excess}$-- (2)

(2)-(1) => 0.5 = $1/2n_2$

Amount of C_2H_6 introduced = n_2 = 1.0 mol or 1.0 **(05)**

(v) The total amount of water formed = $2n_1 + 3n_2$

Amount (moles) of gases after removing water,

$$n_1 + 2n_2 + n_{excess} = \frac{2.1\times10^6\ Pa\ 8.314\times10^{-3}m^3}{8.314\ J\ mol^{-1}K^{-1}\ 300K}$$ **(04+01)**

$n_1 + 2n_2 + n_{excess} = 7.0\ mol$ or 7.0 **(05)**

Therefore, from part (iv) equation (2),

$n_1 = ½(12.5- (n_1 + 2n_2 + 3n_2 + n_{excess})) = ½(12.5-10.0)$mol = 1.25 mol

(I) The total amount of water formed = $2n_1 + 3n_2$ = (2x1.25+3x1.0)mol = 5.5 mol or 5.5 **(05)**

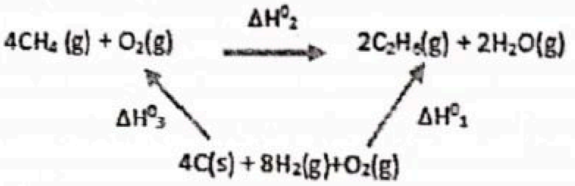
(II) The amount of water formed from C_2H_6 combustion = $3n_2$ = 3.0 mol or 3.0 **(05)**

(III) The amount of water formed from CH_4 combustion = $2n_1$ = 2.5 mol or 2.5 **(05)**

(IV) The amount of O_2 introduced initially = (12.0 –(1.25+1.0))mol = 9.75 mol or 9.75 **(05)** (*b*) (i) Using a **thermochemical cycle** and the data given, calculate the standard enthalpy change for the reaction given below.

$$4\,CH_4(g) + O_2(g) \rightarrow 2\,C_2H_6(g) + 2\,H_2O(g)$$

	$\left(\Delta H_f^{\circ}\right)$ (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
$CH_4(g)$	−74.8	186.3
$C_2H_6(g)$	−84.7	229.6
$CO_2(g)$	−393.5	213.7
$H_2O(g)$	−214.8	188.8
C(s), graphite	0.0	5.7
$O_2(g)$	0.0	205.1
$H_2(g)$	0.0	130.7



To award marks for a reaction, the physical state and stoichiometry of all the species on both sides of an arrow must be correct. If the physical state and stoichiometry are correct then award **(02 marks)** per species.

(02 marks x 7 = 14)

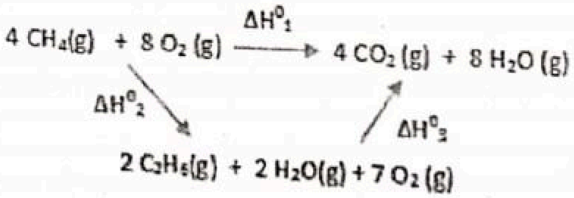
$\Delta H^0_2 = \Delta H^0_1 - \Delta H^0_3$ Or $\Delta H_2^0 = \sum \Delta H^0(products) - \sum \Delta H^0(reactants)$ **(03)**

$\Delta H_2^0 = [\overset{\textbf{(06)}}{-84.7\times2}\ \overset{\textbf{(06)}}{-\ 214.8\times2}\ \overset{\textbf{(06)}}{-\ (-74.8}\overset{\textbf{(02)}}{\times4)}]$ kJ mol^{-1}

$= -299.8$ kJ mol^{-1}

(03+01)

Alternate thermodynamic cycle



To award marks for a reaction, the physical states and stoichiometry of all the species on both sides of an arrow must be correct. If the physical state and stoichiometry are correct then award **(02 marks)** per species.

(02 marks x 7 = 14)

$\Delta H^0_1 = (\overset{\textbf{(02)}}{-393.5\times4}\ \overset{\textbf{(02)}}{-214.8\times8} - (\overset{\textbf{(02)}}{-74.8\times4} + \overset{\textbf{(01)}}{0\times}\overset{\textbf{(02)}}{8)})$ kJ mol^{-1}

$= -2993.2$ kJ mol^{-1}

$\Delta H^0_3 = ((\overset{\textbf{(02)}}{-393.5\times4}\ \overset{\textbf{(02)}}{-214.8\times8}) - (\overset{\textbf{(02)}}{-84.7\times2}\ \overset{\textbf{(02)}}{-\ 214.8\times2}\ \overset{\textbf{(01)}}{-\ 0\times}\overset{\textbf{(02)}}{7)})$ kJ mol^{-1}

$= -2693.4$ kJ mol^{-1}

$\Delta H^0_2 = \Delta H^0_1 - \Delta H^0_3$

$= (-2993.2-(-2693.4))$ kJ mol^{-1} **(03)**

$= -299.8$ kJ mol^{-1}

(03+01)

(ii) Calculate the standard entropy change for the reaction in (*b*)(i) above.

$\Delta S^0 = \sum S^0(products) - \sum S^0(reactants)$ **(04)**

(02) **(02)** **(02)** **(02)** **(01)**

ΔS^0 = ((229.6x2 + 188.8x2 – (186.2x4 + 205.1x1)) J mol^{-1} K^{-1}

= -113.5 J mol^{-1} K^{-1} **(02+01)**

(iii) Calculate the standard Gibbs energy change (ΔG^0) for the reaction in (*b*)(i) above at 500 K.

$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$ **(04)**

= -299.8 kJ mol^{-1} – (500 K x (-113.5 x10^{-3}) kJ mol^{-1} K^{-1}) **(04+01)**

= -243.05 kJ mol^{-1} **(02+01)**

(iv) State, giving reasons, whether increase in temperature favours the reaction in (*b*)(i) above. Assume that the enthalpy change and entropy change are independent of temperature.

Increasing temperature does not favour the forward reaction. **(03)**

(Or increasing temperature makes Gibbs energy change less negative)

Because the reaction has a negative change in entropy. **(03)**

Note: If the sign of entropy change is incorrect, but prediction agrees with the sign of the entropy change award 06 marks

5(b) : 75 marks

6. (*a*) (i) Consider the reversible reaction **a A(aq) $\rightleftharpoons$ b B(aq) + c C(aq)** that occurs in the aqueous medium. Considering that both forward and reverse steps are elementary reactions, write expressions for the rate of the forward reaction (R_1) and the rate of the reverse reaction (R_2). Rate constants for the forward reaction and the reverse reaction are k_1 and k_2, respectively.

$R_1 = k_1\,[A(aq)]^a$ **(05+01)**

$R_2 = k_2\,[B(aq)]^b\,[C(aq)]^c$ **(05+01)**

[expression 05 marks, physical states 01 mark]

(ii) Write the relationship between R_1 and R_2 at equilibrium.

At equilibrium, $R_1 = R_2$ **(05)**

(iii) Write down the expression for equilibrium constant K_C. Also give the relationship between K_C, k_1 and k_2.

$$K_c = \frac{[B(aq)]^b[C(aq)]^c}{[A(aq)]^a}$$ **(05+01)**

[expression 05 marks, physical states 01 mark]

$$K_C = \frac{k_1}{k_2}$$ **(05)**

(iv) To study the above equilibrium, three experiments were carried out at a constant temperature. In these experiments, different amounts of A, B and C were mixed, and the system was allowed to reach equilibrium. The following data were obtained at equilibrium.

Experiment Number	Concentration at equilibrium (mol dm^{-3})		
	[A]	[B]	[C]
1	1.0×10^{-1}	1.0×10^{-2}	1.0×10^{-3}
2	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-3}
3	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-5}

I. Obtain three relationships by substituting the concentrations of A, B and C given in the table for experiments 1, 2 and 3 in the equilibrium constant expression written in (*a*)(iii) above.

$$K_c = \frac{(1.0\times10^{-2})^b\,(1.0\times10^{-3})^c}{(1.0\times10^{-1})^a} \quad \text{--(1)}$$ **(06)**

$$K_c = \frac{(1.0\times10^{-3})^b\,(1.0\times10^{-3})^c}{(1.0\times10^{-2})^a} \quad \text{--(2)}$$ **(06)**

$$K_c = \frac{(1.0\times10^{-2})^b\,(1.0\times10^{-5})^c}{(1.0\times10^{-2})^a} \quad \text{--(3)}$$ **(06)**

II. Prove that a = b = 2c using these relationships.

From (1)/(2)=> $1 = \frac{10^b}{10^a}$ **(05)**

$10^a = 10^b$

a=b **(05)**

From (2)/(3) => $1 = \frac{10^{2c}}{10^b}$ **(05)**

$10^b = 10^{2c}$

b = 2c **(05)**

Therefore, a = b = 2c

Alternate answer 1 for **(iv) (II)**

Using equations (1), (2) and (3) in (iv)(I)

$K_C = 10^{-2b-3c+a}$ ---------- (4) **(04)**

$K_C = 10^{-3b-3c+2a}$ --------- (5) **(04)**

$K_C = 10^{-2b-5c+2a}$ --------- (6) **(04)**

Log K_c = -2b-3c+a ---------(7)

Log K_c = -3b-3c+2a ---------(8)

Log K_c = -2b-5c+2a ---------(9)

(4)/(5) or (7)-(8) → a = b **(04)**

(5)/(6) or (8)-(9) → a = 2c **(04)**

Therefore, a = b = 2c

Alternate answer 2 for **(iv) (II)**

Using equations (1), (2) and (3) in (iv)(I)

$K_C = (0.01)^b(0.001)^c(0.1)^{-a}$ ---------- (4)

$K_C = (0.001)^b(0.001)^c(0.01)^{-a}$ -------- (5)

$K_C = (0.01)^b(0.00001)^c(0.01)^{-a}$ ------ (6)

(1)/(2)→ $1 = 10^b \times 10^{-a}$ **(05)**

$10^a = 10^b$

a=b **(05)**

(1)/(3) → $1 = 10^{2c} \times 10^{-a}$ **(05)**

$10^a = 10^{2c}$

a = 2c **(05)**

Therefore, a = b = 2c

III. Using the smallest integers for the stoichiometric coefficients a, b and c, calculate the value of the equilibrium constant, K_C of the above reaction.

Using the smallest set of integers,

a = 2, b=2, c=1

Calculation of K_C

$$K_C = \frac{(1.0\times10^{-2} mol\ dm^{-3})^2(1.0\times10^{-3} mol\ dm^{-3})^1}{(1.0\times10^{-1} mol\ dm^{-3})^2}$$ **((02+01)x3=09)**

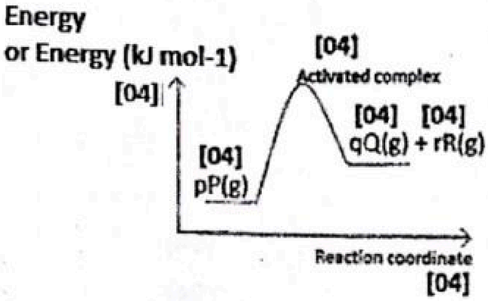
$K_C = 1.0 \times 10^{-5} mol\ dm^{-3}$ **(04+01)**

Note: a, b and c must be correct to award marks for K_c

6(a) : 80 marks

(*b*) Consider the reaction, **p P(g) ⇌ q Q(g) + r R(g)** that takes place in gas phase.

(i) The enthalpy change and activation energy of the forward reaction, **p P(g) ⟶ q Q(g) + r R(g)** are 50.0 kJ mol^{-1} and 90.0 kJ mol^{-1}, respectively. Draw the labelled energy diagram (the graph of energy vs reaction coordinate) for this reaction. Show the positions of P, Q and R by marking them on the energy diagram. Also, mark the position of the activated complex as 'activated complex' on it.



(ii) Calculate the activation energy for the reverse reaction.

Activation energy of the reaction = E_a

E_a = (90.0 – 50.0) kJ mol^{-1} **(05+01)**

= 40.0 kJ mol^{-1} **(04+01]**

(iii) Explain the effect of increasing temperature on the equilibrium constant of this reaction.

When the temperature is increased, the equilibrium constant is increased **(05)**
because the reaction has a positive change in enthalpy **(05)**
When the temperature is increased, the rate constant of the forward reaction is increased more than the rate constant of the reverse reaction. **(05)**

(iv) Explain the effect of a catalyst
I. on the rates of forward and reverse reactions.
II. on the equilibrium constant.

(I) Increases the rate of forward reaction **(05)**
and the rate of the reverse reaction **(05)**
by the same factor (extent). **(05)**

(II) The value of the equilibrium constant is not changed. **(05)**

Alternate answer

(iv) Addition of a catalyst,

(I) It provides a new pathway for the reaction **(05)** with higher rate constants for forward and reverse reactions **(05)**.

The ratio between the two rate constants does not change **or** Rate constants of the forward and reverse reactions are increased by the same factor (extent). **(05)**

(II) The value of the equilibrium constant is not changed. **(05)**

6(b) : 70 marks

7. (*a*) You are provided with the three metal rods **L**, **M**, **N** and the three solutions L^{2+} (1.0 mol dm^{-3}), M^{2+} (1.0 mol dm^{-3}), N^{2+} (1.0 mol dm^{-3}). When the metal **N** is dipped in the solution of M^{2+} ions, M^{2+} is reduced to **M**, whereas when **N** is dipped in the solution of L^{2+} ions, L^{2+} does not get reduced to **L**.

(i) Giving reasons arrange the three metals, **L**, **M** and **N** in the increasing order of their reducing ability.

$N(s) + M^{2+}(aq) \rightarrow N^{2+}(aq) + M(s)$ is spontaneous or $M^{2+}(aq)$ is reduced by N(s) **(02)**

Reducing ability N > M or $[E^0_{N2+(aq)/N(s)} < E^0_{M2+(aq)/M(s)}]$ **(03)**

$N(s) + L^{2+}(aq) \rightarrow N^{2+}(aq) + L(s)$ is not spontaneous or $L^{2+}(aq)$ is not reduced by N(s) **(02)**

Reducing ability of L > N or $[E^0_{L2+(aq)/L(s)} < E^0_{N2+(aq)/N(s)}]$ **(03)**

Increasing order of reducing ability M < N < L **(05)**

(Or increasing order of oxidizing ability L< N < M)

(ii) Electromotive forces of the two electrochemical cells prepared using $L^{2+}(aq)/ L(s)$ electrode and each of the other two electrodes are +0.30 V and +1.10 V. Using this information and your answer to (i) above, calculate $E^{\circ}_{M^{2+}(aq)/M(s)}$ and $E^{\circ}_{N^{2+}(aq)/N(s)}$.
$\left(E^{\circ}_{L^{2+}(aq)/L(s)} = -0.80\text{ V}\right)$

Out of the two cells one has E_{cell} = 0.30 V and the other has E_{cell} = 1.10 V

Highest E_{cell} is between $L^{2+}(aq)/L(s)$ electrode and $M^{2+}(aq)/M(s)$ electrode.

The lowest E_{cell} is between $L^{2+}(aq)/L(s)$ electrode and $N^{2+}(aq)/N(s)$ electrode.

$E^0_{M2+(aq)/M(s)} - E^0_{L2+(aq)/L(s)} = 1.10\text{ V}$ **(04+01)**

$E^0_{M2+(aq)/M(s)} = 1.10\text{ V} - 0.80\text{ V} = 0.30\text{ V}$ **(04+01)**

And

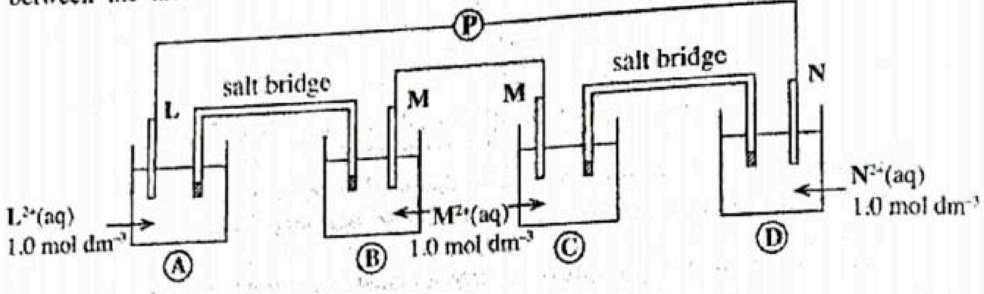
$E^0_{N2+(aq)/N(s)} - E^0_{L2+(aq)/L(s)} = 0.30\text{ V}$ **(04+01)**

$E^0_{N2+(aq)/N(s)} = 0.30\text{ V} + (-0.80\text{V}) = -0.50\text{ V}$ **(04+01)**

Note: Do not deduct marks if physical states are not indicated when writing E^0

Alternate answer
Based on the order of reducing ability, $L^{2+}_{(aq)}/L_{(s)}$ should be the anode in both the cells.
$E^0_{cathode} - E^0_{L2+(aq)/L(s)} = 1.10\text{ V}$
Therefore $E^0_{cathode} = 1.10\text{ V} - 0.80\text{ V} = 0.3\text{ V}$ **(04+01)**
$E^0_{cathode} - E^0_{L2+(aq)/L(s)} = 0.3\text{ V}$
Therefore $E^0_{cathode} = 0.3\text{ V} - 0.80\text{ V} = -0.5\text{ V}$ **(04+01)**
Therefore,
$E^0_{M2+(aq)/M(s)} = 0.3\text{ V}$ **(04+01)**
$E^0_{N2+(aq)/N(s)} = -0.5\text{ V}$ **(04+01)**

(iii) You are provided with the following arrangement, where a potentiometer (**P**) is connected between the metal rods **L** and **N**.



I. Calculate the potentiometer reading.

II. Write the electrode reactions that occur at each of the electrodes Ⓐ, Ⓑ, Ⓒ and Ⓓ separately when the potentiometer is removed and **L** and **N** are connected by a conductor.

Potentiometer reading (P),

$P = E^0_{cell(1)} + E^0_{cell(2)}$ **(05)**

$= (E^0_{M2+(aq)/M(s)} - E^0_{L2+(aq)/L(s)}) + (E^0_{N2+(aq)/N(s)} - E^0_{M2+(aq)/M(s)})$ **(05)**

$= E^0_{N2+(aq)/N(s)} - E^0_{L2+(aq)/L(s)}$ **(05)**

$= -0.50\ V - (-0.80\ V)$

$= 0.30\ V$ **(04+01)**

II. Write the electrode reactions that occur at each of the electrodes Ⓐ, Ⓑ, Ⓒ and Ⓓ separately when the potentiometer is removed and **L** and **N** are connected by a conductor.

Electrode reactions when a current is drawn.

Electrode (A) $L(s) \rightarrow L^{2+}(aq) + 2e$ **(05)**

Electrode (B) $M^{2+}(aq) + 2e \rightarrow M(s)$ **(05)**

Electrode (C) $M(s) \rightarrow M^{2+}(aq) + 2e$ **(05)**

Electrode (D) $N^{2+}(aq) + 2e \rightarrow N(s)$ **(05)**

Note: Do not award marks if $\rightleftharpoons$ are used in the reactions.

7(a) : 75 marks

(b) The following questions are based on the element manganese (Mn).

(i) Write the complete electronic configuration of Mn.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

(03)

(ii) Write **three** common oxidation states of Mn.

+2, +3, +4, +7 (any three)

(02 x 3)

(iii) When $MnSO_4 \cdot H_2O$ is dissolved in water, solution **P** is obtained.

I. State the colour of solution **P**.

II. Give the chemical formula and the IUPAC name of the species responsible for this colour.

I. very pale pink/ pale pink/ colourless (03)

II. $[Mn(H_2O)_6]^{2+}(aq)$ (03)

hexaaquamanganese(II) ion (03)

(iv) What would you observe when

I. dilute NaOH is added to solution P?

II. the mixture from (iv)(I) above is exposed to air?

III. conc. HCl is added to the mixture from (iv)(I) above?

I. white/cream precipitate (03)

II. brown precipitate or blackish-brown precipitate (03)

III. yellow / greenish-yellow solution (03)

(v) Give the chemical formulae of **five** oxides of Mn, and write the oxidation state of Mn in each. State the nature of each of the oxides as basic, weakly basic, amphoteric, weakly acidic, acidic.

MnO	+2	basic	(02 x 3)
Mn_2O_3	+3	weakly basic	(02 x 3)
MnO_2	+4	amphoteric	(02 x 3)
MnO_3	+6	weakly acidic	(02 x 3)
Mn_2O_7	+7	acidic	(02 x 3)

(vi) Give the chemical formula of the most common oxoanion of Mn.

MnO_4^- (03)

(vii) Give balanced ionic half equations to indicate how the oxoanion given by you in (vi) above behaves as an oxidizing agent in acidic and basic media.

Acidic

$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ (06)

Alkaline

$MnO_4^-(aq) + 2H_2O(l) + 3e \longrightarrow MnO_2(s) + 4OH^-(aq)$ (06)

(viii) State **one** use of $MnSO_4$ in the analysis of water quality parameters.

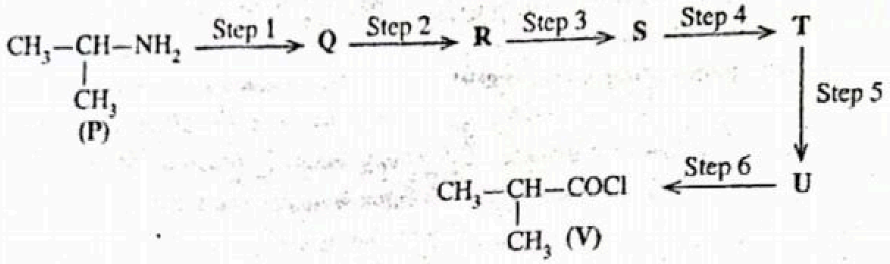
Determination of dissolved O_2 in water samples or Winkler method (03)

7(b) : 75 marks

PART C – ESSAY

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

8. (*a*) Compound **P** was converted to compound **V** using the reaction scheme given below.



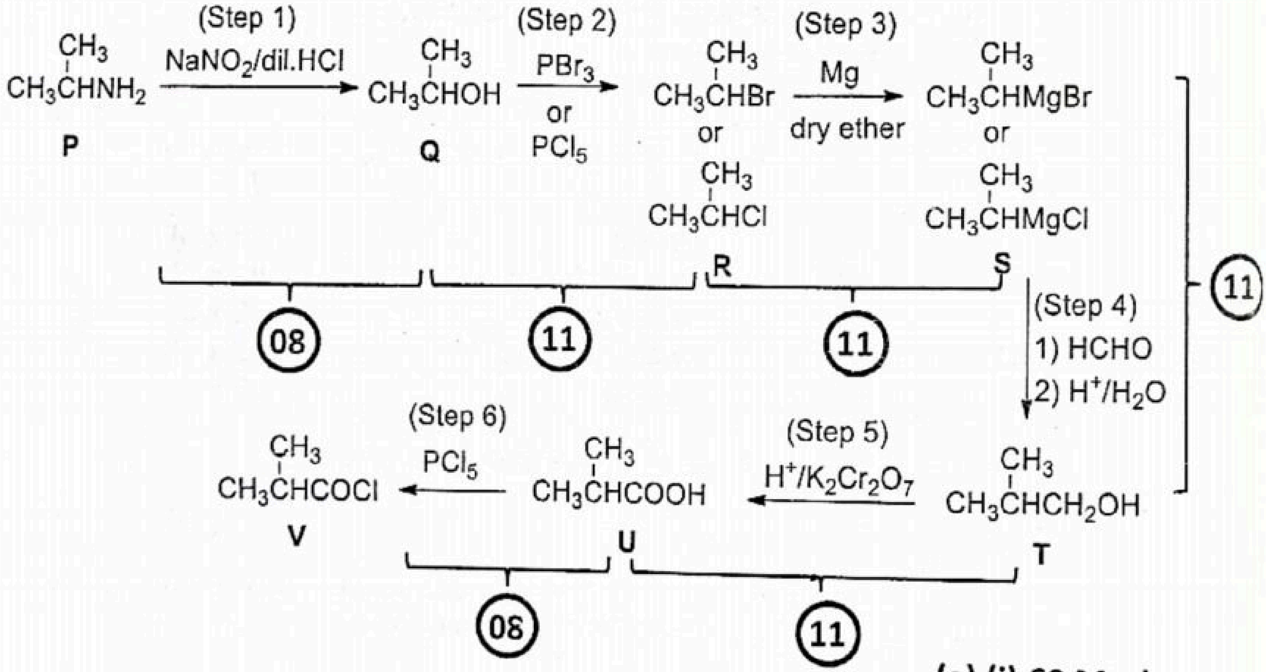
(i) Complete the above reaction sequence by drawing the structures of compounds **Q**, **R**, **S**, **T** and **U** and writing the reagents for steps 1–6 selected only from those given in the list below.

List of reagents
HCHO, Mg/dry ether, $H^+/K_2Cr_2O_7$, PCl_5, PBr_3, $NaNO_2$/dilute HCl, H^+/H_2O

(**Note:** The reaction of a compound with a Grignard reagent and the hydrolysis of the resultant magnesium alkoxide should be considered as **one step** in the above reaction sequence.)

(ii) Draw the structure of the product formed when compounds **P** and **V** react with each other.

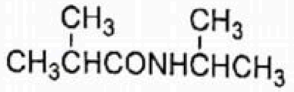
i



(a) (i) 60 Marks

*In **Step 4** the student may have misinterpreted the instruction given in the note in the question and written HCHO and H^+/H_2O without showing the sequence 1 and 2. Award the **11** Marks.

ii



$$CH_3\overset{CH_3}{\overset{|}{C}}HCONH\overset{CH_3}{\overset{|}{C}}HCH_3$$

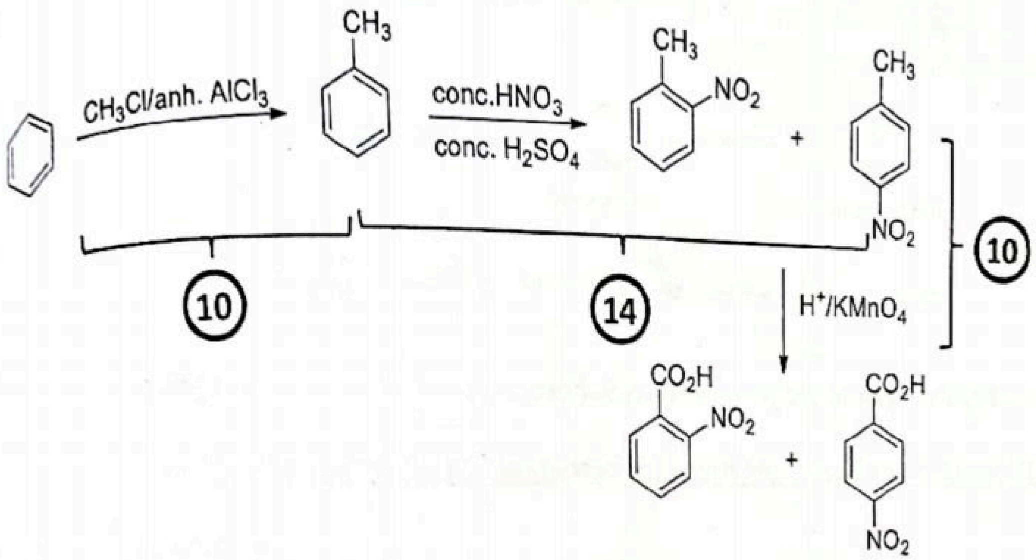
05

(a) (ii) 05 Marks

8(a) : 65 Marks

(b) (i) Propose a method to prepare a mixture of *o*-nitrobenzoic acid and *p*-nitrobenzoic acid from benzene using not more than **three** (03) steps.

i

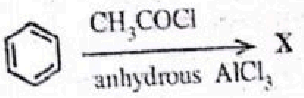


(b) (i) 34 Marks

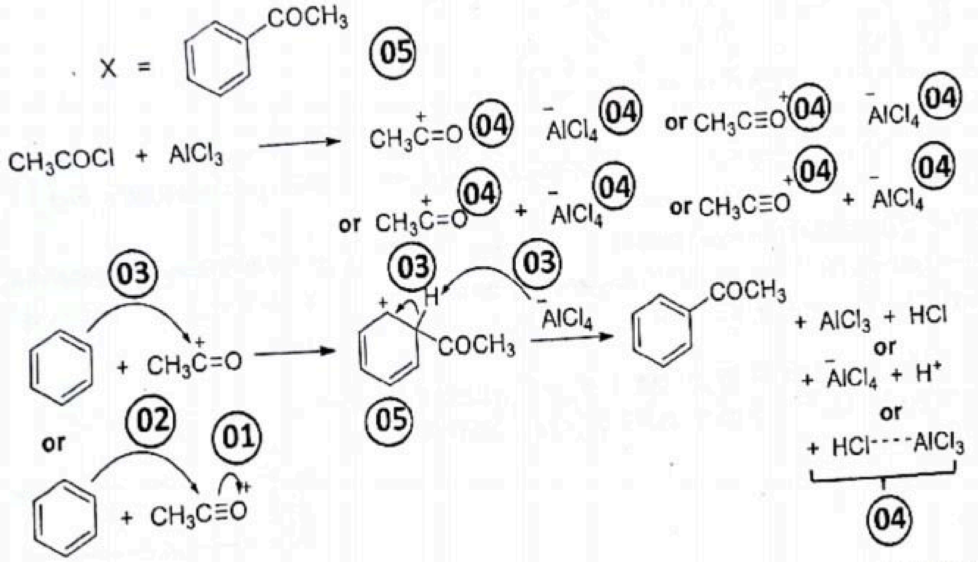
IF only one product is written for the nitration reaction **do not award the 14 marks.**

However, award **05 marks** for the oxidation step.

(ii) Give the structure of the product **X** and the mechanism of the following reaction.



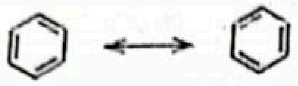
(65 marks)



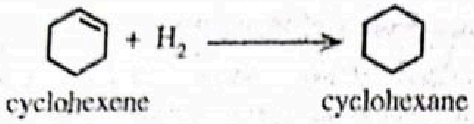
(b) (ii) 31 Marks

8(b): 65 Marks

(c) The structure of benzene is represented as the resonance hybrid of the following two hypothetical six membered cyclic structures (cyclohexatriene).



Using the standard enthalpy data of hydrogenation given below, show that benzene is more stable than hypothetical 'cyclohexatriene'.



$\Delta H^o = -120$ kJ mol^{-1}

Benzene + $3H_2 \longrightarrow$ cyclohexane $\Delta H^o = -208$ kJ mol^{-1}

(20 marks)

Standard enthalpy of hydrogenation of cyclohexene = -120 kJ mol^{-1}

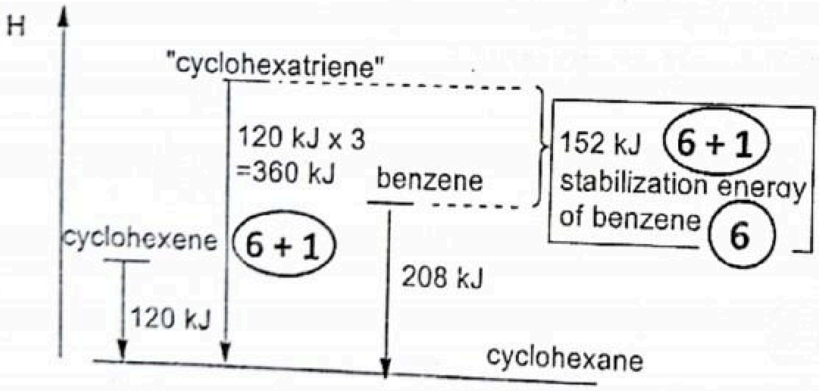
Expected enthalpy of hydrogenation of hypothetical "cyclohexatriene" = -120 × 3 kJ mol^{-1}

= -360 kJ mol^{-1} (6 + 1)

Standard enthalpy of hydrogenation of benzene = -208 kJ mol^{-1}

Stabilization energy of benzene ⑥ = - 152 kJ mol^{-1} (6 + 1)

OR



Note. **07 marks** for calculating the expected enthalpy of hydrogenation of "cyclohexatriene" and **07 marks** for calculating the stabilization energy of benzene.
06 marks for showing that the stabilization energy of benzene is equal to the difference between the two hydrogenation enthalpy values. This **06 marks** can be awarded even if the stabilization energy is not calculated but indicated by a statement such as following.

Hydrogenation of both benzene and "cyclohexatriene" (with $3H_2$) give cyclohexane. However, benzene evolves less energy than "cyclohexatriene" in this process. Therefore, it is more stable.

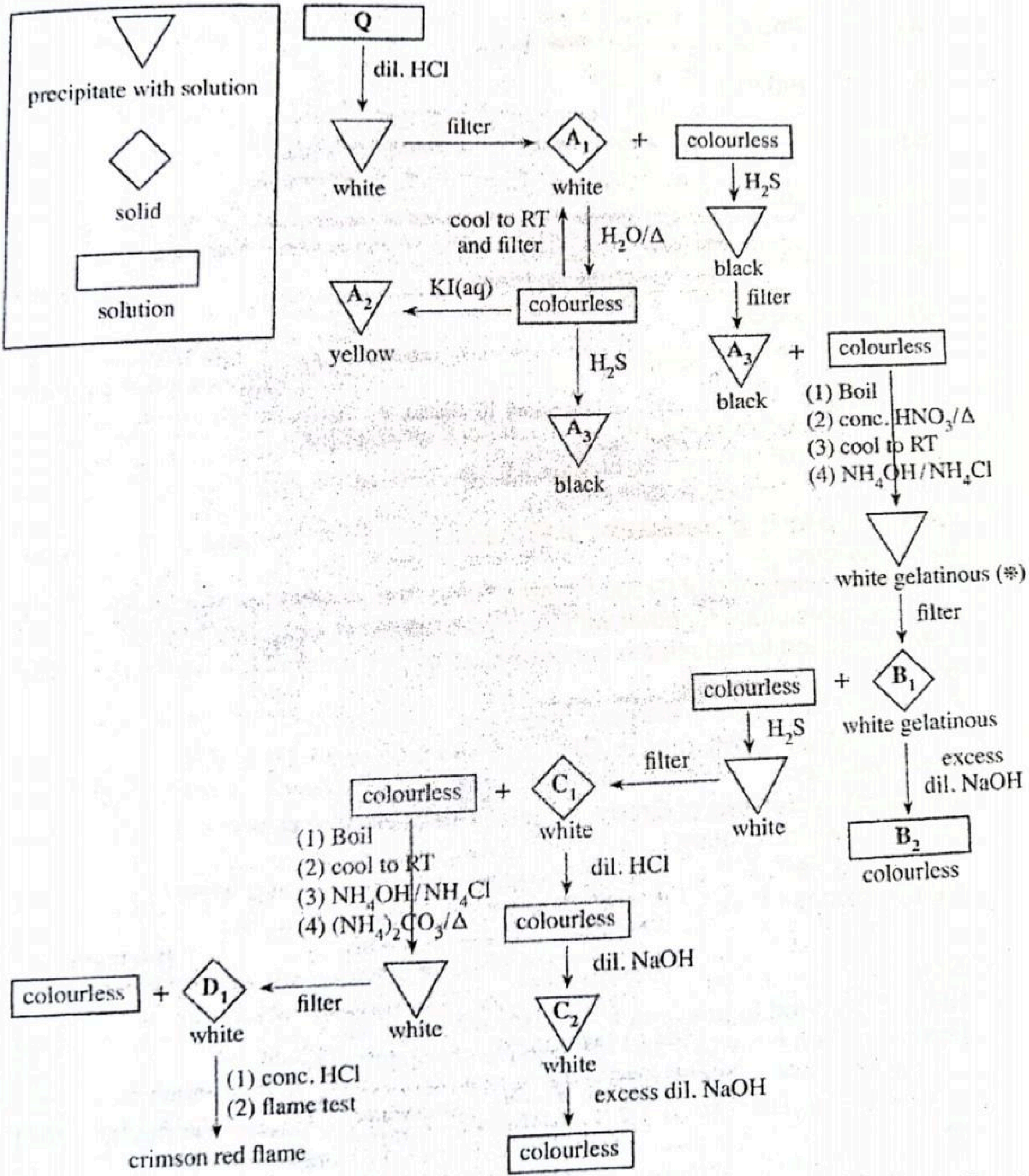
8(c) :20 Marks

9. (*a*) The following question is based on the qualitative analysis of cations.

An aqueous solution **Q** contains **four** cations of metals **A**, **B**, **C** and **D**. **Q** is subjected to the reactions given in the scheme below.

The symbols given in the box are used to represent precipitates with solutions, solids and solutions.

(**Note**: RT – room temperature)



(i) A_1, A_2, A_3, B_1, B_2, C_1, C_2, and D_1 are compounds/species of the four cations **A**, **B**, **C**, and **D**.

Identify A_1, A_2, A_3, B_1, B_2, C_1, C_2, and D_1.

(**Note**: Write **only** chemical formulae. Chemical equations and reasons are **not** required.)

A_1	$PbCl_2$
A_2	PbI_2
A_3	PbS
B_1	$Al(OH)_3$
B_2	$NaAlO_2$ or AlO_2^- or $[Al(OH)_4]^-$ or $Na[Al(OH)_4]$
C_1	ZnS
C_2	$Zn(OH)_2$
D_1	$SrCO_3$

(08 marks x 8 = 64 marks)

(ii) Give a reason for the use of NH_4OH/NH_4Cl as a reagent when obtaining the white gelatinous precipitate (✻). *(75 marks)*

NH_4OH is added to precipitate the Group III ions (Fe^{3+}, Al^{3+} and Cr^{3+}) as hydroxides. **(02)**

Then, the hydroxides of Group IV metal ions (Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}) may also precipitate together with the hydroxides of Group III metal ions. **(02)**

NH_4Cl is added to reduce the concentration of OH^- (common ion effect). **(02)**

or

Addition of NH_4Cl shifts the equilibrium position of NH_4OH

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ and the concentration of OH- is reduced

The K_{sp} of hydroxides of Group IV metal ions is greater than those of the Group III metal ions. **(02)**

This allows Fe^{3+}, Al^{3+} and Cr^{3+} hydroxides to be precipitated while the hydroxides of Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} remain in solution. **(03)**

(11 marks)

Alternate Answer

NH_4OH is added to precipitate Al^{3+} as the hydroxide. **(02)**

However, then both Zn^{2+} and Al^{3+} can be precipitated as their hydroxides. **(02)**

NH_4Cl is added to reduce the concentration of OH^- (common ion effect). **(02)**

or

Addition of NH_4Cl shifts the equilibrium position of NH_4OH

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ and the concentration of OH- is reduced

K_{sp} of $Zn(OH)_2 >$ $Al(OH)_3$ **(02)**

Therefore, precipitation of $Zn(OH)_2$ can be prevented by using NH_4Cl / NH_4OH **(03)**

(11 marks)

(b) A mixture **X** contains only aluminium sulfide (Al_2S_3) and ferric sulfide (Fe_2S_3). The following procedure was carried out to calculate the mass percentages of Al_2S_3 and Fe_2S_3 in **X**. When a mass **m** of mixture **X** was heated at high temperature under H_2 gas, Al_2S_3 remains unchanged but Fe_2S_3 was converted to iron (Fe) metal. The final mass obtained was 0.824 g. When another mass **m** of mixture **X** was heated at high temperature in air, both Al_2S_3 and Fe_2S_3 decomposed, giving SO_2 gas. This SO_2 gas was bubbled through a solution of H_2O_2 and oxidized to H_2SO_4 acid, which is the only product. When this entire solution was titrated with a standard 1.00 mol dm^{-3} NaOH solution in the presence of phenolpthalein indicator, the burette reading was 36.00 cm^3.

(i) Write the balanced chemical equation for the reaction of Fe_2S_3 with hydrogen gas.

$Fe_2S_3 + 3H_2 \rightarrow 2Fe + 3H_2S$ **(04)**

(ii) Write the balanced chemical equation for the reaction of SO_2 with H_2O_2 to give H_2SO_4.

$SO_2 + H_2O_2 \rightarrow H_2SO_4$ **(04)**

(iii) Calculate the mass percentages of Al_2S_3 and Fe_2S_3 in mixture **X**.

$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$ or $Al_2S_3 : SO_2 = 1 : 3$ **(03)**

$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$ or $Fe_2S_3 : SO_2 = 1 : 3$ **(03)**

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ or $H_2SO_4 : NaOH = 1 : 2$ **(03)**

Molar mass of Al_2S_3 = (27x2)+(32x3) = 150 **(02)**

Molar mass of Fe_2S_3 = (56x2)+(32x3) = 208 **(02)**

Assume mass of Al_2S_3 to be m_1 and Fe_2S_3 to be m_2

Mass of Fe from Fe_2S_3 after heating under H_2

$$\frac{m_2}{208}\times 56\times 2$$ **(04)**

Total mass after heating under H_2

$$m_1+\frac{m_2}{208}\times 56\times 2=0.824g \text{ —— } [1]$$ **(08]**

From heating under air

Mols of H_2SO_4 from Al_2S_3 $=\frac{m_1}{150}\times 3$ **(04)**

Mols of H_2SO_4 from Fe_2S_3 $=\frac{m_2}{208}\times 3$ **(04)**

Total mols from both Fe_2S_3 and Al_2S_3 $=\frac{m_1}{150}\times 3+\frac{m_2}{208}\times 3$ **(04)**

Mols of NaOH for titration $=\frac{1}{1000}\times 36$ **(02)**

Mols of H_2SO_4 from titration $= \frac{1}{1000} \times \frac{36}{2} = 18 \times 10^{-3}$ (02)

$$\frac{3m_1}{150} + \frac{3m_2}{208} = 18 \times 10^{-3}\, g \quad \rightarrow [2]$$ (08)

$$m_1 + \frac{m_2}{208} \times 112 = 0.824\, g \quad \rightarrow [1]$$

$$\frac{3m_1}{150} + \frac{3m_2}{208} = 18 \times 10^{-3}\, g \quad \rightarrow [2]$$

Solving equations [1] and [2] for m_1 and m_2

$$\frac{m_1}{50} + \frac{3m_2}{208} = 0.018 \quad \rightarrow [3]$$

$$\frac{m_1}{50} + \frac{3m_2}{208} = 0.018 \quad \rightarrow [3]$$

[3] x 50

$$m_1 + \frac{150m_2}{208} = 50 \times 0.018 \quad \rightarrow [4]$$

[4] - [1]

$$\frac{150m_2}{208} - \frac{112m_2}{208} = 0.900 \times 0.824$$

$m_2 =$ 0.416 g

(02)

$m_2 =$ 0.416 g in eq [1]

$$m_1 + \frac{0.416 \times 112}{208} = 0.824$$

$m_1 =$ 0.600 g

(02)

$$\% m_1 = \frac{0.600}{0.416 + 0.600} \times 100\% = 59.06\%$$ or 59 % (04)

$$\% m_2 = 100 - 59.06 = 40.94\%$$ or 41 % (04)

Alternate answer 01 for (iii)

$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$ or $Al_2S_3 : SO_2 = 1:3$ **(03)**

$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$ or $Fe_2S_3 : SO_2 = 1:3$ **(03)**

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ or $H_2SO_4 : NaOH = 1:2$ **(03)**

Molar mass of $Al_2S_3 = (27\text{x}2)+(32\text{x}3) = 150$ **(02)**

Molar mass of $Fe_2S_3 = (56\text{x}2)+(32\text{x}3) = 208$ **(02)**

Assuming mols of Al_2S_3 is n_1 and mols of Fe_2S_3 as n_2

Mols of Fe from Fe_2S_3

$n_2 \times 56 \times 2$ **(04)**

Total mass after heating under H_2

$150n_1 + 112n_2 = 0.824 \rightarrow [1]$ **(08)**

Mols of NaOH for titration $= \frac{1}{1000} \times 36$ **(02)**

Mols of H_2SO_4 from titration $= \frac{1}{1000} \times \frac{36}{2} = 18 \times 10^{-3}$ **(02)**

Mols of H_2SO_4 from Al_2S_3 = $3n_1$ **(04)**

Mols of H_2SO_4 from Fe_2S_3 = $3n_2$ **(04)**

Total mols of H_2SO_4 = $3n_1 + 3n_2$ **(04)**

Therefore,

$3n_1 + 3n_2 = 0.018 \rightarrow [2]$ **(08)**

Solving equation [1]and [2] for n_1 and n_2

[2] x 50 $150n_1 + 150n_2 = 0.9 \rightarrow [3]$

[3] –[1] $38n_2 = 0.076$

$n_2 = 2 \times 10^{-3}$ mol **(02)**

Substituting n_2 in [2]

$3n_1 + 3 \times 0.002 = 0.018$

$n_1 = 0.004$ mol **(02)**

Mass of Al_2S_3 = 0.004 mols x 150 $gmol^{-1}$ = 0.600 g

Mass of Fe_2S_3 = 0.002 mols x 208 $gmol^{-1}$ = 0.416 g

% mass of Al_2S_3 $= \frac{0.600}{0.600+0.416} \times 100\% = 59.06$ or 59 % (04)

% mass of Fe_2S_3 $= 100 - 59.06 = 40.94$ or 41 % (04)

Alternate answer 02 for (iii)

$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$ or $Al_2S_3 : SO_2 = 1:3$ (03)

$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$ or $Fe_2S_3 : SO_2 = 1:3$ (03)

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ or $H_2SO_4 : NaOH = 1:2$ (03)

Molar mass of Al_2S_3 = (27x2)+(32x3) = 150 (02)

Molar mass of Fe_2S_3 = (56x2)+(32x3) = 208 (02)

Assume mass of Al_2S_3 in the mass of 0.824 g is as *y*

$n_{Fe} = \frac{(0.824-y)}{56} mol$ (06)

$n_{Fe_2S_3} = \frac{1}{2}\frac{(0.824-y)}{56} mol$ ——— [1] (06)

$n_{SO_2} = 3 \times \frac{y}{150} + 3 \times \frac{1}{2}\frac{(0.824-y)}{56} mol$ (10)

Mols of NaOH for titration $= \frac{1}{1000} \times 36 mol$ (02)

Mols of H_2SO_4 from titration $= \frac{1}{1000} \times \frac{36}{2} = 18 \times 10^{-3} mol$ (02)

Therefore, $n_{SO_2} = 0.018 mol$

$n_{SO_2} = 3 \times \frac{y}{150} + 3 \times \frac{1}{2}\frac{(0.824-y)}{56} = 0.018$ ——— [2] (10)

Solving equation [2] for *m*

$$\frac{y}{150} + \frac{(0.824-y)}{112} = 0.006$$

$$112y + 150(0.824-y) = 0.006 \times 150 \times 112$$

$$38y = 22.8$$

$$y = m_{Al_2S_3} = 0.60\,g$$ **(02)**

Substituting $y = 0.60$ g in equation [1]

$$n_{Fe_2S_3} = \frac{1}{2}\frac{(0.824 - 0.60)}{56}mol = 0.002\,mol$$

$$m_{Fe_2S_3} = 0.002 \times 208\,g\,mol^{-1} = 0.416\,g$$ **(02)**

Therefore

% mass of Al_2S_3 $= \frac{0.600}{0.600 + 0.416} \times 100\% = 59.06\%$ or 59 % **(04)**

% mass of Fe_2S_3 $= 100\% - 59.06\% = 40.94\%$ or 41% **(04)**

Note: If the steps are combined award marks accordingly

(iv) If the above titration is carried out using methyl orange as the indicator instead of phenolpthalein, would there be a change in the burette reading? Explain your answer.
(Relative atomic mass: Al=27, S=32, Fe=56) (75 *marks*)

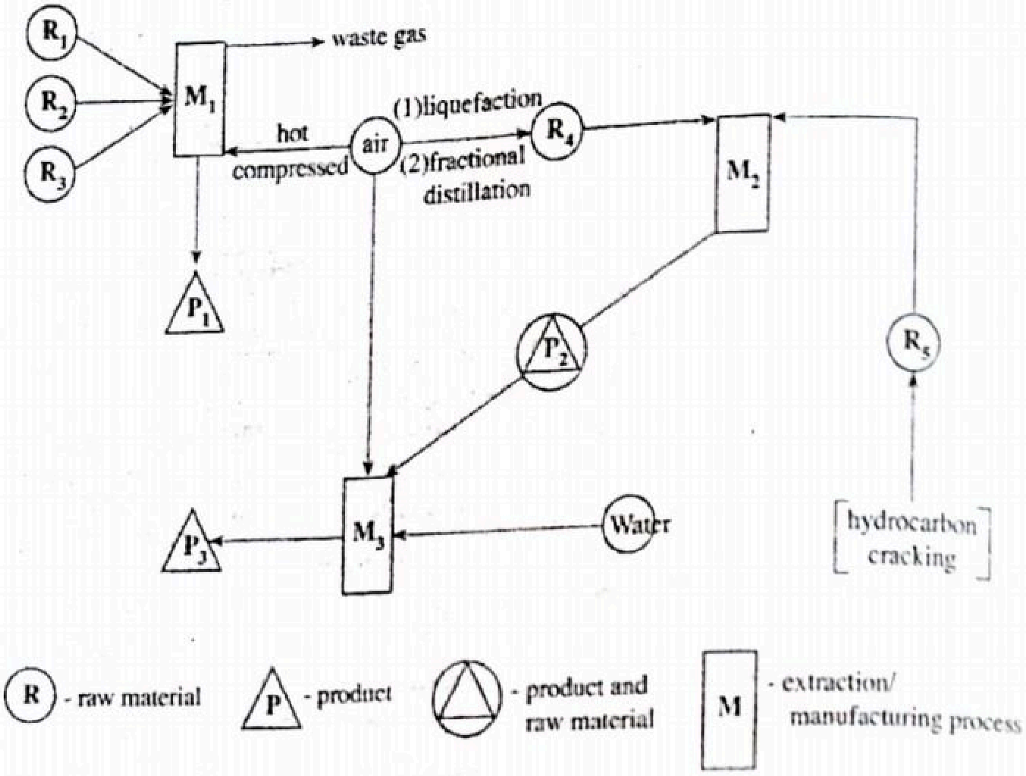
No **(02)**

Because this is a strong acid- strong base titration **(02)**

So the color change pH interval of methyl orange and phenolphthalein both falls into vertical region of the titration curve. **(02)**

9(b): 75 marks

10. *(a)* The following flow chart shows the industrial extraction/production of three important elements/ compounds P_1, P_2 and P_3.
There is evidence to show that our ancestors produced P_1 thousands of years ago. P_1 is used as a catalyst in M_2. P_3 is used in the manufacture of explosives.



(i) Name the manufacturing processes M_2 and M_3. (e.g.: Manufacture of Na_2CO_3 is named as Solvay process.)

M_2 - Manufacture of NH_3 by Haber Process (02)
M_3 – Manufacture of HNO_3 by Ostwald Process (02)

(ii) Identify the process M_1 and name the main constituent of its waste gas.

M_1 – extraction of Fe (02)
N_2 gas (02)

(iii) Give the common names of the raw materials R_1, R_2 and R_3 used in M_1.

R_1 – coke (02)
R_2 – iron ore / hematite (02)
R_3 – limestone (02)

(iv) Write a balanced chemical equation for the role of R_1 as a reducing agent in M_1 process.

As a reducing agent: $FeO(s) + C(s) \rightarrow Fe(l) + CO(g)$ (02)

Or

$CO_2(g) + C(s) \rightarrow 2CO(g)$

Or

$2FeO(s) + C(s) \rightarrow 2Fe(l) + CO_2(g)$

(v) Identify R_4 and R_5.

R4 – $N_2(g)$
R5 – $H_2(g)$
(02)
(02)

(vi) Give balanced chemical equations for reactions taking place in the processes M_1, M_2 and M_3. Appropriate conditions (temperature, pressure, catalysts, etc.) must be stated as required. (**Note**: For the M_1 process, give only the reactions showing the conversion of R_2 to P_1.)

M1:

$3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g)$ **(02)**

$Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g)$ **(02)**

$FeO(s) + CO(g) \rightarrow Fe(l) + CO_2(g)$ --(A)

$2FeO(s) + C(s) \rightarrow 2Fe(l) + CO_2(g)$ --(B)

Either (A) or (B) **(02)**

M2:

$$N_2(s) + 3H_2(g) \underset{400 - 500\ ^{\circ}C\ \mathbf{(01)}}{\overset{200 - 300\ atm\ \mathbf{(01)}}{\rightleftharpoons}} 2NH_3(s)$$ **(02)**

Fe catalyst **(01)**

K_2O and Al_2O_3 promoters **(01)**

Note: Any pressure between 200 – 300 atm and any temperature between 400 – 500 °C accepted. Physical states are not required

M3:

$$4NH_3(g) + 5O_2 \underset{\text{Pt or Pt-Rh catalyst}\ \mathbf{(01)}}{\overset{800 - 900\ ^{\circ}C\ \mathbf{(01)}}{\rightleftharpoons}} 4NO + 6H_2O(g)$$ **(02)**

$2NO(g) + O_2 \rightarrow 2NO_2$ **(02)**

$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3$ **(02)**

Note: Any temperature between 800 – 900 °C accepted. Physical states are not required

(vii) Give **two** uses each of P_1, P_2 and P_3 (**other than** what is indicated in the flow chart or given in the question).

P1 – to make alloy steel / construction industry to provide strength to structures / in machinery and tool manufacture **(01 x 2)**

P2 – production of fertilizers / production of nylon / in petroleum industry to neurtralize acide in crude oil constituents / water and waste water treatment / as refrigerant / to prevent coagulation of rubber **(01 x 2)**

P3 – manufacture of fertilizer / in industries which require nitrates such as KNO_3 in explosive manufacture and $AgNO_3$ in photography / to clean surfaces when welding metals / aqua regia **(01 x 2)**

(viii) State whether the M_2 process would be favoured at very high temperatures. Explain your answer using ΔH, ΔS and ΔG. **(50 marks)**

Reaction is exothermic. ΔH is (-ve)

No of gaseous moles decrease. ΔS decreases (-ve) **(01)**

According to ΔG = ΔH – TΔS

When ΔS is negative, –TΔS term is +ve. **(01)**

As temperature increases, +ve term overrides -ve term, making ΔG +ve. **(01)**

Therefore not favoured at high temperature. **(01)**

10(a): 50 marks

(*b*) The following questions are based on photochemical smog and water pollution.

(i) State the major types of gaseous chemical pollutants and conditions that are required for the formation of photochemical smog.

NO_x (NO or NO_2), Volatile hydrocarbon (VOC), sunlight/solar radiation, temperature above 15 °C

(02 x 4)

(ii) State why the strength of photochemical smog is low in the morning and evening.

(03)

The intensity of solar radiation is low during morning and evening.

Therefore photochemical smog is weak in the morning and evening.

(iii) Using balanced chemical equations, explain how ozone is formed in the lower atmosphere due to photochemical smog.

$2NO(g) + O_2(g) \rightarrow 2NO2(g)$

$NO_2(g) \rightarrow NO(g) + O(g)$

$O(g) + O_2(g) \rightarrow O_3(g)$

(03 x 3)

(iv) State **four** major products (excluding ozone) of photochemical smog.

PAN (peroxy acetyl nitrate)

PBN (peroxy benzoyl nitrate)

Short chain (volatile) aldehydes

Particles (particulate matter)

(02 x 4)

(v) State **three** free radicals produced during the formation of photochemical smog.

$OH^{\cdot}$ (hydroxyl radical), $ROO^{\cdot}$(peroxy radical), $R^{\cdot}$ (alkyl radical), $RO^{\cdot}$ (Alkoxy radical), $O^{\cdot}$ (oxygen radical), NO

(02 x 3)

(vi) Many countries now promote the use of electric vehicles. State how the use of electric vehicles affect the formation of photochemical smog.

Electric vehicles do not release ingredients for photochemical smog. **(02)**

Therefore, electric vehicles contribute for the reduction of photochemical smog/ no contribution for photochemical smog. **(02)**

(vii) State an environmental problem, other than photochemical smog, that could ease due to the use of electric vehicles.

Global warming/acid rain

(03)

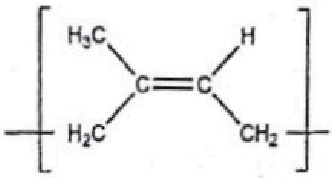
(viii) A ship carrying the following chemicals sank in the sea.
Na_2HPO_4, HNO_3, $Pb(CH_3COO)_2$
State an effect from each chemical on the water quality parameters of the water surrounding the ship, by the release of the above chemicals. *(50 marks)*

PO_4^{3-}, NO_3^-, Reduction of dissolved oxygen level.
HNO_3 Increases the acidity/decreases pH
Pb^{2+} -Increases the heavy metal level of sea water /Increases the lead level of water
(03 x 3)

10(b): 50 marks

(c) The following questions are based on natural rubber and additives used for polymer related products.

(i) Sketch the repeating unit of natural rubber. **(10)**



Note: square brackets are not required. Do not award marks if 'n' is written.

(ii) Give a compound that can be used to prevent coagulation of natural rubber latex. **(04)**

NH_3 solution

(iii) State a compound that can be used to coagulate natural rubber latex and explain how it acts. **(04)**

weak Acids such as acetic/formic acid.
H+ can neutralize the COO- groups, making the surface of rubber particles neutral. Particles can then combine together and become as a mass. **(02 x 4 = 08)**

(iv) Briefly state how the 'vulcanization' of natural rubber is carried out.

rubber is heated (or 140-160 °C) with 1-3% sulfur **(03 x 3 = 09)**

(v) State **two** types of substances used to increase the efficiency of vulcanization.
Organic catalysts
Catalyst promoters or ZnO **(03 x 2 = 06)**

(vi) Give **three** properties, which can be enhanced by adding additives to polymer products.

Increase flexibility
Decrease flammability
Prevent damage by UV rays
Increase mechanical and/or physical strength **(Any three)** **(03 x 3 = 09)**

10(c): 50 marks