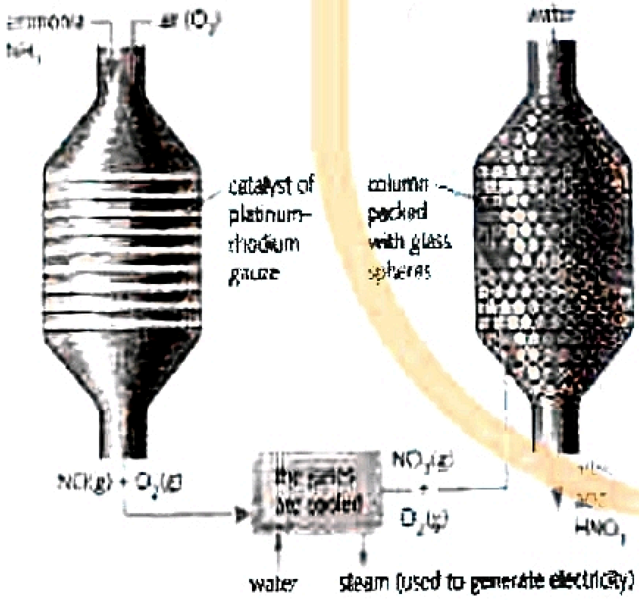
Confidential

Department of Examinations - Sri Lanka

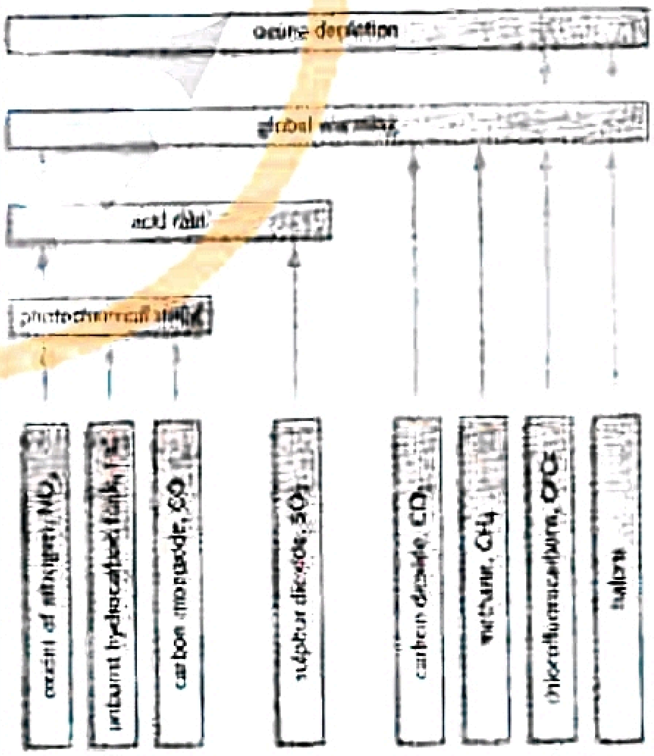
G.C.E. (A/L) Examination - 2018

02 - Chemistry

Marking Scheme



Producing nitric acid by the oxidation of ammonia.



A summary of various atmospheric pollution problems caused by human activity.

This document has been prepared for the use of Marking Examiners. Some changes would be made according to the views presented at the Chief Examiners' meeting.

Amendments to be included

ශ්‍රී ලංකා විභාග දෙපාර්තමේන්තුව
இலங்கைப் பரீட்சைத் திணைக்களம்

අ.පො.ස. (උ.පෙළ) විභාගය/ க.பொ.த. (உயர் தர)ப் பரீட்சை - 2018

විෂයය අංකය / பாட இலக்கம்: **02** විෂයය / பாடம்: **Chemistry**

ලකුණු දීමේ පටිපාටිය/புள்ளி வழங்கும் திட்டம்

I පත්‍රය/பத்திரம் I

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

✪ විශේෂ උපදෙස්/ விசேட அறிவுறுத்தல் :

එක් පිළිතුරකට/ ஒரு சரியான விடைக்கு 01 ලකුණු බැගින්/புள்ளி வீதம்

මුළු ලකුණු/மொத்தப் புள்ளிகள் 1 × 50 = 50

PART A — STRUCTURED ESSAY

Answer all four questions on this paper itself. *(Each question carries 10 marks.)*

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

(i) The polarizability of halide ions increases with increasing size. ....**True**.......

(ii) The O—N—O bond angle of NO_2 is greater than that of NO_2^-. ....**True**.......

(iii) London dispersion forces among CCl_4 molecules are smaller than the London dispersion forces among SO_3 molecules. ....**False**.......

(iv) The shape of the HSO_4^- ion is trigonal bipyramidal. ....**False**.......

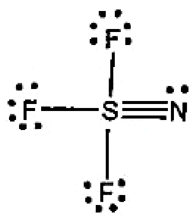
(v) All 3*d* atomic orbitals of an atom are represented by quantum numbers (*n*, *l*, m_l) 3, 2, 1. ....**False**.......

(vi) The addition of an electron to a gaseous phosphorus atom is an exothermic process whereas for a gaseous nitrogen atom it is endothermic. ....**True**.......

(✓ = True ✗ = False can be accepted.) **(04 marks x 6 = 24)**

1(a) = 24 marks

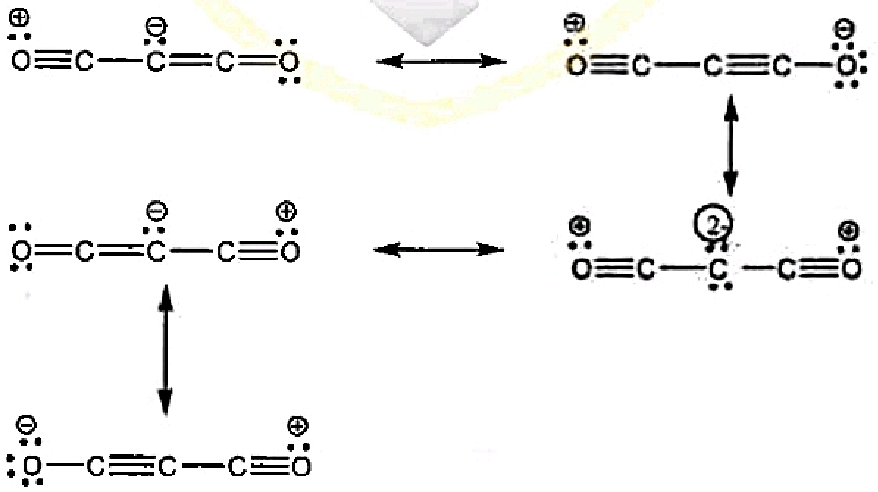
(*b*) (i) Draw the **most** acceptable Lewis structure for the molecule SF_3N.



(08)

(ii) The most stable Lewis structure for the molecule C_3O_2 (carbon suboxide) is shown below. Draw another **two** Lewis structures (resonance structures) for this molecule.

(**Note**: Marks will not be awarded for Lewis structures drawn with octet rule violated.)



(any two) **(07 marks x 2 = 14)**

(resonance arrows are not required for award of marks)

(iv) In each of the following instances, give a balanced chemical equation to indicate the action of **Y**.

I. **Y** as an oxidizing agent

$2Na(s) + 2NH_3(l) \longrightarrow 2NaNH_2(s) + H_2(g)$

$3Mg(s) + 2NH_3(l) \longrightarrow Mg_3N_2(s) + 3H_2(g)$

$6Li(s) + 2NH_3(l) \longrightarrow 2Li_3N(s) + 3H_2(g)$

(Any one) **(03)**

II. **Y** as a reducing agent

$3Cl_2(g) + 2NH_3(g) \longrightarrow N_2(g) + 6HCl(g)$

$3Cl_2(g) + 8NH_3(g) \longrightarrow N_2(g) + 6NH_4Cl(s)$

$3Cl_2(g) + NH_3(g) \longrightarrow NCl_3(l) + 3HCl(g)$

$3CuO(s) + 2NH_3(g) \longrightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$

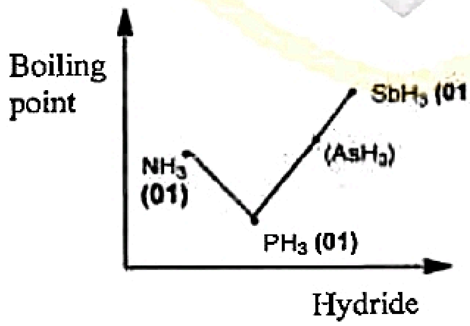
$3O_2(g) + 4NH_3(g) \longrightarrow 2N_2(g) + 6H_2O(l)$

$5O_2(g) + 4NH_3(g) \longrightarrow 4NO(g) + 6H_2O(l)$

(Any one) **(03)**

Note: Physical states are not required for award of marks.

(v) Consider the hydrides of the elements in the group to which **X** belongs, which are analogous to **Y**. Sketch the variation in boiling points of these hydrides (including **Y**) in the graph below. In your sketch indicate the hydrides using their chemical formulae. (**Note:** Values of boiling points are **not** required.)



(05)

Note: Shape (02). Shape needs to be correct for award of marks for labeling.
(i.e. Max. SbH_3; Min. PH_3; In between NH_3)

(vi) Give reasons for the variation in boiling points in part (v) above.

As molecular mass / size increases, boiling point increases. **(03)**

But with NH_3, boiling point is higher than expected because of H-bonding between NH_3 molecules. **(03)**

(vii) I. Write what you would observe when an excess of an aqueous solution of **Y** is added to a solution of $Al_2(SO_4)_3$.

white precipitate / white gelatinous precipitate (03)

II. Write the chemical formula of the species that gives rise to your observation in part I above.

$Al(OH)_3$ (03)

(viii) Give **one chemical** test to identify **Y**.

Test: Test with Nessler's reagent (03)

Observation: Brown precipitate / Brown coloration (03)

OR

Test with HCl vapour (03)

White fumes (03)

OR

Test with red litmus (03)

Red litmus turns blue (03)

OR

Add to a solution of Cu(II) ions (03)

Deep blue colour solution (03)

(ix) **Z** is an oxo-acid of **X** and a strong oxidizing agent.

I. Identify **Z**. HNO_3 **OR** Nitric acid (03)

II. State the products obtained when hot concentrated **Z** reacts with sulphur.

$H_2SO_4(l)$, $NO_2(g)$, $H_2O(l)$ **(01+01+01)**

Note: physical states are not required.

2(a) = 60 marks

(*b*) **A** and **B** are compounds of two *p*-block elements that belong to the same group in the Periodic Table. **A** exists as a colourless, odourless liquid at room temperature and atmospheric pressure. It is also found in the gaseous and solid states. The solid state of **A** is less dense than its liquid state. Ionic and polar compounds are readily soluble in **A**.

B is a colourless gas at room temperature and atmospheric pressure. A filter paper moistened with lead acetate turns black on treatment with **B**.

(i) Identify **A** and **B**.

A - H_2O **B** - H_2S **(04 + 04)**

(ii) Sketch the shapes of A and B showing lone pairs of electrons where necessary.

A **B** **(03 + 03)**

(iii) Giving reasons, state whether A or B has the larger bond angle.

Oxygen is more electronegative than suphur. **(01)**
Therefore, bonding pairs of electrons are located closer to the oxygen atom in H_2O, than to the sulphur atom in H_2S. **(01)**
Therefore, repulsion of bonding electron pairs is greater in H_2O than in H_2S. **(01)**
Bond angle of A/$H_2O$is greater than bond angle of B/H_2S **(02)**

(iv) In each of the following instances, give a balanced chemical equation to indicate the action of A.

I. A as an acid: $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (OR $NH_4OH(aq)$) **(03)**
OR
$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$
(OR any other metal that reacts with water liberating H_2)

(Note: $\longrightarrow$ accepted)

II. A as a base: $H_2O(l) + HCl(aq) \longrightarrow H_3O^+(aq) + Cl^-(aq)$ OR **(03)**
$H_2O(l) + CH_3COOH(aq) \longrightarrow H_3O^+(aq) + CH_3COO^-(aq)$

(v) Write the balanced chemical equation for the reaction of B with aqueous lead acetate.

$Pb(CH_3COO)_2(aq) + H_2S(g) \longrightarrow PbS(s) + 2CH_3COOH(aq)$ **(03)**
(OR $2CH_3COO^- + 2H^+$)

(vi) I. Write what you would observe when A and B are added separately to an acidified solution of $BiCl_3$.

with A (excess) - white precipitate / white solid/ white turbidity **(03)**

with B - black precipitate **(03)**

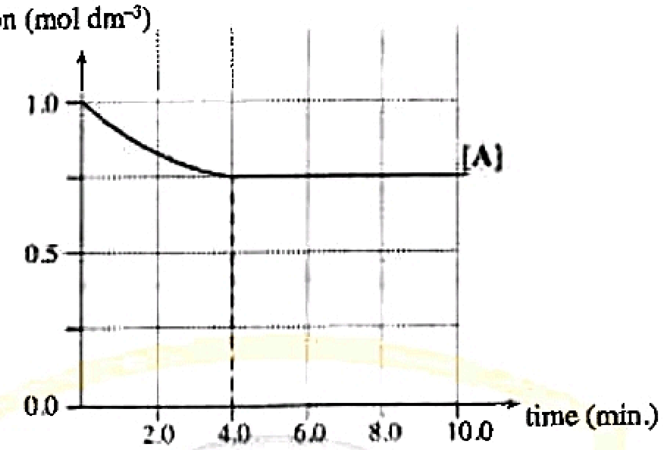
II. Write balanced chemical equations for your observations in part I above.

$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$ **(03)**
($\longrightarrow$ can be accepted.)
$2BiCl_3(aq) + 3H_2S(g) \longrightarrow Bi_2S_3(s) + 6HCl(aq)$ **(03)**

Note: Physical states are not required for parts (iv), (v), (vi)

2(b) = 40 marks

3. The reaction $A + B \rightleftharpoons 2C + D$ (elementary in both directions) was carried out at 25 °C. Initially, the reaction mixture was made by dissolving 0.10 mol of **A** and 0.10 mol of **B** in distilled water (total volume 100.00 cm^3). Variation in the concentration of **A** in this solution with time is shown in the graph.



(i) Calculate the amount of **A** (in moles) reacted during the first 4.0 minutes of the reaction.

Initial amount of A = 0.1 mol

Concentration of A after 4.0 min = 0.75 mol dm^{-3}

Amount of A reacted = $(0.1 - 0.75) \times 100 \times 10^{-3}$ mol (04+01)

= 0.025 mol. (04+01)

(ii) Would the rate of the forward reaction be less than the rate of the reverse reaction after 4.0 minutes? Explain your answer.

No (05)

Forward and reverse rates will be equal after 4.0 min.

OR The reaction has reached the equilibrium. (05)

(iii) Given that the rate constant of the forward reaction ($k_{forward}$) is 18.57 $mol^{-1}\ dm^3\ min^{-1}$, calculate the initial rate of the forward reaction.

Rate of the forward reaction, $R_f = k[A][B]$ (05)

Initial rate of the forward reaction = 18.57 $mol^{-1}\ dm^3\ min^{-1} \times 1.0\ mol\ dm^{-3} \times 1.0\ mol\ dm^{-3}$ (04+01)

= 18.57 $mol\ dm^{-3}\ min^{-1}$ (04+01)

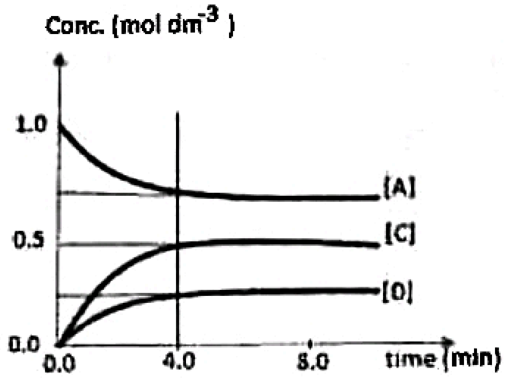
(iv) Calculate the concentrations of **C** and **D** at equilibrium.
Draw the relevant curves showing the variation of the concentrations of **C** and **D** with time in the above graph and **label** them.

Concentration of C at equilibrium = $2 \times 0.025\ mol/(100.00 \times 10^{-3}\ dm^3)$ (02+01)

= 0.50 mol dm^{-3} (02+01)

Concentration of D at equilibrium = $0.025\ mol/(100.00 \times 10^{-3}\ dm^3)$ (02+01)

= 0.25 mol dm^{-3} (02+01)



Curve C (04)

Curve D (04)

Note : Do not award marks if the curves do not become flat after 4.0 min, if the curves do not reach the respective concentrations at 4.0 min, if the curves for C and D are not labeled and if the curves do not start from zero.

(v) Write the expression for the equilibrium constant K_c of the above reaction and calculate its value.

(Equilibrium constant), $K_c = \frac{[C]^2\,[D]}{[A]\,[B]}$ (05)

$K_c = \frac{(0.5\ mol\ dm^{-3})^2(0.25\ mol\ dm^{-3})}{(0.75\ mol\ dm^{-3})(0.75\ mol\ dm^{-3})}$ (04+01)

$K_c = 1.11\ \times 10^{-1}\ mol\ dm^{-3}$ (04+01)

(vi) Calculate the value of the rate constant ($k_{reverse}$) of the reverse reaction.

Using $K = \frac{k_f}{k_r}$, k_r can be calculated $k_r = \frac{18.57\ mol^{-1} dm^3 min^{-1}}{1.11 \times 10^{-1}\ mol\ dm^{-3}}$ (04+01)

$k_r = 1.67 \times 10^2 mol^{-2} dm^6 min^{-1}$ (04+01)

(vii) After reaching equilibrium, the volume of the solution was doubled by adding 100.00 cm^3 of distilled water. Predict the direction of the net reaction soon after doubling the volume of the solution, by means of a suitable calculation.

New concentrations,

[A] = 0.75/2 mol dm^{-3}, [B] = 0.75/2 mol dm^{-3}, [c] = 0.5/2 mol dm^{-3}, [D]= 0.25/2 mol dm^{-3}

Rate of forward reaction,

R_f = 18.57 mol^{-1} dm^3 min^{-1} (0.75/2 mol dm^{-3})^2 (05+01)

= 2.61 mol dm^{-3} min^{-1}

Rate of the reverse reaction,

R_r = 1.67x10^2 mol^{-2} dm^6 min^{-1} (0.5/2 mol dm^{-3})^2(0.25/2 mol dm^{-3}) (05+01)

= 1.30 mol dm^{-3} min^{-1}

$R_f > R_r$ Net reaction occurs in the forward direction. (03)

Alternate answer

$Q = \frac{(\frac{0.5}{2}\ mol\ dm^{-3})^2(\frac{0.25}{2}\ mol\ dm^{-3})}{(\frac{0.75}{2}\ mol\ dm^{-3})^2}$ (05+01)

$Q = 0.056\ \ mol\ dm^{-3}$ (05+01)

$Q < K$, therefore, the net reaction occurs in the forward direction. (03)

(viii) Consider that the above experiment was conducted at a temperature lower than 25 °C. How would this affect the rate of the reverse reaction? Explain your answer giving reasons.

Rate of the reverse reaction will decrease (01)

Because

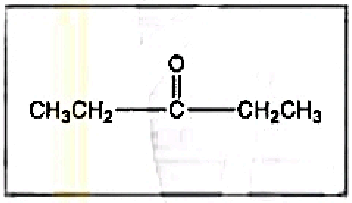
the fraction of molecules having sufficient energy to overcome the activation energy barrier decreases (02)

and

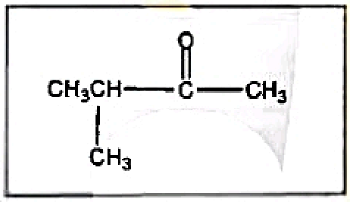
the collision rate decreases. (02)

Q3 = 100 marks

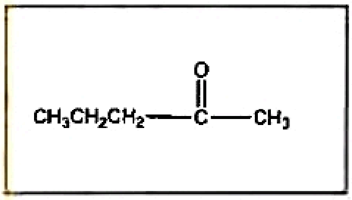
4. (*a*) (i) Compounds **A**, **B** and **C** are structural isomers of each other having the molecular formula $C_5H_{10}O$. All three compounds give yellow-orange precipitates with 2, 4–DNP. None of them give a silver mirror in the silver mirror test. When **A**, **B** and **C** were separately reacted with $NaBH_4$, compounds **D**, **E** and **F** respectively were obtained. Only **E** and **F** showed optical isomerism. When **B** and **C** were separately reacted with $CH_3CH_2CH_2MgBr$ followed by hydrolysis, compounds **G** and **H** respectively, were obtained. Only **G** showed optical isomerism. Draw the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G** and **H** in the boxes given below. (It is **not** necessary to show stereoisomeric forms.)



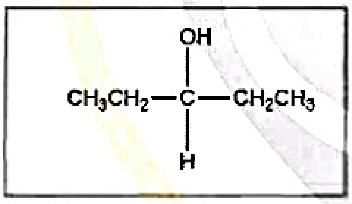
A



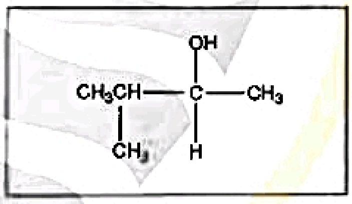
B



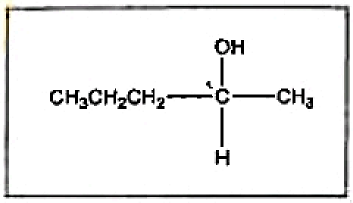
C



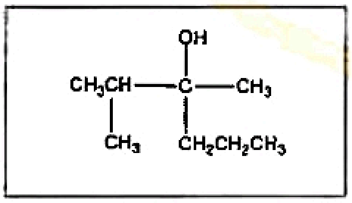
D



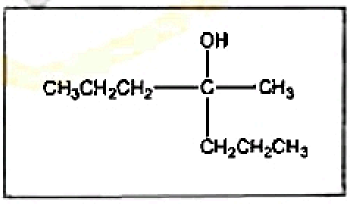
E



F



G



H

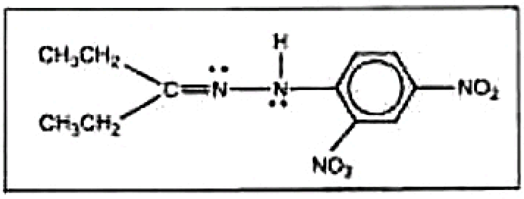
Note: C_3H_7 can be accepted in place of $CH_3CH_2CH_2$. C_2H_5 can be accepted in place of CH_3CH_2.

(05 marks x 8 = 40 marks)

Note: A, B, C should be correct to award marks for D, E, F
B, C should be correct to award marks for G, H

(ii) Draw the structure of the product of the following reaction.

A $\xrightarrow[\text{(2) dehydration}]{\text{(1) 2, 4–DNP}}$

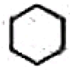
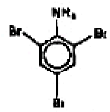
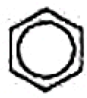


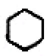
(05)

Note : Lone pairs are not necessary. Award mark if B or C is used instead of A with the correct corresponding product.

4.(a): 45 marks

(*b*) Draw the structure of the **major** organic **product** in each of the following reactions.

(i) C_6H_6	H_2/Raney Ni, 150 °C		(04)
(ii) $C_6H_5-NH_2$	Br_2 water		(04)
(iii) CH_3CHO	(1) aqueous NaOH (2) dehydration	$CH_3CH{=}CH-\overset{O}{\overset{\Vert}{C}}-H$	(04)
(iv) $C_6H_5-\overset{\oplus}{N_2}\overset{\ominus}{Cl}$	H_3PO_2, Δ		(04)
(v) $C_2H_5CONH_2$	aqueous NaOH, Δ	$C_2H_5-\overset{O}{\overset{\Vert}{C}}-O^-Na^+$	(04)
(vi) $CH_3CH{=}CH_2$	conc. H_2SO_4	$CH_3-\underset{OSO_3H}{\underset{\vert}{CH}}-CH_3$	(03)
(vii) CH_3COCl	NH_3	$CH_3-\overset{O}{\overset{\Vert}{C}}-NH_2$	(03)
(viii) $C_2H_5CO_2H$	PCl_5	$C_2H_5-\overset{O}{\overset{\Vert}{C}}-Cl$	(03)
(ix) C_2H_5OH	$H^+/KMnO_4$	CH_3COOH	(03)
(x) $C_2H_5COCH_3$	HCN	$C_2H_5-\overset{OH}{\overset{\vert}{\underset{CN}{\underset{\vert}{C}}}}-CH_3$	(03)

(i) strcture showing hydrogens on  can be accepted.

(iii) $CH_3CH{=}CHCHO$ can be accepted. No marks for $CH_3CH{=}CHCOH$

(iv)  can be acepted

(v) Charges on O and Na are not required for award of marks. No marks if given as O—Na

(vi) OSO_2OH can be accepted.

(vii) CH_3CONH_2 can be accepted.

(viii) C_2H_5COCl can be accepted.

(ix) CH_3CO_2H can be accepted.

4(b): 35 marks

(04)

(08)

(08)

OR (for third step)

(02)

4.(c): 20 marks

Note: if no half arrow are drawn, deduct (01) mark once in each line.

Radical needs to be shown for award of marks.

Mark each step as an independent step.

PART B — ESSAY

Answer two questions only. (Each question carries 15 marks.)

5. (a) Consider the following reactions.

$$M(CO_3)_2 \cdot nH_2O(s) \rightarrow M(CO_3)_2(s) + nH_2O(g)$$

$$M(CO_3)_2(s) \rightleftharpoons MO_2(s) + 2CO_2(g)$$

A small amount (0.10 mol) of $M(CO_3)_2 \cdot nH_2O(s)$ is present in an evacuated rigid container of volume 0.08314 m^3. The temperature of the container was raised to 400 K. The metal carbonate, $M(CO_3)_2$ does not decompose at this temperature but the crystalline water evaporates completely. The pressure of the container was measured to be 1.60×10^4 Pa. Volume occupied by the solids is negligible.

Determine the value of 'n' in the formula $M(CO_3)_2 \cdot nH_2O(s)$.

$M(CO_3)_2.nH_2O$ (s) → $M(CO_3)_2(s)$ + n $H_2O(g)$

$M(CO_3)_2(s) \rightleftharpoons MO_2$ (s) + $2CO_2(g)$

The amount of $M(CO_3)_2.nH_2O$ used = 0.10 mol

Water is completely evaporated.

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

$$n_{H2O} = \frac{1.60 \times 10^4 Pa \times 0.08314\, m^3}{8.314\, J\, mol^{-1} K^{-1} \times 400 K}$$ **(04+01)**

= 0.40 mol **(04+01)**

0.1 mol of $M(CO_3)_2.nH_2O$ (s) has generated 0.40 mol of H_2O. Therefore, n = 4 **(04+01)**

5 (a) = 20 marks

(b) The temperature of the above system was then increased to 800 K. It was observed that some amount of the solid metal carbonate is decomposed and is in equilibrium with the gas phase. The pressure of the container was measured to be 4.20×10^4 Pa.

(i) Calculate the partial pressure of water vapour in the container at 800 K.

Partial pressure of H_2O at 800 K,

$$P_{H2O} = \frac{n_{H2O}RT}{V}$$

$$= \frac{0.4\, mol \times 8.314\, J mol^{-1} K^{-1} \times 800\, K}{0.08314\, m^3}$$ **(04+01)**

= 3.20×10^4 Pa **(04+01)**

Alternate Answer 01

Total pressure at 800 K, P_T = 4.20×10^4 Pa

Total number of moles $n_T = \frac{4.20 \times 10^4\ Pa \times 0.08314\, m^3}{8.314\ J\, mol^{-1} K^{-1} \times 800\, K}$ **(04+01)**

= 0.525 mol

Partial pressure of water = P_{H2O} = P_T X $_{H2O}$

= 3.20×10^4 Pa **(04+01)**

Alternate Answer 02

Because V and n_{H2O} are constant, at 800 K,

partial pressure of water = P_{H2O} = $2 \times 1.60 \times 10^4$ Pa **(04+01)**

= 3.20×10^4 Pa **(04+01)**

(ii) Calculate the partial pressure of CO_2 in the container at 800 K.

Partial pressure of CO_2 at 800K,

$P_{CO2} = P_{total} - P_{H2O}$

$= 4.2 \times 10^4$ Pa $- 3.2 \times 10^4$ Pa (04+01)

$= 1.00 \times 10^4$ Pa (04+01)

(iii) Write an expression for the pressure equilibrium constant, K_p for the decomposition of $M(CO_3)_2(s)$. Calculate K_p at 800 K.

$K_P = P^2_{CO2}$ (05)

$K_P = (1.0 \times 10^4 \text{ Pa})^2 = 1.00 \times 10^8 \text{ Pa}^2$ (04+01)

(iv) Calculate the molar percentage of the metal carbonate decomposed at 800 K.

Initial amount = 0.10 mol

Amount of CO_2 generated = n_{CO2}

$$n_{CO2} = \frac{P_{CO2}V}{RT}$$

$$n_{CO2} = \frac{1.0\times10^4 Pa \times 0.08314\ m^3}{8.314\ J\ mol^{-1}K^{-1}\times 800K} \quad or \quad \frac{3.2\times10^4 Pa}{1.0\times10^4\ Pa} = \frac{0.4}{n_{CO2}}$$ (04+01)

$n_{CO2} = 0.125$ mol

Amount of $M(CO_3)_2$ decomposed = ½ amount of CO_2 generated.

mol % of $M(CO_3)_2$ decomposed $= \frac{0.0625\ mol}{0.10\ mol} \times 100$ (03)

$= 62.5\ \%$ (02)

(v) Enthalpy change (ΔH) for the decomposition of the metal carbonate under the above conditions is 40.0 kJ mol^{-1}. Calculate the corresponding entropy change (ΔS).

System is at equilibrium, therefore $\Delta G = 0$. (05)

$$\Delta S = \frac{\Delta H}{T}$$

$$\Delta S = \frac{40.0\times10^3 J\ mol^{-1}}{800\ K}$$ (04+01)

$\Delta S = 50.0$ J mol^{-1} K^{-1} OR 0.05 kJ mol^{-1} K^{-1} (04+01)

Note : ΔS^0 , ΔH^0 cannot be accepted.

(vi) Suggest **two** ways to drive the decomposition reaction of $M(CO_3)_2(s)$ in the forward direction.

Increase temperature (05)

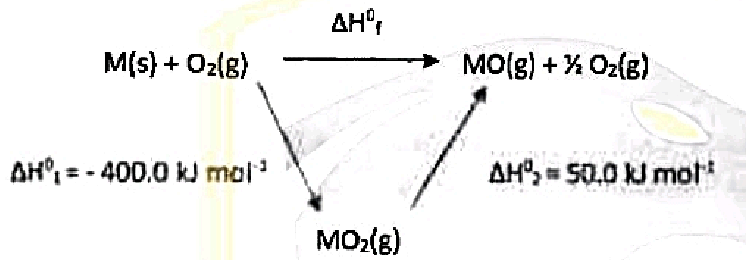
Remove CO_2 (05)

5 (b) = 65 marks

(c) With the aid of thermochemical cycles and the data given in the table, answer the following questions.

Species	Standard enthalpy of formation (ΔH_f°) (kJ mol^{-1})
M(s)	0.0
M(g)	800.0
$O_2(g)$	0.0
O(g)	249.2
$MO_2(g)$	−400.0

(i) Given that $MO(g) + \frac{1}{2} O_2(g) \rightarrow MO_2(g)$ $\Delta H^\circ = -50.0$ kJ mol^{-1}, calculate the standard enthalpy of formation of MO(g).



(02+02+02 =06)

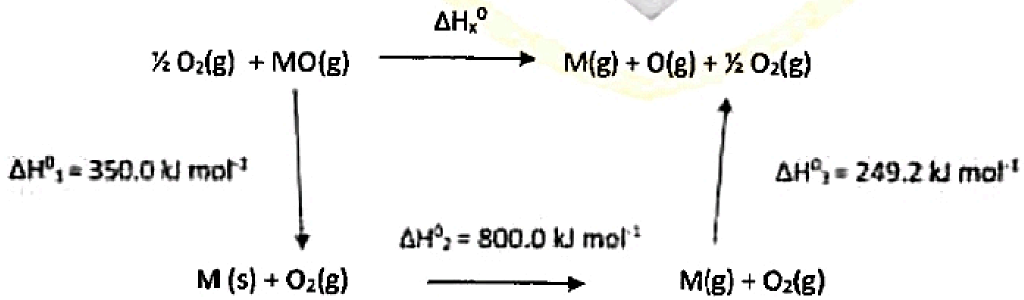
Note : To award marks for the cycle, reactions must be balanced and physical states must be given.

Standard formation enthalpy of MO(g), ΔH^0_f

$\Delta H^0_f = (-400.0 + 50.0)$ kJ mol^{-1} **(04+01)**

$= -350.0$ kJ mol^{-1} **(04+01)**

(ii) Calculate M–O bond dissociation enthalpy in MO(g).



(02+02+02 +02 = 08)

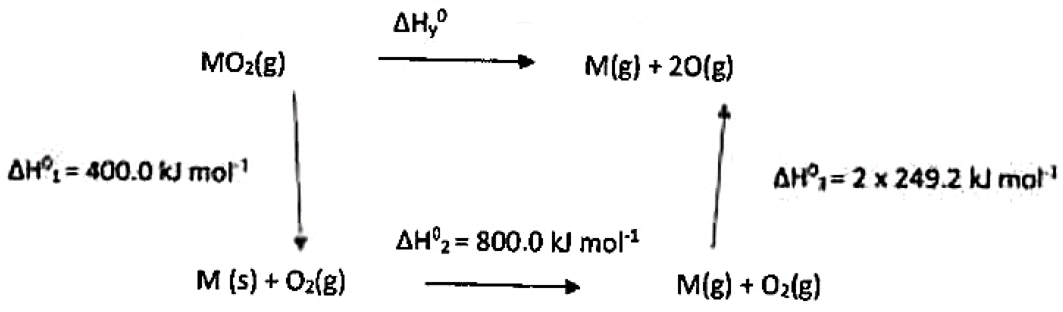
Note : To award marks for the cycle, reactions must be balanced and physical states must be given.

MO bond dissociation enthalpy change = ΔH_x^0

$\Delta H_x^0 = (350.0 + 800.0 + 249.2)$ kJ mol^{-1} **(04+01)**

$= 1399.2$ kJ mol^{-1} **(02+01)**

(iii) Calculate M–O bond dissociation enthalpy in $MO_2(g)$.



(02+02+02+02 =08)

Note : To award marks for the cycle, reactions must be balanced and physical states must be given.

$\Delta H_y^0 = (400.0 + 800.0 + 2 \times 249.2)$ kJ mol^{-1} **(04+01)**

$= 1698.4$ kJ mol^{-1}

MO bond dissociation energy in $MO_2 = \frac{1}{2}\,\Delta H_y^0 = 849.2$ kJ mol^{-1} **(04+01)**

(iv) By means of a suitable calculation, predict whether the reaction, $MO_2(g) \rightarrow MO(g) + \frac{1}{2}\ O_2(g)$ is spontaneous under standard conditions and 2000 K. Standard entropy change of this reaction is $30.0\,J\,K^{-1}\,mol^{-1}$.

$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$ **(03)**

For the reaction, $MO_2(g) \longrightarrow MO(g) + \frac{1}{2}\,O_2(g)$ at 2000 K,

$\Delta G^0 = 50.0\times10^3$ J mol^{-1} – 2000 K x 30.0 J K^{-1} mol^{-1} **(04+01)**

$= -10000.0$ J mol^{-1} = -10.0 kJ mol^{-1} **(04+01)**

The given reaction is spontaneous at 2000K. **(02)**

Note : Standard states are required for award of marks.

5 (c) = 65 marks

6. (*a*) An experiment was carried out to determine the partition coefficient of iodine (I_2) between water (**A**) and an organic solvent (**B**) which form an immiscible liquid system.

20.00 cm^3 of **B** containing 'n' moles of I_2 is mixed with 20.00 cm^3 of **A** and allowed to reach equilibrium at room temperature.

The concentration of I_2 in phase **A** is determined by titrating a 5.00 cm^3 sample drawn from phase **A** with a 0.005 mol dm^{-3} solution of $Na_2S_2O_3$. The volume of $Na_2S_2O_3$ required to reach the end point was 22.00 cm^3. The concentration of I_2 in phase **B** was determined to be 0.040 mol dm^{-3}.

(i) Write the balanced chemical equation for the reaction between $Na_2S_2O_3$ and I_2.

$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

OR

$2\,S_2O_3^{2-} + I_2 \longrightarrow 2\,I^- + S_4O_6^{2-}$ **(10)**

(ii) Calculate the concentration of I_2 in phase A.

Concentration of I_2 in phase $A = \dfrac{22.00\ cm^3 \times 0.005\ mol\ dm^{-3}}{2 \times 5.0\ cm^3}$ **(04+01)**

$= 0.011$ mol dm^{-3} **(04+01)**

(iii) Calculate the value of the partition coefficient, K_D where $K_D = \frac{[I_2]_B}{[I_2]_A}$.

Partition coefficient, $K_D = \frac{[I_2]_B}{[I_2]_A} = \frac{0.04\ mol\ dm^{-3}}{0.011\ mol\ dm^{-3}}$ **(04+01)**

(iv) Calculate the total number of moles of I_2 in the two phases **A** and **B**.

$K_D = 3.64$ **(04+01)**

Total number of moles of I_2

$n_{I_2} = 0.04\ mol\ dm^{-3} \times 20.0 \times 10^{-3} dm^3 + 0.011\ mol\ dm^{-3} \times 20.0 \times 10^{-3} dm^3$

2 x (04+01)

$= 1.02 \times 10^{-3}$ mol **(04+01)**

6 (a) = 45 marks

(*b*) The above experiment was repeated under the same conditions, that is, at the same temperature, using the same amount of I_2 and the same volumes, but with the addition of I^- ions to phase **A**. The system was then thoroughly shaken and allowed to reach equilibrium. The volume of 0.005 mol dm^{-3} $Na_2S_2O_3$ solution required to titrate the I_2 in a 5.00 cm^3 sample of phase **A** was 41.00 cm^3. The concentration of I_2 in phase **B** was then determined to be 0.030 mol dm^{-3}.

(i) Calculate the amount of I_2 (moles) expected in 5.00 cm^3 of phase **A**, based on the partition coefficient for the distribution of I_2 between the phases **A** and **B**.

Concentration of I_2 in phase A (when excess I^- is added)

$[I_2]_A = [I_2]_B/K_D$ **(05)**

$[I_2]_A = \frac{0.030\ mol\ dm^{-3}}{3.64}$ **(02+01)**

$= 8.242 \times 10^{-3}$ mol dm^{-3} **(01+01)**

The amount of I_2 in 5.00 cm^3 of phase A = n

n $= 8.242 \times 10^{-3}$ mol $dm^{-3} \times 5.00 \times 10^{-3}$ dm^3 **(02+01)**

$= 4.121 \times 10^{-5}$ mol **(01+01)**

(ii) Calculate the amount (moles) of I_2 reacted with $Na_2S_2O_3$ in the above titration.

The amount of I_2 in 5.00 cm^3 of phase A, after the addition of iodide = n/

n/ = 0.005 mol $dm^{-3} \times 41.00 \times 10^{-3}$ $dm^3 \times 0.5$ **(04+01)**

$= 1.025 \times 10^{-4}$ mol (or 1.03×10^{-4} mol) **(04+01)**

(iii) Considering the different iodine species present in phase **A**, explain why the answers obtained in parts (*b*)(i) and (*b*)(ii) above are different.

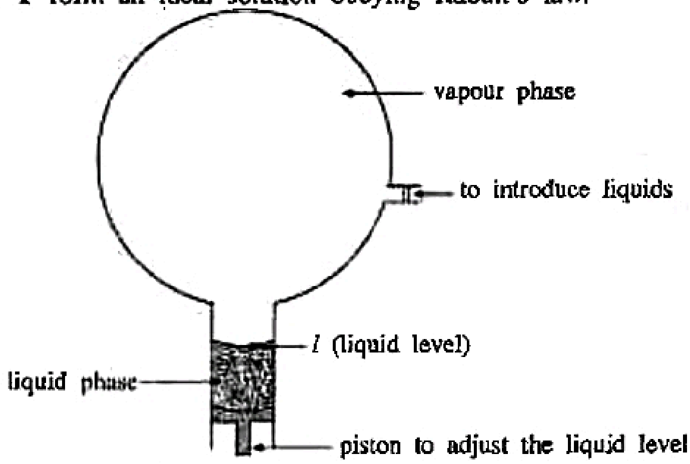
When I^- ions are added to the phase A, I_2 and I^- combine to form I_3^-. **(05)**

When phase A is titrated with $Na_2S_2O_3$, I_2 released from I_3^- is also reacted with $Na_2S_2O_3$.

Therefore, n/ > n. **(05)**

6 (b) = 35 marks

(*c*) Liquids **X** and **Y** form an ideal solution obeying Raoult's law.



Initially only liquid **X** was introduced in to an evacuated rigid container as shown in the figure.

Maintaining the liquid level at *l*, the system was allowed to reach equilibrium at 400 K. The pressure of the container was measured to be 3.00×10^4 Pa. The volume of the vapour phase when the liquid level is at *l* was 4.157 dm^3. Then liquid **Y** was introduced in to the container mixed with liquid **X** and the system was allowed to reach equilibrium at 400 K. The liquid level was maintained at *l*. The molar ratio of **X** : **Y** in the liquid phase was found to be 1 : 3 The pressure of the container was measured to be 5.00×10^4 Pa.

(i) What is the saturated vapour pressure of **X** at 400 K?

Saturated vapour pressure of X at 400K = 3.00×10^4 Pa. **(04+01)**

(ii) Calculate the mole fractions of **X** and **Y** in the liquid phase at equilibrium.

Mole fraction of X in the liquid phase = $\frac{1}{(1+3)}$ **(04+01)**

$= \frac{1}{4}$ or 0.25

Mole fraction of Y in the liquid phase = $\frac{3}{(1+3)}$ **(04+01)**

$= \frac{3}{4}$ *or* 0.75

(iii) Calculate the partial pressure of **X** at equilibrium after the addition of **Y**.

At equilibrium, $P_x = P_x^0 X_A$ **(05)**

$= 0.25 \times 3.0 \times 10^4$ Pa **(02+01)**

$= 7.5 \times 10^3$ Pa **(01+01)**

(iv) Calculate the partial pressure of **Y** at equilibrium.

$P_y = P_{total} - P_x$

$= 5.0 \times 10^4 \text{ Pa} - 7.5 \times 10^3 \text{ Pa}$ **(02+01)**

$= 4.25 \times 10^4$ Pa **(01+01)**

(v) Calculate the saturated vapour pressure of **Y**.

Saturated vapour pressure of Y, $P_y^0 = \frac{P_y}{X_y}$

$$P_y^0 = \frac{4.25 \times 10^4 Pa}{0.75}$$ **(04+01)**

$$= 5.67 \times 10^4 Pa$$ **(04+01)**

(vi) Calculate the amounts (in moles) of **X** and **Y** in the vapour phase.

The amount of X in the gas phase, $n_x = P_xV/RT$

$$n_x = \frac{7.5 \times 10^3 Pa \times 4.157 \times 10^{-3} m^3}{8.314\ J\ mol^{-1}\ K^{-1} \times 400K}$$ **(04+01)**

$n_x = 9.38 \times 10^{-3}$ mol **(04+01)**

Similarly,

$$n_y = \frac{4.25 \times 10^4 Pa \times 4.157 \times 10^{-3} m^3}{8.314\ J\ mol^{-1}\ K^{-1} \times 400K}$$ **(04+01)**

$n_y = 5.31 \times 10^{-2}$ mol **(04+01)**

(vii) When a mixture of the liquids **X** and **Y** is subjected to fractional distillation, state which compound would distill out first from the fractional distillation column. Give reason/s for your answer.

Compound **Y** can be obtained first. **(05)**

Y is the more volatile compound or saturated vapour pressure of **Y** (P^0_Y) is high. Therefore, its vapour comes out first from the fractional distillation column.

(05)

Note :To award marks for (vii) answers for P_x^o and P_y^o must have been calculated. Prediction must be according to the calculated P_x^o and P_y^o values.

6 (c) = 70 marks

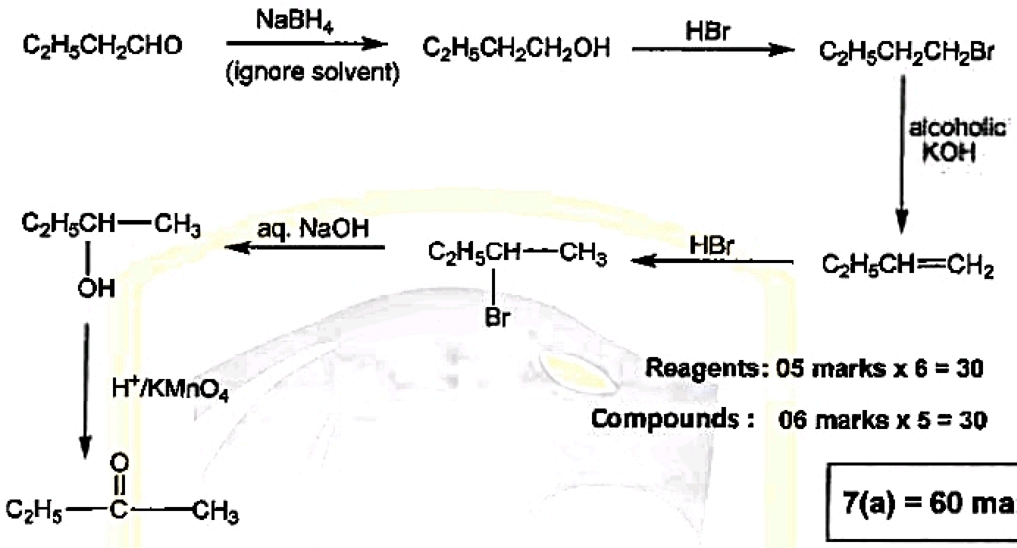
7. (*a*) Using only the chemicals given in the list, show how you would carry out the following conversion

$$C_2H_5CH_2CHO \longrightarrow C_2H_5COCH_3$$

List of chemicals
aqueous NaOH, HBr, alcoholic KOH, $NaBH_4$, $H^+/KMnO_4$

Your conversion should not exceed 7 steps.

7 (a)



Reagents: 05 marks x 6 = 30

Compounds : 06 marks x 5 = 30

7(a) = 60 marks

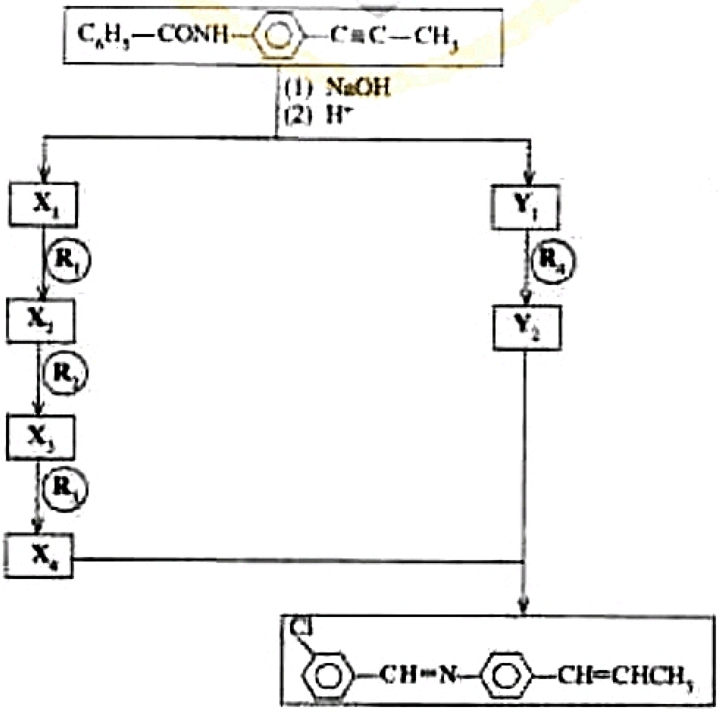
Note : Do not award 60 marks if there are more than seven steps. Do not award marks for $C_2H_5CH_2CHO$ and $C_2H_5COCH_3$.

<u>Marking of partially correct answer</u>

Mark from the beginning till an incorrect answer (reagent or product) is found. Mark from the end till an incorrect answer (reagent or product) is found. Add the marks. Do not award marks for any isolated correct steps in the middle.

To award marks for reagent, both reactant and product have to be correct.

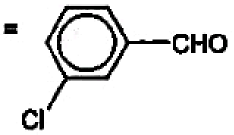
(*b*) Identify R_1—R_4 and X_1—X_4 and Y_1, Y_2 in order to complete the following reaction scheme

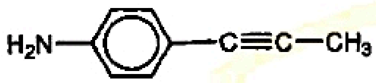
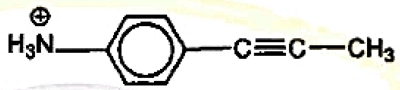


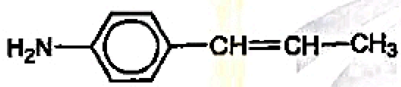
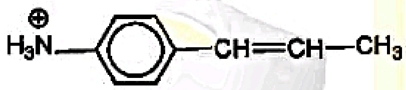
$X_1 = C_6H_5CO_2H$ **(06)**

$X_2 = C_6H_5CH_2OH$ **(06)**

$X_3 = C_6H_5CHO$ **(06)**

$X_4 =$  **(06)**

$Y_1 =$  OR  **(06)**

$Y_2 =$  OR  **(06)**

$R_1 =$ 1. $LiAlH_4$ 2. H_2O **OR** H_2O/H^+ **(06)**

$R_2 =$ PCC **(06)**

$R_3 =$ $FeCl_3/Cl_2$ **OR** Fe/Cl_2 **OR** Lewis acid/Cl_2 **(06)**

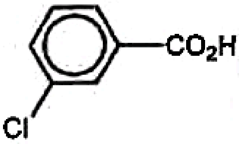
$R_4 =$ 1. NaOH 2. $H_2/Pd/BaSO_4$/quinoline **OR** **(06)**
1. NaOH 2. Lindlar/ H_2

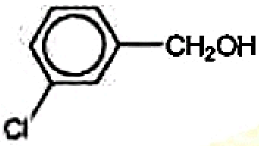
(Note : NaOH is not required for award of 06 marks) **(06 marks x 10 = 06)**

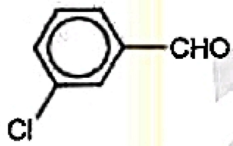
7(b) = 60 marks

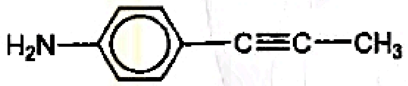
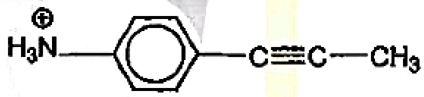
Alternative Pathway

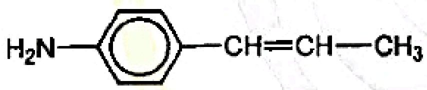
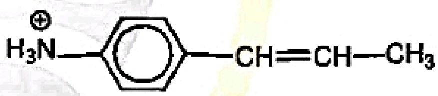
7 (b) X_1 = $C_6H_5CO_2H$ **(06)**

X_2 =  **(06)**

X_3 =  **(06)**

X_4 =  **(06)**

Y_1 =  OR  **(06)**

Y_2 =  OR  **(06)**

R_1 = $FeCl_3/Cl_2$ OR Fe/Cl_2 OR Lewis acid/Cl_2 **(06)**

R_2 = 1. $LiAlH_4$ 2. H_2O OR H_2O/H^+ **(06)**

R_3 = PCC **(06)**

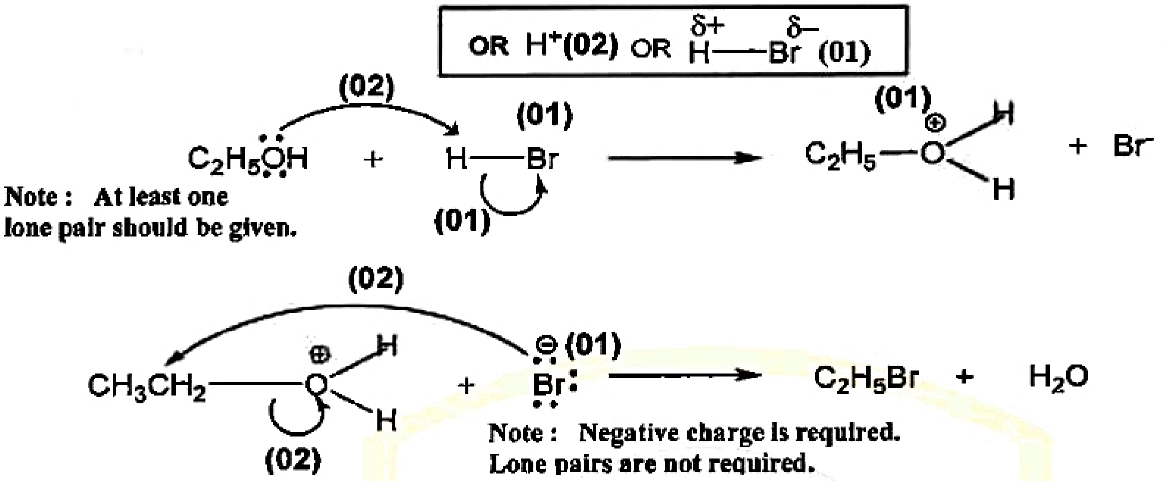
R_4 = 1. NaOH 2. $H_2/Pd/BaSO_4$/quinoline OR **(06)**
1. NaOH 2. Lindlar/H_2
(Note : NaOH is not required for award of 06 marks)

(06 marks x 10 = 60)

7(b) = 60 marks

(*c*) (i) Give the mechanism of the following reaction.

$$C_2H_5OH + HBr \longrightarrow C_2H_5Br + H_2O$$



(10 marks)

(ii) State whether the above reaction is a nucleophilic substitution reaction or an electrophilic substitution reaction. Identify the nucleophile or electrophile as appropriate.

(ii) Nucleophilic substitution, $Br^{\ominus}$ **(02 + 02)**

(iii) State giving reasons which of the two compounds, phenol (C_6H_5OH) or ethanol (C_2H_5OH) is more acidic.

$$C_2H_5OH + H_2O \rightleftharpoons C_2H_5O^{\ominus} + H_3O^{\oplus} \quad (02)$$

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^{\ominus} + H_3O^{\oplus} \quad (02)$$

Note: If H_2O is not included in the equations, only (01) per equation

- In the above equilibria the equilibrium point for phenol is more toward the right than ethanol. **(02)**
- This is because the stability of phenate ion relative to phenol is greater than the stability of the alkoxide relative to alcohol. **(02)**
- The phenate ion is more stable because its negative charge gets delocalized by resonance. **(02)**
- Resonance structures drawn **(02)**
- In alkoxide ion there is no such charge dispersion/ No resonance **(02)**
- Phenol is more acidic than ethanol. **(02)**

7(c) = 30 marks

PART C — ESSAY

Answer two questions only. (Each question carries 15 marks.)

8. (*a*) An aqueous solution **P** contains **two** cations and **two** anions. The following experiments were carried out to identify these cations and anions.

Cations

	Experiment	Observation
①	**P** was acidified with dilute HCl and H_2S was bubbled through the solution.	A clear solution was obtained.
②	The above solution was boiled till all the H_2S was removed. A few drops of conc. HNO_3 were added and the solution was heated further. The resulting solution was cooled and NH_4Cl/NH_4OH was added.	A brown precipitate (**Q**) was formed.
③	**Q** was removed by filtration and H_2S was bubbled through the filtrate.	A pale pink precipitate (**R**) was formed.
④	**R** was removed by filtration and the filtrate was boiled till all the H_2S was removed. $(NH_4)_2CO_3$ was added to the solution.	A clear solution was obtained.
⑤	Dilute NaOH was added to a **fresh portion** of **P**.	A dirty-green precipitate and a white precipitate were formed.

Experiments for precipitates **Q** and **R**:

	Experiment	Observation
⑥	**Q** was dissolved in dil. HNO_3 and a salicylic acid solution was added.	A light purple solution was obtained.
⑦	**R** was dissolved in dilute acid and dil. NaOH was added to the solution.	A white precipitate was formed. It turned brown on standing.

Anions

		Test	Observation
⑧	I.	$BaCl_2$ solution was added to **P**.	A white precipitate was formed.
	II.	The white precipitate was separated by filtration and dil. HCl was added to the precipitate.	The white precipitate was not dissolved.
⑨		Cl_2 water and chloroform were added to a portion of the filtrate from ⑧ II, and the mixture was throughly shaken.	Chloroform layer turned yellowish-brown.

(i) Identify the **two** cations and the **two** anions in solution **P**. (Reasons are **not** required.)

Cations: Fe^{2+} and Mn^{2+} **(10 + 10)**

Anions: SO_4^{2-} and Br^- **(08 + 07)**

Note: First correct anion (08), second anion (07)

(ii) Write the chemical formulae of the precipitates **Q** and **R**.

Q - $Fe(OH)_3$ **(10)**

R - MnS **(10)**

(iii) Give reasons for the following:

I. Removal of H_2S in experiment ② for cations.

- If H_2S is not removed MnS/FeS/ cations of group IV will also precipitate when NH_4OH/NH_4Cl solution is added. **(10)**

OR

- H_2S can be oxidized to sulphur by conc. HNO_3. **(05)**
- A fine precipitate of sulphur would be formed in solution if H_2S is not removed. **(05)**

II. Heating with conc. HNO_3 in experiment ② for cations.

- K_{sp} of $Fe(OH)_2 > K_{sp}$ of $Fe(OH)_3$ **(05)**
- Therefore, Fe^{2+} needs to be converted to Fe^{3+} to be completely precipitated. **(05)**

OR

- Conc. HNO_3 must be added to oxidize iron if present, to the ferric state. **(04)**
- If originally present, it would have been reduced by the H_2S to the ferrous ion. **(02)**
- Ferrous ion is not completely precipitated by NH_4OH/NH_4Cl solution.(will get a mixture of Fe^{2+} and Fe^{3+}) **(04)**

8(a): 75 marks

(*b*) The sample **X** contains lead, copper and an inert material. The following procedure was carried out to analyse lead and copper in **X**.

Procedure:

A mass of 0.285 g of **X** was dissolved in a slight excess of dil. HNO_3. A clear solution was obtained. A NaCl solution was added to the resulting clear solution. A white precipitate (Y) was formed. The precipitate was separated by filtration and the precipitate (**Y**) and filtrate (**Z**) were analysed separately.

Precipitate (Y)

The precipitate was dissolved in hot water. A solution of K_2CrO_4 was added in excess. A yellow precipitate was formed. The precipitate was separated by filtration and dissolved in dil. HNO_3. An orange coloured solution was obtained. Excess KI was added to this solution and the liberated I_2 was titrated with 0.100 mol dm^{-3} $Na_2S_2O_3$, with starch as the indicator. The volume of $Na_2S_2O_3$ required to reach the end point was 27.00 cm^3.

(Assume that the NO_3^- ions do **not** interfere with the titration.)

Filtrate (Z)

The filtrate was neutralized and excess KI was added to it. The liberated I_2 was titrated with 0.100 mol dm^{-3} $Na_2S_2O_3$, with starch as the indicator. The volume of $Na_2S_2O_3$ required to reach the end point was 15.00 cm^3.

(**Note**: Assume that the inert material was soluble in dil. HNO_3 and did **not** interfere with the experiment.)

(i) Calculate the mass percentages of lead and copper in **X**. Write balanced chemical equations where relevant.

Determination of Cu

$2Cu^{2+} + 4I^- \rightarrow I_2 + 2CuI$ ----------(1) **(05)**

OR

$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2$ ----------(1) **(05)**

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ ----------(2) **(05)**

From (1) and (2) $Cu^{2+} \equiv S_2O_3^{2-}$ **OR** Identification of correct stoichiometry **(02)**

Moles of $S_2O_3^{2-}$ $= \frac{0.10}{1000} \times 15.0$ **(03)**

Therefore, moles of Cu^{2+} $= \frac{0.10}{1000} \times 15.0$ **(03)**

Mass of Cu $= \frac{0.10}{1000} \times 15.0 \times 63.5$ **(03)**

$= 0.095$ g **(03)**

Therefore, %Cu $= \frac{0.095}{0.285} \times 100$ **(03)**

$=$ **33.4%** **(03)**

(30 marks)

Determination of Pb

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ ----------(3) **(07)**

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ ----------(4)

From (3) + 3x (4) $Cr_2O_7^{2-} \equiv 6S_2O_3^{2-}$ **OR** Identification of correct stoichiometry **(03)**

Moles of $S_2O_3^{2-}$ $= \frac{0.10}{1000} \times 27.0$ **(03)**

Moles of $Cr_2O_7^{2-}$ $= \frac{1}{6} \times \frac{0.10}{1000} \times 27.0$ **(03)**

$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$ **(03)**

Therefore, moles of Cr $= 2 \times \frac{1}{6} \times \frac{0.10}{1000} \times 27.0$ **(03)**

Yellow precipitate is $PbCrO_4$ **(03)**

Therefore, moles of Pb $= 2 \times \frac{1}{6} \times \frac{0.10}{1000} \times 27.0$ **(03)**

Therefore, mass of Pb $= 2 \times \frac{1}{6} \times \frac{0.10}{1000} \times 27.0 \times 207$ **(03)**

$= 0.186$ g **(03)**

Therefore, %Pb $= \frac{0.186}{0.285} \times 100$ **(03)**

$= 65.3\%$ **(03)**

(40 marks)

Alternate method

Determination of Pb

$2CrO_4^{2-} + 6I^- + 16H^+ \rightarrow 2Cr^{3+} + 3I_2 + 4H_2O$ ----------(3)

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ ----------(4)

OR

$CrO_4^{2-} + 8H^+ + 3e \rightarrow Cr^{3+} + 4H_2O$

$2I^- \rightarrow I_2 + 2e$

From equations $CrO_4^{2-} \equiv 3S_2O_3^{2-}$ **OR** Identification of correct stoichiometry **(03)**

Moles of $S_2O_3^{2-}$ $= \frac{0.10}{1000} \times 27.0$ **(03)**

Moles of I_2 $= \frac{1}{2} \times \frac{0.10}{1000} \times 27.0$ **(03)**

Moles of Cr^{3+} $= \frac{2}{3} \times \frac{1}{2} \times \frac{0.10}{1000} \times 27.0$ **(03)**

$= 9 \times 10^{-4}$

Therefore, moles of $PbCrO_4$ $= \frac{2}{3} \times \frac{1}{2} \times \frac{0.10}{1000} \times 27.0 = 9 \times 10^{-4}$ **(03)**

Therefore, moles of Pb $= \frac{2}{3} \times \frac{1}{2} \times \frac{0.10}{1000} \times 27.0 = 9 \times 10^{-4}$ **(03)**

Therefore, mass of Pb $= 9 \times 10^{-4} \times 207$ g **(03)**

$= 0.186$ g **(03)**

Therefore, %Pb $= \frac{0.186}{0.285} \times 100$ **(03)**

$= 65.3\%$ **(03)**

(30 marks)

(ii) What is the colour change at the end point in the titration carried out in the analysis of precipitate **Y**?

(Cu = 63.5, Pb = 207)

Blue → Green **(05)**

8(b): 75 marks

9. (a) The following questions are based on the environment and related issues.

(i) Identify **three** greenhouse gases that contribute to global warming. State **two** consequences of global warming.

Greenhouse gases that contribute to global warming.

CO_2, NO_x, N_2O, O_3, CFC, methane, volatile hydrocarbons **(03 + 03 + 03)**

Consequences:

- Melting of polar ice caps
- Change in weather patterns
- Drying up of freshwater reservoirs
- Sinking of low lying countries due to thermal expansion of sea water/ sea level rise
- desertification
- loss of soil moisture
- changes in biodiversity
- decrease in dissolved oxygen content
- increase in populations of certain insects

(Any two) **(03 + 03)**

(ii) Global environmental issues caused by coal power plants are well known. Identify **one** such issue that contributes **significantly** to change in certain water quality parameters in rivers and lakes.

Acid rain **(03)**

(iii) Name the chemical species responsible for the environmental issue identified in (ii) above and state **three** water quality parameters that are likely to be affected by this issue.

SO_2/ SO_3 / H_2SO_3 / H_2SO_4 **(03)**

Water parameters affected:

- pH (decreases) / acidity (increases)
- Salinity (increases)
- Concentration of heavy metals (increases)
- Hardness (increases)
- Conductivity (increases)

(Any three) **(03 + 03 + 03)**

(iv) Identify **two** environmental issues that change (increase or decrease) the ozone level in the atmosphere and explain briefly how these changes take place with the aid of balanced chemical equations.

photochemical smog (Ozone **increases**) **(03)**

How

Vehicle emissions contain NO_x **(03)**

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g)$$ **(03)**

$$M + O(g) + O_2(g) \longrightarrow O_3(g) + \overset{*}{M}$$ **(03)**

(**M** = third body)

ozone layer depletion (Ozone **decreases**) **(03)**

How

Ozone destroyed by free radicals (X) (e.g. $\dot{H}$, $N\dot{O}$, $\dot{O}H$, $\dot{C}l$) which act as a catalyst. **(03)**

$$O_3(g) + \dot{X}(g) \longrightarrow \dot{O}X(g) + O_2(g) \quad \text{---------(1)}$$ **(03)**

$$O_2(g) \longrightarrow 2O(g) \quad \text{---------(2)}$$ **(03)**

$$X\dot{O}(g) + O(g) \longrightarrow \dot{X}(g) + O_2(g) \quad \text{---------(3)}$$ **(03)**

(1)x2 + (2) + (3)x2

$$2O_3(g) \longrightarrow 3O_2(g)$$ **(03)**

(v) I. "Most of the harmful gases in vehicle exhausts are converted to relatively harmless gases by catalytic converters." Briefly explain this statement.

Catalytic converters convert

- $NO(g)$ formed to $N_2(g)$ **(03)**
- $CO(g)$ formed to $CO_2(g)$ **(03)**
- Unburnt or partially burnt hydrocarbons to $CO_2(g) + H_2O(g)$ **(03)**

II. Name the harmful gas (except CO_2) that is not converted to a less harmful gas by the catalytic converter. State briefly how this harmful gas is formed in the vehicle engine.

SO_2 **(03)**

Certain fossil fuels contain sulphur. **(02)**

Burning of sulphur produces SO_2. **(01)**

9(a): 75 marks

(vii) Give balanced chemical equations with appropriate conditions, for reactions taking place in M_1, M_2 and M_3.

M_1: $N_2(g) + 3H_2(g) \underset{(400-450)\,^\circ C\ (01)}{\overset{(200-250)\ atm\ (01)}{\rightleftharpoons}} 2NH_3(g)$ **(02)**

Fe (catalyst) **(01)**

K_2O and Al_2O_3 (promoters) **(01)**

M_2: $4NH_3(g) + 5O_2(g) \underset{\text{Pt or Pt-Rh(catalyst)}\ (01)}{\overset{(800-900)\,^\circ C\ (01)}{\rightleftharpoons}} 4NO(g) + 6H_2O(g)$ **(02)**

$2NO(g) + O_2(g) \xrightarrow{150\,^\circ C\ (01)} 2NO_2$ **(02)**

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

M_3: $2NH_3(l) + CO_2(l) \overset{(180-210)\,^\circ C\ (01),\ (30-150)\ atm\ (01)}{\rightleftharpoons} NH_2COONH_4(s)$ **(02)**

$NH_2COONH_4(s) \longrightarrow (NH_2)_2CO(aq) + H_2O(l)$ **(02)**

↓ Concentrate by evaporation **(01)**

$(NH_2)_2CO(s)$ **(02)**

Note: Physical states are not required.

(viii) I. Give one use of each compound P_1 and P_2 other than those mentioned above.

P_1:

- Neutralizing acidic constituents in industry / emissions/ effluents / water treatment plants
- In stack emission control systems to neutralize sulphur oxides from combustion of sulphur-containing fuels
- As a refrigerant
- In the rubber industry / for the stabilization of natural and/or synthetic latex / to prevent premature coagulation
- In the paint industry

(Any one) **(02)**

P_2:

- To manufacture nitrates **OR**
  $NaNO_3$ - meat preservative **OR**
  $AgNO_3$ - prepare photographic films and paper
- For the preparation of aqua regia
- Used to clean soldering surfaces

(Any one) **(02)**

II. Give one use of R_1 in the manufacturing process P_1 other than being used as a raw material.

As a fuel **OR** to heat the system (to 450 °C) **(02)**

9(b): 75 marks

10. *(a)* **A** and **B** are **complex ions**, (i.e. metal ion and ligands coordinated to it) with an octahedral geometry. They have the same atomic composition of $MnC_5H_3N_6$. In each complex ion, two types of ligands are coordinated to the metal ion. When an aqueous solution containing **A** is treated with a potassium salt, the **coordination compound C** is formed. **C** gives four ions in aqueous solution. When an aqueous solution containing **B** is treated with a potassium salt the **coordination compound D** is formed. **D** gives three ions in aqueous solution. Both **C** and **D** have an octahedral geometry.

(**Note:** The oxidation states of manganese in **A** and **B** do not change on treatment with the potassium salt).

(i) Identify the ligands coordinated to manganese in **A** and **B**.

CN^- and NH_3 **(05 + 05)**

(ii) Give the structures of **A, B, C** and **D.**

A: $[Mn(CN)_5(NH_3)]^{3-}$	**OR**	$[Mn(NH_3)(CN)_5]^{3-}$	**(10)**
B: $[Mn(CN)_5(NH_3)]^{2-}$	**OR**	$[Mn(NH_3)(CN)_5]^{2-}$	**(10)**
C: $K_3[Mn(CN)_5(NH_3)]$	**OR**	$K_3[Mn(NH_3)(CN)_5]$	**(15)**
D: $K_2[Mn(CN)_5(NH_3)]$	**OR**	$K_2[Mn(NH_3)(CN)_5]$	**(15)**

(iii) Write the electronic configurations of the manganese ions in **A** and **B**.

A, oxidation state of Mn = +2
Therefore, electronic configuration of Mn in **A** is, $1s^22s^22p^63s^23p^63d^5$ **(03)**

B, oxidation state of Mn = +3
Therefore, electronic configuration of Mn in **B** is, $1s^22s^22p^63s^23p^63d^4$ **(02)**

(iv) Write the IUPAC names of **C** and **D**.

C potassium amminepentacyanidomanganate(II) **(05)**

D potassium amminepentacyanidomanganate(III) **(05)**

Note : If spelling is incorrect do not award marks.

10(a): 75 marks

(*b*) (i) I. Write the reduction half reaction corresponding to the electrode, $Ag(s) | AgCl(s) | Cl^-(aq)$.

$AgCl(s) + e \longrightarrow Ag(s) + Cl^-(aq)$ **(05)**

($\rightleftharpoons$ accepted). Physical states are required.

II. State whether the electrode potential of $Ag(s) | AgCl(s) | Cl^-(aq)$ depends on the Ag^+ concentration in the solution. Explain your answer.

No. **(05)**

$Ag^+(aq)$ does not appear in the electrode reaction (half reaction). **(05)**

(ii) Consider the following reaction.

$$Fe(s) + 2H^+(aq) + \frac{1}{2}O_2(g) \longrightarrow Fe^{2+}(aq) + H_2O(l)$$

I. Write the oxidation and reduction half reactions relevant to the above reaction.

$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e$ (oxidation half reaction) **(08)**

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e \longrightarrow H_2O(l)$ (reduction half reaction) **(08)**

($\rightleftharpoons$ accepted) Physical states are required.

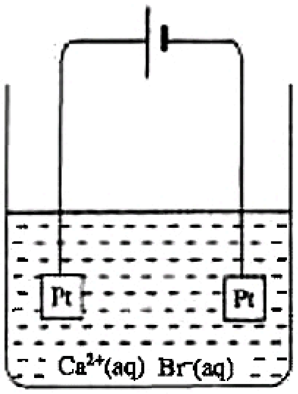
II. Given that the above reaction is the cell reaction of an electrochemical cell, determine the standard electromotive force of the cell.

$E^{o}_{Fe^{2+}(aq)/Fe(s)} = -0.44\ V$ $E^{o}_{H^+(aq)/O_2(g)/H_2O(l)} = 1.23\ V$

Standard cell potential = 1.23V – (-0.44V) **OR** (1.23 – (-0.44))V **(01+01) + (01+01)**

= 1.67 V **(04+01)**

(iii) A constant current of 100 mA was passed through 100.00 cm^3 of a 0.10 mol dm^{-3} aqueous $CaBr_2$ solution as shown in the diagram. The temperature of the system was maintained at 25 °C.



I. Write the oxidation and reduction reactions that take place at the electrodes.

Oxidation half reaction,

$2Br^-(aq) \longrightarrow Br_2(g) + 2e$ **OR** $2Br^-(aq) \longrightarrow Br_2(l) + 2e$ **(05)**

Reduction half reaction,

$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-(aq)$ **(05)**

($\rightleftharpoons$ accepted). Physical states are required.

II. Calculate the time taken for the commencement of precipitation of $Ca(OH)_2(s)$. Solubility product of $Ca(OH)_2$ at 25 °C is 1.0×10^{-5} $mol^3\,dm^{-9}$. Neglect the ionization of water. Assume that the volume of the aqueous phase remains constant.

$K_{sp} = [Ca^{2+}(aq)][OH^-(aq)]^2$ **(05)**

Required concentration of OH^- to start precipitation of $Ca(OH)_2$ = $[OH^-]$

$$[OH^-] = \sqrt{\frac{1.0\times10^{-5} mol^3 dm^{-9}}{0.1\ mol\ dm^{-3}}}$$ **OR** 1.0×10^{-2} mol dm^{-3} **(04+01)**

The amount of OH^- required to provide the above concentration = n_{OH^-}

$n_{OH^-} = 1.0 \times 10^{-2}$ mol $dm^{-3} \times 100 \times 10^{-3}$ dm^3 **OR** 1.0×10^{-3} mol **(04+01)**

Amount of charge, that must be passed through the solution, Q,

$Q = 1.0 \times 10^{-3}$ mol x 96500 C mol^{-1} **OR** 96.5 C **(04+01)**

Time required to pass the charge Q, when the current flow is 100 mA, = t

$$t = \frac{96.5\ C}{100 \times 10^{-3} C s^{-1}}$$ **OR** 965 s **OR** 16.08 min **(04+01)**

(For the Faraday constant, a value between 96500 ± 100 C mol^{-1} is accepted, If the symbol F is used for the Faraday constant, and t is calculated using F, full marks can be awarded. t = 16.08 min **OR** t = 16 min accepted.)

10 (b) = 75 marks