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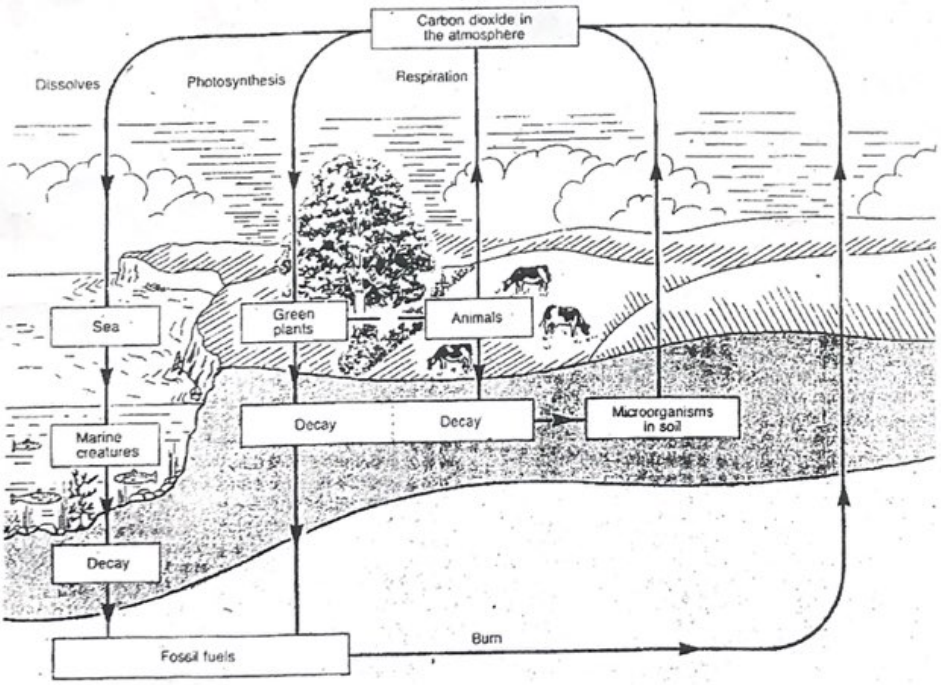
Department of Examinations - Sri Lanka

G.C.E. (A/L) Examination - 2017

02 - Chemistry

Marking Scheme

[For the purpose of marking the Chemistry paper of G.C.E. (A/L) - 2017 only.]



This has been prepared for the use marking examiners. Changes would be made according to the views presented at the Chief / Assistant 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 - 2017

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

✪ 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) (i) I. Complete the expression given below to determine the charge (Q) of an atom in a Lewis structure by inserting the terms N_A, N_{LP} and N_{BP} in the appropriate boxes, where,

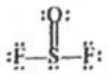
N_A = number of valence electrons in the atom

N_{LP} = number of electrons in lone pairs

N_{BP} = number of electrons in bonding pairs around the atom

$$Q = \boxed{N_A}_{(01)} - \boxed{N_{LP}}_{(01)} - \frac{1}{2}\boxed{N_{BP}}_{(01)}$$

II. Fill in the values for N_A, N_{LP} and N_{BP} in the appropriate boxes and calculate the charge on S, Q(sulfur), in the structure SOF_2 given below.

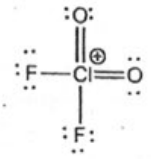


$$Q(\text{sulfur}) = \boxed{6}_{(01)} - \boxed{2}_{(01)} - \frac{1}{2}\boxed{8}_{(01)} = \underset{(04)}{\text{.....0.....}}$$

(10 marks)

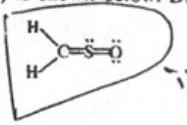
Mark independently

(ii) Draw the **most** acceptable Lewis structure for the ion, $ClO_2F_2^+$.

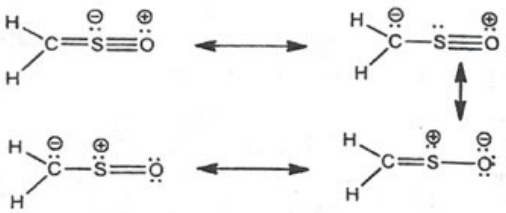


(07 marks)

(iii) The most stable Lewis structure for the molecule CH_2SO (sulfine) is shown below. Draw another **two** Lewis structures (resonance structures) for this molecule.



in question



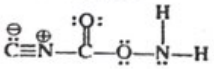
Disregard the double headed arrows

(Any two)

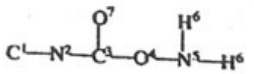
(07 marks x 2 = 14 marks)

(iv) Based on the hypothetical Lewis structure given below, state the following regarding the C, N and O atoms given in the table below.

I. VSEPR pairs around the atom
II. electron pair geometry around the atom
III. shape around the atom
IV. hybridization of the atom



The atoms are numbered as follows:



		N^2	C^3	O^4	N^5
I.	VSEPR pairs	2	3	4	4
II.	electron pair geometry	Linear	trigonal planar	tetrahedral	tetrahedral
III.	shape	Linear	trigonal planar	V/angular	pyramidal
IV.	hybridization	*sp*	sp^2	sp^3	sp^3

(01 mark x 16 = 16 marks)

(v) Identify the atomic/hybrid orbitals involved in the formation of the following σ bonds in the Lewis structure given in part (iv) above. (Numbering of atoms is as in part (iv).)

I. $N^2—C^3$ N^2 ..sp.., C^3 ..sp^2..

II. $O^4—N^5$ O^4 ..sp^3.., N^5 ..sp^3..

III. $N^5—H^6$ N^5 ..sp^3.., H^6 ..$1s/s$..

IV. $C^3—O^7$ C^3 ..sp^2.., O^7 ..sp^2 OR $2p$..

(01 marks x 8 = 08 marks)

1(a): 55 marks

(b) (i) Identify the sub-shells (atomic orbitals) along with their azimuthal quantum number (l), and magnetic quantum number/s (m_l) for the energy level with principal quantum number $n=3$ in an atom. What is the maximum number of electrons present in each sub-shell?

Write your answers in the table given below.

Sub-shell	Azimuthal quantum number (l)	Magnetic quantum number/s (m_l)	Maximum number of electrons in each sub-shell
3s/s	0	0	2
3p/p	1	-1, 0, +1	6
3d/d	2	-2, -1, 0, +1, +2	10

(01 marks x 12 = 12 marks)

(ii) Identify the type/s of intermolecular forces present in I, II and III given below.

I. Ar gas
London dispersion forces (Induce dipole)

II. NO gas
dipole-dipole + London dispersion forces

III. water sample containing a small amount of dissolved KCl
Ion dipole + Hydrogen bonding + London dispersion.

(01 marks x 6 = 06 marks)

(iii) "The boiling point of *n*-butane (C_4H_{10}) is higher than the boiling point of propane (C_3H_8)." Giving reasons, state whether this statement is **true** or **false**.

True (05) (04)
n-butane and propane do not possess dipole moments or n-butane and propane are nonpolar molecules (02)
Forces acting are London dispersion forces (02)
Since n-butane is greater in size or molar mass than propane (02)
London dispersion forces between n-butane molecules are greater than in propane molecules (02)
Therefore, boiling point of C_4H_{10} > C_3H_8 (12)

(iv) Arrange the following in the **decreasing** order of the property indicated in parentheses. (Reasons are **not** required.)

I. Li_2CO_3, Na_2CO_3, K_2CO_3 (solubility in water)
K_2CO_3 > Na_2CO_3 > Li_2CO_3 (05)

II. NF_3, NH_3, NOCl, NO_2^+ (bond angle)
NO_2^+ > NOCl > NH_3 > NF_3 (05)

III. $COCl_2$, CO_2, HCN, CH_3Cl (electronegativity of carbon)
CO_2 > HCN > $COCl_2$ > CH_3Cl (05)

1(b): 45 marks

2. (*a*) **X**, **Y** and **Z** are elements that belong to the same group in the Periodic Table. They are in three successive periods respectively on descending the group. **Y** exists as a non-metallic coloured liquid at room temperature.

(i) Identify **X**, **Y** and **Z**. (Give atomic symbols.)

X = Cl **Y** = Br **Z** = I

Note: Do not award marks for X: Cl_2 Y: Br_2 Z: I_2

(04 marks x 3 = 12 marks)

(ii) Indicate the relative magnitudes of the following with regard to **X**, **Y** and **Z**.

I. Atomic size	I Z	>	Br Y	>	Cl X
II. Electron affinity	Cl X	>	Br Y	>	I Z
III. First ionization energy	Cl X	>	Br Y	>	I Z

Note: X, Y and Z have all to be identified correctly in order to award marks for 2(a)(ii)
provided all three elements are identified correctly X, Y & Z can be used to fill boxes

(03 marks x 3 = 09 marks)

(iii) You are provided with aqueous solutions of the anions of **X**, **Y** and **Z**, each in a separate test-Suggest a **single** reagent that could be used to identify these anions.

[**Note**: You are required to state the observation for each anion.]

Reagent: $AgNO_3$ solution (04)

Observation: (for the anions)
X: white precipitate (02)
Y: pale yellow precipitate (02)
Z: dark yellow precipitate (02)

OR

Reagent: Cl_2/CCl_4 (04)

Observation: (for the anions)
X: colourless organic layer (02)
Y: red-orange organic layer (02)
Z: violet organic layer (02)

Note: X, Y and Z have all to be identified correctly in order to award marks for 2(a)(iii)
Even if X, Y and Z have been identified as Cl_2, Br_2, and I_2 marks can be awarded

(iv) Give balanced chemical equations for the reactions of $X_2(g)$ with the following.

I. $NH_3(g)$ $3Cl_2(g) + 2NH_3(g) \rightarrow N_2(g) + 6HCl(g)$ (03)

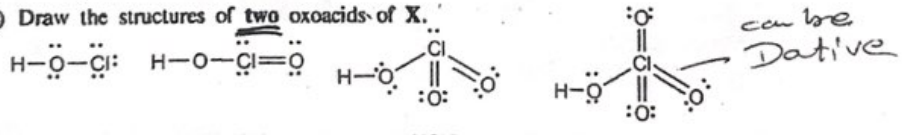
Or $3Cl_2(g) + NH_3(g) \rightarrow NCl_3(g) + 3HCl(g)$

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

II. dil. NaOH $Cl_2(g) + 2NaOH(aq) \rightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$ (03)

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

(v) Draw the structures of **two** oxoacids of **X**.



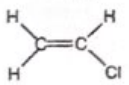
HOCl $HClO_2$ $HClO_3$ $HClO_4$

Any two (Neglect shapes and lone pairs however all bonds must be shown)

(03 x 2 = 06 marks)

(vi) Name **one** natural source of **X**. Sea water/Rock salt (NaCl)/KCl (Sylvine)/$KCl.MgCl_2$ (Carnalllite) (02)

(vii) I. A monomer that contains **X** forms an addition polymer that is widely used in the manufacture of water pipes. Draw the structure of the monomer.



$CH_2=CHCl$.

(03)

II. Write the **full name** of the polymer. Polyvinyl chloride (02)

2(a): 50 marks

(b) An aqueous solution **Q** contains **three** anions. The following tests were carried out to identify these anions.
(Fresh portions of solution **Q** were used for each test ① to ⑤).

		Test	Observation
①	I	Dilute HCl was added.	A colourless gas was evolved. A clear solution was obtained.
	II	The gas evolved was tested with filter paper moistened with lead acetate.	No colour change
②	I	A $BaCl_2$ solution was added.	A white precipitate was obtained.
	II	The white precipitate was separated by filtration, and dil. HCl was added to it.	The white precipitate dissolved with the evolution of a gas.
	III	The gas evolved was tested with a filter paper moistened with acidified potassium dichromate.	The colour changed from orange to green.
③		Conc. HNO_3 and an excess of ammonium molybdate solution were added and the mixture was warmed.	A yellow precipitate did not form.
④		Devarda's alloy and NaOH solution were added and the mixture was heated.	A gas that turned Nessler's reagent brown was evolved.
⑤		A $FeCl_3$ solution was added.	A blood red coloured solution was obtained.

(i) Identify the **three** anions in solution **Q**.

NO_3^- , SCN^- and SO_3^{2-} **(12 x 3 = 36 marks)**

(ii) Write the balanced chemical equation for the reaction taking place in test number ② III. **(14)**

$3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$

Or **(03)**

$3(SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e)$ **(03)**

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$ **(02)**

$3SO_2 + 6H_2O + Cr_2O_7^{2-} + 14H^+ \rightarrow 3SO_4^{2-} + 12H^+ + 2Cr^{3+} + 7H_2O$ **(06)**

$3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$

$3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

2(b): 50 marks

3. (a) Methylamine, CH_3NH_2 is a weak base. The following equilibrium exists in an aqueous solution of methylamine.

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

(i) Write the expression for K_b of methylamine.

Note: Correct Physical states are necessary **(05)**

$$K_b = \frac{[CH_3NH_3^+(aq)][OH^-(aq)]}{[CH_3NH_2(aq)]}$$

(ii) At 25 °C, the pH value of a 0.20 mol dm^{-3} aqueous solution of methylamine is 11.00. Calculate K_b.

$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$ **(02)**

As the pH= 11, $pOH = 3$ **(02)**

$\therefore [OH^-(aq)] = [CH_3NH_3^+(aq)] = 1.0 \times 10^{-3}\ mol\ dm^{-3}$ **(02 + 01)**

$$\therefore K_b = \frac{1.0 \times 10^{-3}\ mol\ dm^{-3} \times 1.0 \times 10^{-3}\ mol\ dm^{-3}}{0.2\ mol\ dm^{-3}}$$ **(02 + 01)**

$$= 5.0 \times 10^{-6}\ mol\ dm^{-3}$$

(iii) A volume of 25.00 cm^3 of the solution in (ii) above was titrated with 0.20 mol dm^{-3} HCl at 25 °C. Calculate the pH value of the solution at the equivalence point. ($K_w = 1.0 \times 10^{-14}$ $mol^2\,dm^{-6}$ at 25 °C.)

Reaction of $CH_3NH_2(aq)$ with HCl is,

$CH_3NH_2(aq) + HCl(aq) \rightleftharpoons CH_3NH_3Cl(aq)$ (or $CH_3NH_3^+(aq)$) **(03)**

Stoichiometry of the reaction,

$CH_3NH_2(aq) : HCl(aq) : CH_3NH_3Cl(aq) = 1 : 1 : 1$

Equivalence point = 25.00 cm^3 **(02)**

$\therefore [CH_3NH_3^+(aq)]$ at the equivalence point $= \dfrac{0.2\ mol\,dm^{-3} \times 25 \times 10^{-3}\ dm^3}{50 \times 10^{-3}\ dm^3}$

$= 0.10\ mol\,dm^{-3}$ **(04 + 01)**

pH at the equivalence point is determined by the reaction;

$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$ ---------- (A) **(03)**

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

(02)

For the Reaction **(A)**:

$$\mathbf{K_a} = \frac{[CH_3NH_2(aq)][H_3O^+(aq)]}{[CH_3NH_3^+(aq)]} = \frac{K_w}{K_b}$$ **(02)**

$$= \frac{1.0 \times 10^{-14}\ mol^2\,dm^{-6}}{5.0 \times 10^{-6}\ mol\,dm^{-3}} = 2.0 \times 10^{-9}\ mol\,dm^{-3}$$ **(03)**

$$\therefore 2.0 \times 10^{-9} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$ **(02 + 03)**

$$2.0 \times 10^{-10} = x^2$$

$$x = 1.41 \times 10^{-5}\ mol\,dm^{-3}$$ **(04 + 01)**

$\therefore$ pH = $-\log(1.41 \times 10^{-5}) = 4.85$ **(05)**

3(a): 50 marks

(*b*) In an experiment, a limited volume of 1.00 mol dm^{-3} HNO_3 was added to a precipitate MX(s) and the system was allowed to reach equilibrium at 25 °C. This resulted in partial dissolution of the precipitate giving rise to a clear solution. The HX(aq) formed behaves as a weak acid.

(i) Write chemical reactions for the equilibria existing in the above solution.

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ **(04)**

$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$ **(04)**

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ **(02)**

(ii) Calculate $[X^-(aq)]$ in the solution assuming that the dissociation of HX(aq) is negligible. (Solubility product of MX at 25 °C, $K_{sp(MX)} = 3.6 \times 10^{-7}\ mol^2\,dm^{-6}$.)

$MX(s) + HNO_3(aq) \rightarrow M^+(aq) + NO_3^-(aq) + HX(aq)$ **(05)**

The concentration of $M^+(aq)$ = 1.0 mol dm^{-3} **(04 + 01)**

$K_{sp(MX)} = [M^+(aq)]\,[X^-(aq)]$ **(05)**

$$\therefore [X^-(aq)] = \frac{3.6 \times 10^{-7}\ mol^2\,dm^{-6}}{1.0\ mol\,dm^{-3}} = 3.6 \times 10^{-7}\ mol\,dm^{-3}$$

(04 + 01)

(iii) Giving reasons explain whether $[X^-(aq)]$ in a saturated aqueous solution of MX at 25 °C is equal to, smaller than or greater than the value obtained in (*b*)(ii) above.

In an aqueous solution, $[X^-(aq)]$ is determined only by K_{sp} **(05)**

$K_{sp(MX)} = [M^+(aq)]\,[X^-(aq)] = 3.6 \times 10^{-7}\ mol^2\ dm^{-6}$

$[X^-(aq)]^2 = 3.6 \times 10^{-7}\ mol^2\ dm^{-6}$ **(05)**

$[X^-(aq)] = 6.0 \times 10^{-4}\ mol\ dm^{-3}$ **(05)**

The value is higher than that in (ii) **(05)**

OR $[X^-(aq)]$ is determined only by K_{sp} **(05)**

No common ion effect **(05)**

Solution is saturated **(05)**

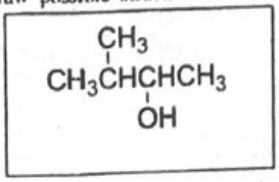
The value is larger **(05)**

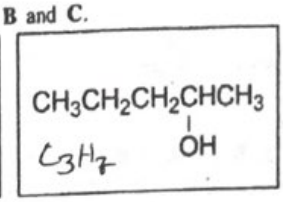
3(b): 50 marks

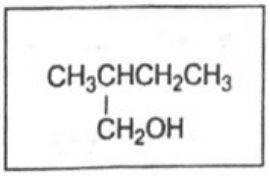
4. (*a*) The alcohols **A**, **B**, **C** and **D** are structural isomers of each other having the molecular formula $C_5H_{12}O$. **A**, **B** and **C** show optical isomerism.

(i) Draw possible structures for **A**, **B** and **C**.

(12)







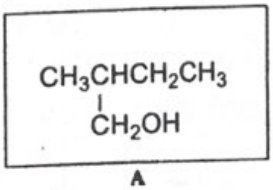
(12)

Structures can be drawn in any order

When **B**, **C** and **D** are reacted with acidic $K_2Cr_2O_7$, **X**, **Y** and **Z** are formed respectively. The products **X**, **Y** and **Z** can be converted back to **B**, **C** and **D** respectively by reacting with $NaBH_4$.

(ii) What is the structure of **A**?

(OH)



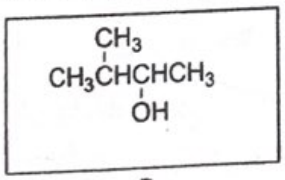
(OH)

A

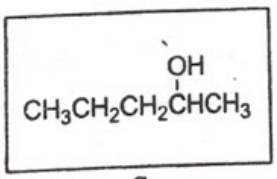
On heating with conc. H_2SO_4 **A** and **B** gave **E** and **F**, respectively, while **C** and **D** gave the same product **G**. **G** shows diastereoisomerism. All three compounds **E**, **F** and **G** have the molecular formula C_5H_{10}. When **E** and **F** are reacted with HBr the same product **H** was formed.

(iii) Draw the structures of **B**, **C**, **D**, **E**, **F** and **H**.

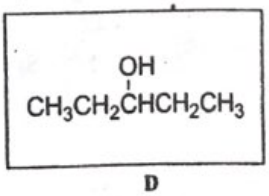
(12)



B



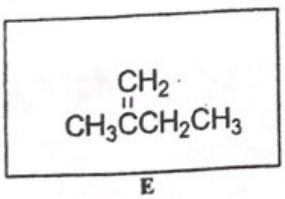
C



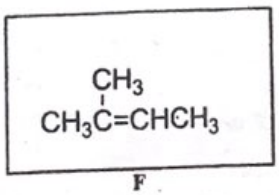
D

(12)

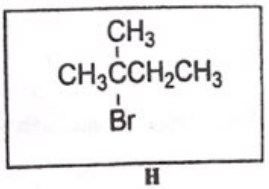
(12)



E



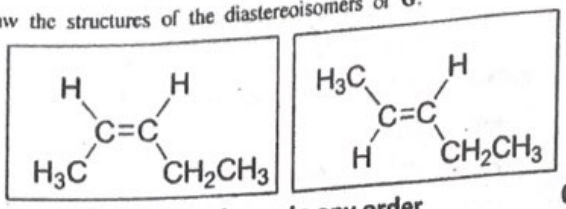
F



H

(12)

(iv) Draw the structures of the diastereoisomers of G.

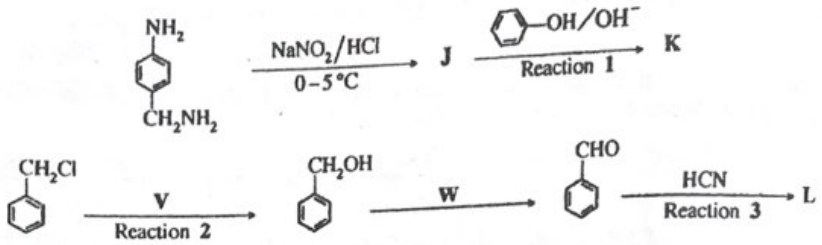


Structures can be drawn in any order

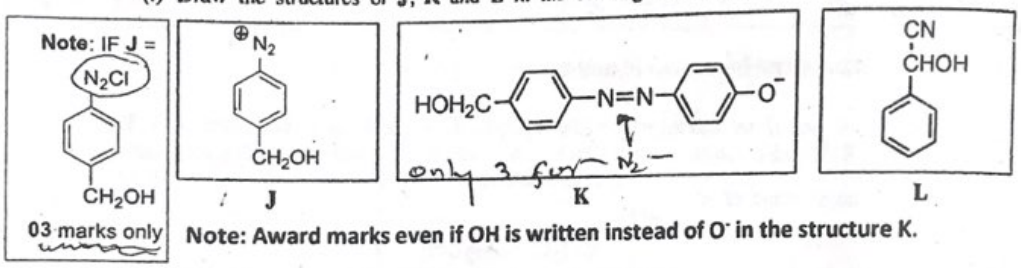
04 marks X 12 = 48 marks

4(a): 48 marks

(b) Consider the two reaction schemes given below.



(i) Draw the structures of J, K and L in the boxes given below.



Note: Award marks even if OH is written instead of O^- in the structure K.

(ii) Write the reagents V and W in the boxes given below.

V = **NaOH Or OH^-** W = **PCC** ~~cu/300°C~~ not accepted

(iii) Writing A_E, A_N, S_E, S_N or E in the appropriate box, classify each of the reactions 1, 2 and 3 as electrophilic addition (A_E), nucleophilic addition (A_N), electrophilic substitution (S_E), nucleophilic substitution (S_N) or elimination (E) reaction.

Reaction 1 **S_E** Reaction 2 **S_N** Reaction 3 **A_N**

05 marks X 8 = 40 marks

4(b): 40 marks

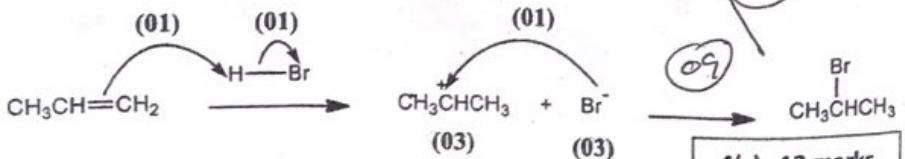
(c) (i) What is the structure of the **major** product of the reaction between $CH_3CH{=}CH_2$ and HBr?

CH_3CHCH_3
Br

(03)

03 12

(ii) Write the mechanism of the above reaction.



Note: Ignore δ+ and δ- if written near the H and Br of HBr and award marks.

4(c): 12 marks

PART B — ESSAY

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

5. (a) The following reaction occurs when $NaHCO_3(s)$ is heated to a temperature above 100 °C.

$$2\ NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

A sample of $NaHCO_3(s)$ was placed in an evacuated closed rigid container of 5.00 dm^3 volume and heated to 328 °C. After the equilibrium was reached, a small amount of $NaHCO_3(s)$ still remained in the container. The pressure of the container was found to be 1.0×10^6 Pa. Assume that the volume of the solids remaining in the container is negligible. RT = 5000 J mol^{-1} at 328 °C.

(i) Calculate the number of moles of $H_2O(g)$ in the container when the equilibrium is reached at 328 °C

$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$

System has $CO_2(g)$ and $H_2O(g)$ as gaseous species,

Assuming ideal behavior or (PV = nRT) **(03)**

$n_{total} = P_{total}V/RT$

$= 1.0 \times 10^6\ Pa \times 5.00 \times 10^{-3}\ m^3 / 8.314\ J\ K^{-1}\ mol^{-1} \times 601\ K$ **(02)**

$= 1.0 \times 10^6\ Pa \times 5.00 \times 10^{-3}\ m^3 / 5000\ J\ mol^{-1}$

$= 1.0\ mol$ **(05)**

$n_{total} = n_{H2O(g)} + n_{CO2(g)}$

According to stoichiometry $n_{H2O(g)} = n_{CO2(g)}$ **(02)**

$\therefore\ n_{H2O(g)} = 0.50\ mol$ **(03)**

(ii) Calculate K_p for the above equilibrium at 328 °C, and hence calculate K_c.

$K_p = P_{H2O(g)} \times P_{CO2(g)}$ **(05)**

in the system, $P_{Total} = P_{H2O(g)} + P_{CO2(g)} = 1.0 \times 10^6\ Pa$ **(05)**

and $P_{H2O(g)} = P_{CO2(g)}$

$\therefore\ P_{H2O(g)} = P_{CO2(g)} = 5.0 \times 10^5\ Pa$ **(04 + 01)**

$\therefore K_p = (5.0 \times 10^5\ Pa)^2 = 2.5 \times 10^{11}\ Pa^2$ **(04 + 01)**

$K_p = K_C(RT)^{\Delta n}$ **(05)**

$\Delta n = 2 - 0 = 2$ **(03)**

$\therefore K_C = K_p / (RT)^2$

$= 2.5 \times 10^{11}\ Pa^2 / (8.314\ J\ K^{-1}\ mol^{-1} \times 601\ K)^2$ **(02)**

$= 2.5 \times 10^{11}\ Pa^2 / (5000\ J\ mol^{-1})^2$

$= 1.0 \times 10^4\ mol^2\ m^{-6}\ (1.0 \times 10^{-2}\ mol^2\ dm^{-6})$ **(04 + 01)**

(Note: Here K_c must be calculated from K_p, other answers are not accepted)

(iii) An extra amount of $CO_2(g)$ was added into the container described above at 328 °C. When the equilibrium is re-established, the partial pressure of $CO_2(g)$ was four (4) times the partial pressure of $H_2O(g)$. Calculate the partial pressures of $CO_2(g)$ and $H_2O(g)$ under this condition.

Take, $P_{H2O(g)} = x\ Pa$

$\therefore\ P_{CO2(g)} = 4x\ Pa$

Now $K_p = P_{H2O(g)} \times P_{CO2(g)} = x.4x = 4x^2$ (05)

As the temperature is constant, (05)

$$2.5 \times 10^{11}\ Pa^2 = 4x^2 \quad (05)$$

$$\left(\frac{2.5}{4}\right) \times 10^{11}\ Pa^2 = x^2$$

$$\left(\frac{25}{4}\right) \times 10^{10}\ Pa^2 = x^2$$

$$x = 2.5 \times 10^5\ Pa$$

$\therefore P_{H2O(g)} = 2.5 \times 10^5$ Pa and (04 + 01)

$P_{CO2(g)} = 1.0 \times 10^6$ Pa (04 + 01)

5(a): 75 marks

(*b*) In order to determine the standard enthalpy change ($\Delta H°$) of the reaction,

$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

the following experiment consisting of two steps (I and II) was carried out at room temperature.

Step I: 0.08 mol of $NaHCO_3(s)$ was added to 100.00 cm^3 of 1.0 mol dm^{-3} HCl acid solution in a beaker. The maximum temperature fall was found to be 5.0 °C.

[The reaction taking place: $NaHCO_3(s) + HCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l) + CO_2(g)$]

Step II: 0.04 mol of $Na_2CO_3(s)$ was added to 100.00 cm^3 of 1.0 mol dm^{-3} HCl acid solution in a beaker. The maximum temperature rise was found to be 3.5 °C.

[The reaction taking place: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2Na^+(aq) + 2Cl^-(aq) + H_2O(l) + CO_2(g)$]

Specific heat capacity at constant pressure and density of HCl acid solution are 4.0 J g^{-1} K^{-1} and 1.0 g cm^{-3} respectively. Assume that the changes in volume and density of the solutions after the addition of solids in the above two steps are negligible.

(i) Calculate the enthalpy changes (in kJ mol^{-1}) of the reactions given in steps I and II above.

Step I:

For the reaction with 0.08 moles of $NaHCO_3(s)$

$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

$Q = ms\theta$ **Or** $Q = mc\theta$ (05)

$= 100\ g \times 4.0\ J\ g^{-1}\ K^{-1} \times 5\ K = 2000\ J = 2.0\ kJ$ (04 + 01)

$\therefore$ for 1 mol

$Q = 2.0\ kJ / 0.08\ mol$ (05)

$Q = \Delta H = +25\ kJ\ mol^{-1}$ (heat loss) (04 + 01)

02 marks for the sign

Step II:

For the reaction with 0.04 moles of $NaHCO_3(s)$

$$Na_2CO_3(s) + 2\,HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

$Q = ms\theta$

$= 100\ g \times 4.0\ J\ g^{-1}\ K^{-1} \times 3.5\ K = 1400\ J = 1.4\ kJ$ **(04 + 01)**

$\therefore$ for 1 mol

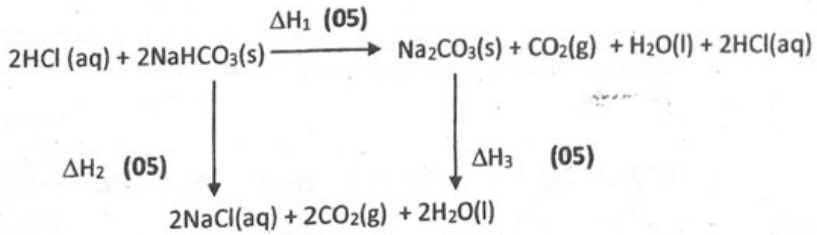
$Q = 1.4\ kJ / 0.04\ mol$

$Q = \Delta H = -35\ kJ\ mol^{-1}$ (heat gain) **(04 + 01)**

(02 marks for the sign)

(ii) Using the values obtained in (i) above and a **thermochemical cycle**, calculate ΔH° of the reaction $2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$.

The reaction, $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$ can be written with the help of following thermochemical cycle,



(To award marks for the thermocycle balanced equations are necessary)

According to Hess's Law, $\Delta H_1 = \Delta H_2 - \Delta H_3$ **(05)**

$\Delta H_1 = 25 \times 2 - (-35)\ kJ\ mol^{-1}$ **(05)**

$\Delta H_1 = +85\ kJ\ mol^{-1}$ **(04 + 01)**

(iii) State the condition under which a heat change of a reaction is equal to its enthalpy change.

At constant pressure. **(05)**

(iv) Identify two sources of error in the above experimental procedure.

Sources of errors

A calorimeter is not used/heat loss (heat loss to environment)

Dissolution enthalpies of solids are different

(03 x 2)

5(b): 75 marks

6. (a) (i) Explain why the rate of a reaction increases when the concentrations of the reactants are increased.

Increase in concentration causes an increase in the number of molecules in unit volume. (05)

This increases the collision rate (Number of collisions in unit time). (05)

(ii) Give two reasons to explain why in general, the rate of a reaction increases with increasing temperature.

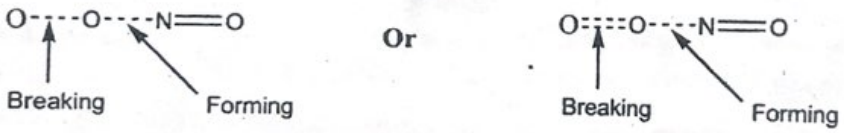
The collision rate and (05)

the fraction of reacting molecules having energy greater than the activation energy increase with increasing temperature. (05)

(iii) What is the relationship between order and molecularity of an elementary reaction?

Molecularity = Order of reaction. (10)

(iv) Sketch the structure of the activated complex of the elementary reaction, $NO + O_2 \rightarrow NO_2 + O$. Label the bonds that are being formed as **'forming'** and the bonds that are being broken as **'breaking'**.



(Correct structure 04 marks labeling 03 +03) (10)

(v) Write the rate expression for the elementary reaction, $xA + yB \rightarrow zC$, where the rate constant is k, and stoichiometric coefficients are x, y, z.

Rate = $k[A]^x[B]^y$ or $\frac{1}{x}\left(\frac{-\Delta[A]}{\Delta t}\right) = k[A]^x[B]^y$ or $\frac{1}{x}\left(\frac{-d[A]}{dt}\right) = k[A]^x[B]^y$

or $\frac{-\Delta[A]}{\Delta t} = k[A]^x[B]^y$ or $\frac{-d[A]}{dt} = k[A]^x[B]^y$ (10)

6(a): 50 marks

(b) The reaction $xA + yB \rightarrow zC$ was studied in a two phase system consisting of an organic solvent and water. The compound **A** is soluble in both phases while compounds **B** and **C** are soluble only in the aqueous phase. The partition coefficient for the distribution of **A** between phases, $K_D = \frac{[A_{(org)}]}{[A_{(aq)}]} = 4.0$.

The compound **A** was added to the two phase system and allowed to reach equilibrium. The reaction was started by injecting the compound **B** to the aqueous phase. Temperature of the system was maintained at a constant value. The results of the experiments carried out are given below.

Experiment No.	Volume of the organic phase (cm^3)	Volume of the aqueous phase (cm^3)	Amount of **A** added to the system (mol)	Amount of **B** injected (mol)	Initial rate, $\left(\frac{-\Delta C_A}{\Delta t}\right)$ (mol dm^{-3} s^{-1})
I	–	100.00	1.00×10^{-2}	1.00×10^{-2}	1.20×10^{-5}
II	100.00	100.00	1.25×10^{-1}	1.00×10^{-2}	7.50×10^{-5}
III	50.00	50.00	6.25×10^{-2}	1.00×10^{-2}	1.50×10^{-3}

Note: Experiment I was carried out without the organic phase.

(i) Calculate the initial concentration of **A** in the aqueous phase in experiments I, II and III above.

Experiment (I)

Concentration of A in the aqueous phase, $[A(I)]_{aq} = 1.00 \times 10^{-2} mol / 100 \times 10^{-3} dm^3 = 0.10$ mol dm^{-3}. **(01 + 01)**

Experiment (II)

$$K = \frac{[A]_{org}}{[A]_{aq}} = 4$$

$$[A(II)]_{aq} = \frac{[A(II)]_{org}}{4.0} \quad \textbf{(03)}$$

Let x be the amount of A in the aqueous phase.

$$\frac{1.25 \times 10^{-1} mol - x}{4 \times 100 \times 10^{-3} dm^{-3}} = \frac{x}{100 \times 10^{-3} dm^{-3}} \quad \textbf{(02 + 01)}$$

$$4x = 1.25 \times 10^{-1} mol - x$$

$$x = 2.5 \times 10^{-2} mol \quad \textbf{(02 + 01)}$$

$$[A(II)]_{aq} = \frac{x}{V} = \frac{2.5 \times 10^{-2} mol}{100 \times 10^{-3} dm^3}$$

$$[A(II)]_{aq} = 2.5 \times 10^{-1} mol\ dm^{-3} \quad \textbf{(02 + 01)}$$

Experiment (III)

Let y be the amount of A in the aqueous phase.

$$[A(III)]_{aq} = \frac{y}{V}$$

$$\frac{y}{V} = \frac{6.25 \times 10^{-2} mol - y}{V \times 4}$$

$$4y = 6.25 \times 10^{-2} mol - y$$

$$y = \frac{6.25 \times 10^{-2} mol}{5} = 0.0125\ mol \quad \textbf{(02 + 01)}$$

$$[A(III)]_{aq} = \frac{0.0125\ mol}{50.0 \times 10^{-3}\ dm^3}$$

$[A(III)]_{aq} = 2.5 \times 10^{-1}$ mol dm^{-3} **(02 + 01)**

(ii) Find the order of the reaction with respect to A.

Finding the order with respect to A

In experiments (I) and (II), the concentration of B in the aqueous phase is the same.

1.2×10^{-5} mol dm^{-3} s^{-1} = k[0.1 mol dm^{-3}]^x [0.1 mol dm^{-3}]^y (02 + 01)

7.5×10^{-5} mol dm^{-3} s^{-1} = k [0.25 mol dm^{-3}]^x [0.1 mol dm^{-3}]^y (02 + 01)

1.5×10^{-3} mol dm^{-3} s^{-1} = k [0.25 mol dm^{-3}]^x [0.2 mol dm^{-3}]^y (02 + 01)

(03)

$$\frac{7.5\times10^{-5}}{1.2\times10^{-5}} = \left(\frac{0.25}{0.1}\right)^x$$

$$\frac{6.25}{1} = \left(\frac{2.5}{1}\right)^x$$

$2.5^2 = 2.5^x$

X=2 (02)

[for calculation of 0.2 M]

(iii) Find the order of the reaction with respect to B.

Finding the order with respect to B

In experiments II and III, the concentration of A in the aqueous phase is the same.

$$\frac{1.5\times10^{-3}}{7.5\times10^{-5}} = \left(\frac{0.2}{0.1}\right)^y$$ (03)

$$\frac{20}{1} = \left(\frac{2}{1}\right)^y$$

Log(20) = y log 2

1.3010 = y x .3010

Y = 4.32 = 4 (02)

(iv) Calculate the rate constant of the reaction.

Finding the rate constant of the reaction.

Using data in experiment (I),

$$k = \frac{Rate\ (I)}{[A(I)]^2[B(I)]^4}$$

(4.32 can be used instead of 4)

$$k = \frac{1.20\times10^{-5} mol\ dm^{-3} s^{-1}}{(1.00\times10^{-1} mol\ dm^{-3})^2\ (1.00\times10^{-1} mol\ dm^{-3})^4}$$ (02 + 01)

k = 1.2 x 10^1 mol^{-4} dm^{12} s^{-1} (wrong unit) (if 4.32 k = 25) (01)

Correct unit: $mol^{-5}\ dm^{15}\ s^{-1}$

(v) In the experiment III above, after adding A and allowing the system to reach equilibrium, if a volume of 10.00 cm^3 was removed from the organic phase, what can be stated about the initial rate of the reaction? Give reason/reasons for your answer.

The initial rate of the reaction will not change. The Concentration of A in the aqueous phase does not change.

(02 + 02)

6(b): 50 marks

(c) A mixture of liquids X and Y behaves ideally. At a constant temperature, when the liquid phase in equilibrium with the vapour phase in a closed rigid vessel contains 1.2 moles of X and 2.8 moles of Y, the total vapour pressure is 3.4×10^4 Pa. At the same temperature, when the composition of the liquid phase in equilibrium with the vapour phase is 1.2 moles of X and 4.8 moles of Y, the total vapour pressure is 3.6×10^4 Pa. Calculate the saturated vapour pressures of X and Y at this temperature.

According to Rault's law, $p_i = x_i p_i^0$ **(05)**

$p_{total} = p_x + p_y = X_x p_x^0 + X_y p_y^0$ **(05)**

For the first condition,

$X_x = \frac{1.2\ mol}{1.2mol+2.8\ mol}$ **(04 + 01)**

$X_x = 0.3$ and therefore $X_y = 0.7$ **(02 + 02 + 01)**

For the second condition,

$X_y = \frac{1.2\ mol}{1.2mol+4.8\ mol}$ **(04 + 01)**

$X_y = 0.2$ and therefore $X_y = 0.8$ **(02 + 02 + 01)**

Using the mole fractions, two equations can be constructed for the two conditions.

$3.4 \times 10^4 Pa = 0.3p_x^0 + 0.7p_y^0$ – (1) **(05)**

$3.6 \times 10^4 Pa = 0.2p_x^0 + 0.8p_y^0$ – (2) **(05)**

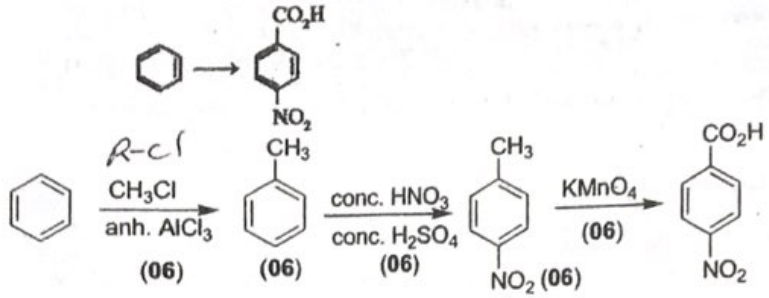
Solving the two equations,

$p_x^0 = 2.0\times10^4$ Pa (04 + 01) **(05)**

$p_y^0 = 4.0\times10^4$ Pa (04 + 01) **(05)**

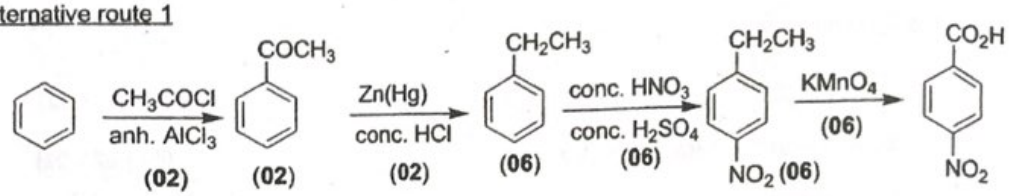
6(c): 50 marks

7. (*a*) Show how you would carry out the following conversion in **not more than five (5) steps.**

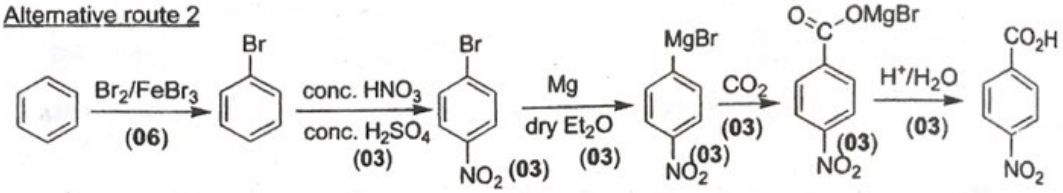


30 marks

Alternative route 1



Alternative route 2

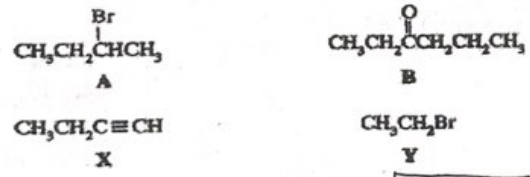


Notes: *Instead of CH_3Cl any other appropriate alkyl halide can be written.

***$(CH_3)_3CCl$ is unacceptable.**

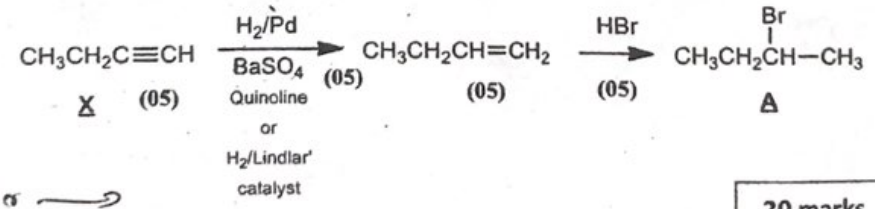
***RCH_2Cl is acceptable provided that the appropriate product is given.**

(*b*) Two compounds **A** and **B** are required to be prepared in the laboratory.



cannot be exceed

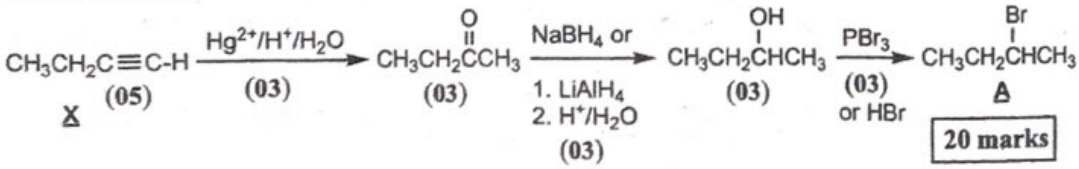
(i) Show how you would prepare **A** and **B** in **not more than five (5) steps** in each case, using **X** and **Y** as required.



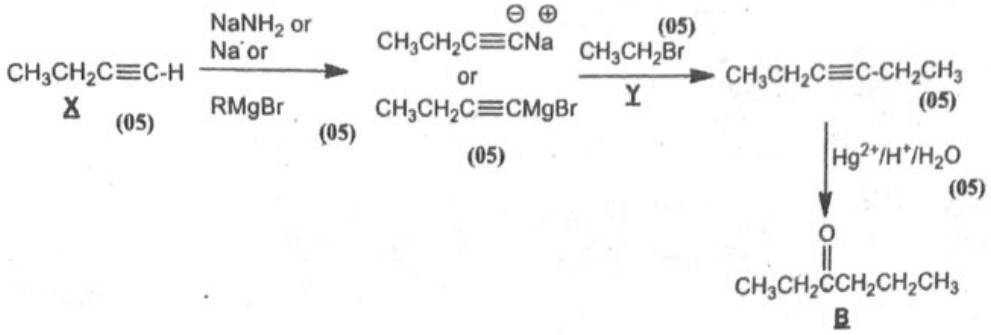
CH3CH2Br ⟶

20 marks

Alternative route



20 marks

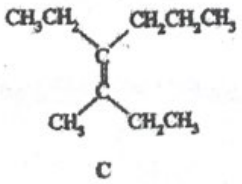


30 marks

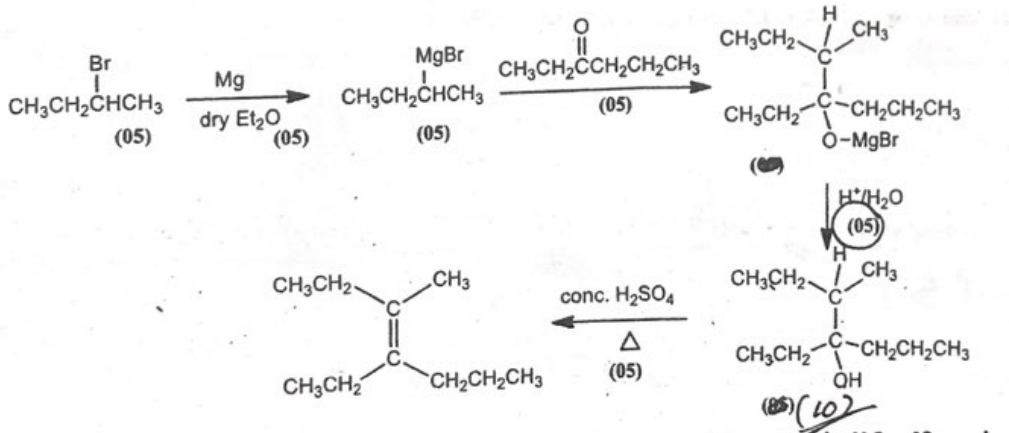
Note : The marks allocated for X and Y in the synthetic pathways can be awarded ONLY if the usage of X and Y is correct/appropriate.

7(b): 05 marks X 10 = 50 marks

(ii) Show how you would prepare the compound C using A and B given above, in not more than five (5) steps.



C

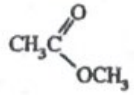


7(b)(ii): 05 marks X 8 = 40 marks

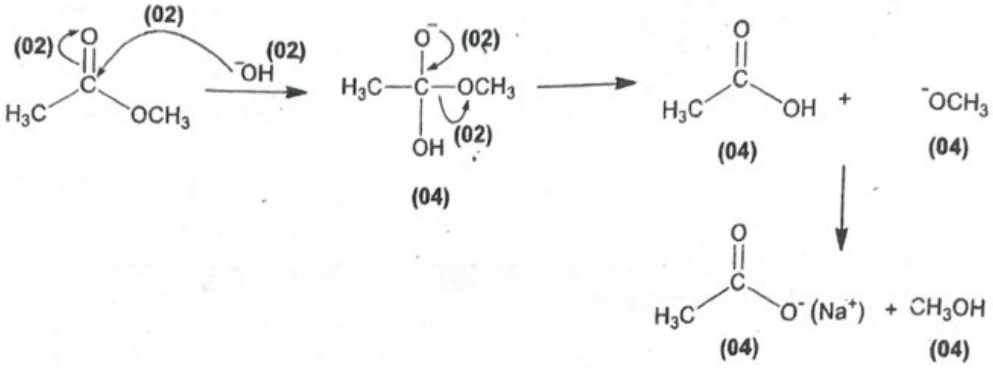
Note: Steps can be combined appropriately. Award marks appropriately for correct Answers.

No marks are awarded for Cu/300^{0}C or heat

(c) Using your knowledge of the mechanism of the reaction between acetyl chloride and NaOH, propose a mechanism for the reaction between



and NaOH.



Notes: ***Steps can be combined appropriately. Award marks appropriately for correct Answers.**

7(c): 30 marks

(7b) $CH_3CH_2Br \xrightarrow[(02)]{Mg/Eth} CH_3CH_2MgBr \xrightarrow[(02)]{CH_3CH_2Br} CH_3CH(CH_2CH_3)MgBr$ (02) (02)

$\xrightarrow[(02)]{H_2O/H^+}$ $CH_3-CH(OH)-CH_2CH_3 \xrightarrow[(02)]{PBr_3}$ $CH_3-CH(Br)-CH_2CH_3$ (product)

$CH_3CH_2Br \xrightarrow[(5)]{Mg/Eth} CH_3CH_2MgBr \xrightarrow[(03)]{n\text{-}C_3H_7\text{-}CHO}$ $CH_3CH_2CH_2-CH(OMgBr)-CH_2CH_3$ (5) (5) (5) (01)

$\xrightarrow[(05)]{H_2O/H^+}$ $CH_3CH_2CH_2-CH(OH)-CH_2CH_3 \xrightarrow[K_2Cr_2O_7/H^+ \text{ or } CrO_3/H^+]{PCC}$ $CH_3CH_2CH_2-C(=O)-CH_2CH_3$ (05)

8. (a) Solution **Y** contains **three** cations.

Ⓐ The following tests were carried out to identify these cations.

	Test	Observation
①	Dilute HCl was added to a small portion of **Y**.	A white precipitate (P_1)
②	P_1 was separated by filtration and H_2S was bubbled through the solution.	A black precipitate (P_2)
③	P_2 was separated by filtration. The filtrate was boiled to remove the H_2S, cooled, and NH_4OH/NH_4Cl was added.	No precipitate
④	H_2S was bubbled through the solution.	A black precipitate (P_3)

Ⓑ The following tests were carried out for precipitates P_1, P_2 and P_3.

Precipitate	Test	Observation
P_1	I. Water was added to P_1 and the mixture was boiled.	Part of P_1 dissolved.
	II. The mixture from I above was filtered while warm and the following tests were carried out on the filtrate (F_1) and residue (R_1).	
	Filtrate (F_1)	
	• Dilute H_2SO_4 was added to warm F_1.	A white precipitate
	Residue (R_1)	
	• R_1 was washed thoroughly with warm water and dilute NH_4OH was added.	R_1 dissolved.
	• Thereafter, a KI solution was added.	A dark yellow precipitate
P_2	P_2 was dissolved in warm dil. HNO_3 and a potassium chromate solution was added.	A yellow precipitate
P_3	I. P_3 was dissolved in warm conc. HNO_3.	A pink coloured solution (**solution 1**)
	II. The following were added to **solution 1** above.	
	• conc. HCl	A blue coloured solution (**solution 2**)
	• dil. NH_4OH	A yellow-brown coloured solution (**solution 3**)

(i) Identify the **three** cations. (Reasons are **not** required.)

Pb^{2+}, Co^{2+}, Ag^+ **(08 x 3)**

(ii) Identify,
I. precipitates P_1, P_2 and P_3
II. species responsible for the colours of **solutions, 1, 2 and 3.**
(**Note:** Write chemical formulae **only**.)

I P_1: $PbCl_2$ and AgCl P_2: PbS P_3: CoS **(05 x 4)**

II Solution **1**: Co^{2+} OR $Co(NO_3)_2$ OR $[Co(H_2O)_6]^{2+}$ **(05)**

Solution **2**: $[CoCl_4]^{2-}$ **(05)**

Solution **3**: $[Co(NH_3)_6]^{2+}$ **(05)**

(iii) Explain **briefly** why the cation/s that precipitate/s in Ⓐ ④ above does not/do not precipitate in acidic medium.

For cations to precipitate from solution as sulfides,

$[M^{2+}][S^{2-}] > K_{sp}$ (04)

In acidic medium, $[S^{2-}]$ is reduced. (03)

$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$ (03)

K_{sp} of sulfides of Group IV cations > K_{sp} of sulfides of Group II cations (Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}) (03)

As $[S^{2-}]$ is reduced in acidic medium, it is not sufficient to precipitate the Group IV cations as sulfides. Therefore, they remain in solution. (03)

8(a): 75 marks

(*b*) A solid sample was found to contain $(NH_4)_2SO_4$, NH_4NO_3 and non-reactive substances. The following procedures were used to determine the amount of ammonium salts present in this sample.

A 1.00 g portion of the solid sample was dissolved in water and diluted to 250.00 cm^3 in a volumetric flask (hereafter referred to as solution **S**).

Procedure 1

A 50.00 cm^3 portion of solution **S** was treated with an excess amount of a strong alkali (NaOH) and the gas liberated was passed into 30.00 cm^3 of 0.10 mol dm^{-3} HCl. The volume of 0.10 mol dm^{-3} NaOH required to neutralize the remaining HCl (using phenolphthalein as the indicator) was 10.20 cm^3.

Procedure 2

To a 25.00 cm^3 portion of solution **S**, Al powder was added followed by an excess of strong alkali, and the mixture was heated. The gas liberated was passed into 30.00 cm^3 of 0.10 mol dm^{-3} HCl. The volume of 0.10 mol dm^{-3} NaOH required to neutralize the remaining HCl (using phenolphthalein as the indicator) was 15.00 cm^3.

(**Note**: Completion of gas evolution in procedures **1** and **2** was checked using litmus paper.)

(i) Identify the gas liberated in procedure **1**.

(ii) Identify the gas liberated in procedure **2**.

(iii) Write balanced chemical equations for the reactions taking place in procedures **1** and **2**.

(iv) Calculate the mass percentage of each of the compounds $(NH_4)_2SO_4$ and NH_4NO_3 in the solid sample. (H = 1, N = 14, O = 16, S = 32)

(i) NH_3 (03)

(ii) NH_3 (03)

(iii) Reactions in Procedure I

$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$ .....(1) (04)

$NH_4NO_3 + NaOH \rightarrow NaNO_3 + NH_3 + H_2O$ .....(2) (04) ? if not

Reactions in Procedure 2

$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$ ..... (3) (03) 07

$NH_4NO_3 + NaOH \rightarrow NaNO_3 + NH_3 + H_2O$ .....(4) (03) 07

$5OH^- + 3NO_3^- + 2H_2O + 8Al \rightarrow 8AlO_2^- + 3NH_3$ .....(5) (05)

Note: Since the question does not ask to write the reactions separately for procedures, students may write only the last three reactions as in the procedure 2. If so, award 07 marks each, to the reactions with NaOH (i.e. reactions 3 and 4).

(iv) Amount of $(NH_4)_2SO_4$ in sample = x g **(01)** Amount of NH_4NO_3 in sample = y g **(01)**

Molar mass of $(NH_4)_2SO_4$ = 132 **(01)** Molar mass of NH_4NO_3 = 80 **(01)**

Moles of $(NH_4)_2SO_4 = \frac{x}{132}$ **(01)** Moles of $NH_4NO_3 = \frac{y}{80}$ **(01)**

Procedure 1

Moles of NaOH $= \frac{0.10}{1000} \times 10.20$ **(01)**

Therefore, moles of HCl reacted with NaOH $= \frac{0.10}{1000} \times 10.20$ **(01)**

Therefore, moles of HCl reacted with NH_3 $= \frac{0.10}{1000} \times 30.0 - \frac{0.10}{1000} \times 10.20$ **(01)**

$= \frac{0.10}{1000} \times 19.80$ **(01)**

Therefore, moles of NH_3(g) liberated $= \frac{0.10}{1000} \times 19.80$ **(01)**

Moles of $(NH_4)_2SO_4$ in 50.00 cm^3 $= \frac{x}{132} \times \frac{1}{5}$ **(01)**

Moles of NH_4NO_3 in 50.00 cm^3 $= \frac{y}{80} \times \frac{1}{5}$ **(01)**

Therefore, Moles of NH_3 given out by 50.00 cm^3 of solution (Eq. (1) & (2)) =

$$\frac{x}{132} \times \frac{1}{5} \times 2 + \frac{y}{80} \times \frac{1}{5} = \frac{0.10}{1000} \times 19.80 \quad \text{.....(6)} \quad \textbf{(07)}$$

Similarly for Procedure 2

Moles of NaOH $= \frac{0.10}{1000} \times 15.00$ **(01)**

Therefore, moles of HCl reacted with NaOH $= \frac{0.10}{1000} \times 15.00$ **(01)**

Therefore, moles of HCl reacted with NH_3 $= \frac{0.10}{1000} \times 30.0 - \frac{0.10}{1000} \times 15.00$ **(01)**

$= \frac{0.10}{1000} \times 15.00$ **(01)**

Therefore, moles of NH_3(g) liberated $= \frac{0.10}{1000} \times 15.00$ **(01)**

Moles of $(NH_4)_2SO_4$ in 25.00 cm^3 $= \frac{x}{132} \times \frac{1}{10}$ (01)

Moles of NH_4NO_3 in 25.00 cm^3 $= \frac{y}{80} \times \frac{1}{10}$ (01)

Moles of NH_3 given out by 25.00 cm^3 of solution (Eq. (3), (4) & (5)) =

$$\frac{x}{132} \times \frac{1}{10} \times 2 + \frac{y}{80} \times \frac{1}{10} + \frac{y}{80} \times \frac{1}{10} = \frac{0.10}{1000} \times 15.00 \quad \text{.....(7)}$$ (07)

$$\frac{x}{132} \times \frac{1}{10} \times 2 + \frac{2y}{80} \times \frac{1}{10} = \frac{0.10}{1000} \times 15.00$$

$$\frac{x}{132} \times \frac{1}{5} + \frac{y}{80} \times \frac{1}{5} = \frac{0.10}{1000} \times 15.00 \quad \text{.....(8)}$$ (01)

Eq.(6) $$\frac{x}{132} \times \frac{1}{5} + \frac{y}{80} \times \frac{1}{10} = \frac{0.10}{1000} \times 19.80 \times \frac{1}{2} \quad \text{.....(6)}$$

Eq. (8) – (6) $$\frac{y}{80} \times \frac{1}{10} = \frac{0.10}{1000} \times 15.00 - \frac{0.10}{1000} \times 9.90$$ (01)

$$y = \frac{0.10}{1000} \times 5.10 \times 800;$$

$$y = 0.408$$ (02)

Substituting $y = 0.408$ in Eq.(8) (y=0.408 can also be substituted to Eq. (6))

$$\frac{x}{132} \times \frac{1}{5} + \frac{0.408}{80} \times \frac{1}{5} = \frac{0.10}{1000} \times 15.00$$

$$\frac{x}{660} = \frac{0.10}{1000} \times 15.00 - \frac{0.408}{400} = \frac{(6.0 - 4.08)}{4000}$$

$$x = 0.317$$ (02)

% of $(NH_4)_2SO_4$ $= \frac{0.317}{1.0} \times 100$ **= 31.7%** (05)

% of NH_4NO_3 $= \frac{0.408}{1.0} \times 100$ **= 40.8%** (05)

8(b)(iv): 75 marks

Alternative Answer 1

Procedure 1

Amount of NH_3 collected = $(30.00 \times 0.10 - 10.20 \times 0.10) \times 10^{-3}$ mol **(02)**

= 1.98×10^{-3} mol **(01)**

Amount of NH_3 from 1 g of sample = $1.98 \times 10^{-3} \times 5$ **(01)**

= 9.90×10^{-3} mol **(01)**

Procedure 2

Amount of NH_3 collected = $(30.00 \times 0.10 - 15.00 \times 0.10) \times 10^{-3}$ mol **(02)**

= 1.50×10^{-3} mol **(01)**

Amount of NH_3 from 1 g of sample = $1.50 \times 10^{-3} \times 10$ mol **(01)**

= 15.0×10^{-3} mol **(01)**

Number of moles of NH_4NO_3 in 1 g of sample = x

Number of moles of $(NH_4)_2SO_4$ in 1 g of sample = y

In Procedure 1, NH_3 from NH_4NO_3 and $(NH_4)_2SO_4$ is evolved.

Therefore, $x + 2y = 9.90 \times 10^{-3}$ mol .....(1) **(07)**

In Procedure 2, NO_3^- is converted to NH_3 and evolved together with NH_3 from NH_4NO_3 and $(NH_4)_2SO_4$

Therefore, $2x + 2y = 15.0 \times 10^{-3}$ mol .....(2) **(07)**

(2) – (1) $x = (15.0 - 9.9) \times 10^{-3}$ mol

= 5.1×10^{-3} mol **(02)**

From (1) $y = \frac{1}{2}(9.9 - 5.1) \times 10^{-3}$ **(02)**

= 2.4×10^{-3} mol **(02)**

% of NH_4NO_3 in sample $= \frac{5.1 \times 10^{-3}\ mol \times 80\ g\ mol^{-1} \times 100}{1.0\ g}$ **(04 + 01** for mol. mass)

= **40.8 %** **(05)**

% of $(NH_4)_2SO_4$ in sample $= \frac{2.4 \times 10^{-3}\ mol \times 132\ g\ mol^{-1} \times 100}{1.0\ g}$ **(04 + 01)**

(04 + 01 for mol. mass)

= **31.7%** **(05)**

Alternative Answer 2

Procedure 1

Initial number of moles of HCl $= \frac{0.10}{1000} \times 30.00$ **(01)**

Number of moles of HCl remaining $= \frac{0.10}{1000} \times 10.20$ **(01)**

HCl : NaOH = 1: 1

Therefore, number of moles of HCl used $= \frac{0.10}{1000} \times 30.00 - \frac{0.10}{1000} \times 10.20$ **(02)**

$= \frac{0.10}{1000} \times 19.80 = 0.00198$ **(02)**

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

Therefore, number of moles of NH_3 evolved (from NH_4NO_3 & $(NH_4)_2SO_4$, in 50.0 cm^3 of solution)

$= 0.00198$ **(01)**

Procedure 2

Initial number of moles of HCl $= \frac{0.10}{1000} \times 30.00$ **(01)**

Number of moles of HCl remaining $= \frac{0.10}{1000} \times 15.00$ **(01)**

Therefore, number of moles of HCl used $= \frac{0.10}{1000} \times 30.0 - \frac{0.10}{1000} \times 15.00$ **(02)**

$= \frac{0.10}{1000} \times 15.00$ **(01)**

$= 0.0015$

Number of moles in 50.00 cm^3 $= 0.00150 \times 2 = 0.003$ **(01)**

Therefore, number of moles of NO_3^- in 50.00 cm^3 = 0.003 - 0.00198 = 0.00102 **(07)**

Mass of NH_4NO_3 in 250.0 cm^3 $= 0.00102 \times 80 \times 5$ g **(01)**

% of NH_4NO_3 in sample $= \frac{0.00102\ mol \times 80\ g\ mol^{-1} \times 100 \times 5}{1.0\ g}$

(04 + 01 for mol. mass)

= 40.8% Substitution **(05)**

Number of moles of NH_3 obtained from NH_4NO_3 (from 50.00 cm^3) = 0.00102

Therefore, number of moles of NH_3 obtained from $(NH_4)_2SO_4$ = 0.00198 – 0.00102 = 0.00096 **(07)**

$(NH_4)_2SO_4$: NH_3 = 1:2

Therefore, number of moles of $(NH_4)_2SO_4$ $= \frac{0.00096}{2} = 0.00048$ **(01)**

Mass of $(NH_4)_2SO_4$ in sample $= 0.00048 \times 132 \times 5$ g **(01)**

% of $(NH_4)_2SO_4$ in sample $= \frac{0.00048\ mol \times 132 g\ mol^{-1} \times 5 \times 100}{1.0\ g}$

(04 +01 for mol. mass)

= 31.7% Subs **(05)**

8(b): 75 marks

9. (a) Consider the following industrial processes.

I. Manufacture of bleaching powder
II. Manufacture of calcium carbide
III. Manufacture of urea
IV. Manufacture of sulphuric acid (contact process)

(i) State the starting materials used in each process.

I Bleaching powder – $CaCO_3$ (lime stone)/CaO (quicklime)/$Ca(OH)_2$ (slakedlime) and Cl_2 gas

II Calcium carbide – CaO (quick lime)/$CaCO_3$(lime stone), and ~~coke (C)~~

III Urea – NH_3 (l or Gas) and CO_2 (l or Gas)

IV H_2SO_4 – sulfur (s)/FeS_2(iron pyrite), air and H_2O

(02 X 9 = 18 marks)
9(a)(i): 18 marks

(ii) Write balanced chemical equations for the reactions taking place in each process, along with proper conditions wherever necessary.

I Bleaching powder

$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$ **(03)**

$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$ **(03)**

$3Ca(OH)_2(s) + 2Cl_2(g) \xrightarrow[12\text{-}15 \text{ hrs. } \textbf{(01)}]{RT \textbf{ (01)}} Ca(OCl)_2.Ca(OH)_2.CaCl_2.2H_2O\ (s)$ **(03)**

9(a)(ii)I: 11 marks

II Calcium carbide

$CaO(s) + 3C(s) \xrightarrow{\sim 2000 \pm 100^\circ C \textbf{ (02)}} CaC_2(s) + CO(g)$ **(03)**

OR

$2CaO(s) + 5C(s) \longrightarrow 2CaC_2(s) + CO_2(g)$

OR

$CaCO_3(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g) + CO_2(g)$ (only for this year)

9(a)(ii)II: 05 marks

III Urea

(for balanced equation)

$2NH_3(l/g) + CO_2(l/g) \xrightarrow[150 \text{ atm. } \textbf{(01)}]{180 - 200\ ^\circ C \textbf{ (01)}} NH_2COONH_4(s)$ **(03)** $\xrightarrow{\text{Decomposes at low pressure (01)}} CO(NH_2)_2$ (solution) $+ H_2O$ **(02)**

(for balanced equation)

Concentrate by evaporation **(01)**

$CO(NH_2)_2(s)$ **(01)**

[9(a)(ii)III: 10 marks]

IV Sulphuric acid

$S(s) + O_2(g) \longrightarrow SO_2(g)$ or $4FeS_2 + 11O_2 \longrightarrow 8SO_2 + 2Fe_2O_3$ (03)

$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5\ (01)} 2SO_3(g)$ (03)

450 °C (01), 1 atm (01) ← high T, P > 1 atm or high P.

$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$ (03)

$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$ (03)

[9(a)(ii)IV: 15 marks]

[9(a)(ii): 41 marks]

Note : Physical states not required for a(i) and (ii)

(iii) State two uses for each of the following:
bleaching powder, calcium carbide, urea and sulphuric acid

Uses

Bleaching powder

- Bleaching agent
- Disinfects water

Calcium carbide

- To induce flowering
- To ripen fruits
- Production of oxyacetylene flame
- Produces acetylene

Urea

- To manufacture nitrogen rich fertilizers
- Manufacture of urea-formaldehyde polymer

H_2SO_4

- Manufacture of phosphate fertilizer.
- Manufacture of $(NH_4)_2SO_4$
- Manufacture of rayon and plastics
- Manufacture of dyes
- Manufacture of explosives
- Manufacture of drugs
- Battery acid
- To dry gases (e.g.Cl_2 gas)
-

(02 + 02) x 4 = 16 marks

Note: For Uses - Award marks for any acceptable uses not listed in the marking scheme after getting approval from Chief Examiner.

9(a)(iii): 16 marks

9(a): 75 marks

(*b*) The major environmental problems we are facing at present are ozone layer depletion (OLD), global warming (GW) and acid rain (AR). The questions given below are related to the environment and the problems mentioned above.

(i) The carbon and nitrogen cycles are two important chemical cycles that operate in the environment.

I. With regard to the carbon cycle, state one main form of carbon that is present in each of the following:
atmosphere, plants, water, Earth's crust

II. State briefly how N_2 gas in the atmosphere is removed and replenished in the nitrogen cycle.

III. State two ways by which microorganisms participate in the carbon cycle.

I

- Atmosphere – CO_2 **(02)**
- Plants – glucose/ starch/ cellulose/ lignin **(02)**
- Water – HCO_3^- / CO_3^{2-} (CO_2(aq)) **(02)**
- Earth's crust –$CaCO_3$ / $CaCO_3.MgCO_3$/ fossil fuel (coal, petroleum) /graphite **(02)**

II Removed *via*

- Industrial fixation (Haber process)/internal combustion engine/high temperature combustion **(02)**
- Biological fixation (nitrogen fixing bacteria) **(02)**
- Atmospheric fixation (by lightning) **(02)**

Replenished *via*

- Denitrifying bacteria that converts NO_3^- to N_2 gas **(02)**

III Under aerobic conditions carbon compounds in soil are converted to CO_2 **(02)**

whereas, under anaerobic conditions they are converted to CH_4 & CO **(02)**

9(b)(i): 20 marks

(ii) Identify the two main nitrogen containing compounds present in the atmosphere that contribute to acid rain. With the aid of balanced chemical equations show how these compounds make rain water acidic.

NO, NO_2 **(02+ 02)**

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

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

OR $2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$

HNO_3 is a strong acid which gives $H^+ + NO_3^-$ **OR** ($HNO_3 \rightarrow H^+ + NO_3^-$) **(02)**

9(b)(ii): 10 marks

(iii) Identify **two** contributing industrial processes **per** environmental problem stated above (OLD, GW, AR). Identify **one** chemical compound that is liberated to the atmosphere by **each** of these industrial processes.

Ozone layer depletion

- Air-conditioning industry (CFC / HCFC / aerosol)
- Refrigerator industry (CFC / HCFC)
- Aircraft industry or supersonic jets (NO_2)
- Agrochemical industry (CH_3Br Weedicide, fumigant)
- Fire extinguisher industry using or releasing Cl_2

(Industry (02) Chemical species (01)) X 2

Global warming

- Agriculture (CH_4, N_2O)
- Air-conditioners (CFC/ HCFC)
- Refrigerator industry (CFC / HCFC)
- Poultry farming (CH_4)
- Coal power plants (CO_2)
- Nitrate fertilizers
- Agrochemical industry (CH_3Br Weedicide, fumigant)
- Halons in fire extinguishers
- Any industry producing / using chlorine gas
- Aerosol / spraying agents

(Industry (02) Chemical species (01)) X 2

Acid rain

- Burning fossil fuels in transportation (NO, NO_2)
- Burning of fossil fuel in coal power plants (SO_2)
- High temperature combustion (NO, NO_2)

(Industry (02) Chemical species (01)) X 2

9(b)(iii): 18 marks

(iv) Identify the main industrial process that contributes significantly to the addition of nitrogen compounds to water and soil. Comment on the pathways by which these compounds are added to water and soil.

Haber Process (NH_3 Production) (Agriculture process). **(04)**

NH_3 can be converted to fertilizers **(01)**

I $NH_3 \xrightarrow[\text{Ostwald Process}]{\text{converted to}} HNO_3$ **(02)** **(03)**

NH_4^+ NO_3^- can come for agriculture 1+1

HNO_3 is used to make fertilizers **(02)** such as KNO_3 **(02)**, NH_4NO_3 **(02)**, urea **(02)** which are added to soil.

Or

II Liquid NH_3 is directly used as a fertilizer. **(01)**

$NH_3 \xrightarrow{H_2O} NH_4^+ \xrightarrow[\text{bacteria}]{\text{nitrifying}} NO_2^- \xrightarrow[\text{bacteria}]{\text{nitrifying}} NO_3^-$

(01) **(02)** **(02)** **(03)** **(02)** **(03)**

9(b)(iv): 18 marks

(v) Inappropriate disposal of solid municipal waste as in the Meethotamulla event contributes significantly to one of the three environmental issues stated above. Identify this environmental issue and state briefly how the disposal of solid municipal waste contributes to it.

As a result of the unregulated disposal of solid waste, large amounts of methane **(02)** are produced (between the layers of solid waste) due to the action of bacteria **(01)** under anaerobic conditions **(02)**. This methane is a greenhouse gas **(01)** and contributes to global warming **(03)**.

9(b)(v): 09 marks

9(b): 75 marks

10. (a) (i) $TiCl_3$ is a violet coloured solid. In water, two hydrated species of $TiCl_3$, **A** and **B** are formed. **A** and **B** are coordination compounds of titanium with an octahedral geometry, containing H_2O and Cl^- as ligands.

A and **B** were separated and their atomic compositions were determined. The compounds were further analysed using the procedures given below.

Analysis of A

When excess $AgNO_3(aq)$ was added to 50.00 cm^3 of a 0.20 mol dm^{-3} solution of **A**, a white precipitate that was soluble in dilute ammonia was obtained. The mass of the precipitate after washing and oven drying (to a constant mass) was 4.305 g.

Analysis of B

When excess $AgNO_3(aq)$ was added to 50.00 cm^3 of a 0.30 mol dm^{-3} solution of **B**, the same white precipitate was obtained as in analysis, **A**. The mass of the precipitate after washing and oven drying (to a constant mass) was also 4.305 g.

(H = 1, O = 16, Cl = 35.5, Ti = 48, Ag = 108)

I. Write the electronic configuration of titanium in **A** and **B**.

II. Deduce the structures of **A** and **B**.

III. Give the IUPAC names of **A** and **B**.

(I) $1s^2 2s^2 sp^6 3s^2 3p^6 4s^0 3d^1$ OR $1s^2 2s^2 sp^6 3s^2 3p^6 3d^1$ **(02)**

OR $[Ar]\ 3d^1\ 4s^0$ **(Only for this year)**

(Note: Oxidation state of Ti in both **A** and **B** is the same.)

(II) **Structure of A**

White precipitate is AgCl (Relative mol mass = 143.5) **(02)**

Number of moles of **A** in solution = $\frac{0.20}{1000} \times 50.00 = 0.010$ **(02)**

Number of moles of AgCl in 4.305 g of precipitate = $\frac{4.305}{143.5} = 0.03$ **(02)**

Therefore, **A** contains three ionic chlorides ($3Cl^-$) **(02)**

Therefore, charge of coordination sphere/ complex ion has to be +3 **(02)**

Oxidation state of Ti ion is +3 **(02)**

Therefore, only neutral ligands could be coordinated to Ti. **(02)**

Since the complex has an octahedral geometry, six ligands (monodentate) need to be coordinated to Ti. **(02)**

(10)

Structure of **A** $[Ti(H_2O)_6]Cl_3$ **(07)**

Structure of B

Number of moles of **B** in solution = $\frac{0.30}{1000} \times 50.00 = 0.015$ **(02)**

Number of moles of AgCl in 4.305 g of precipitate = $\frac{4.305}{143.5} = 0.03$ **(02)**

Therefore, **B** contains two ionic chlorides ($2Cl^-$) **(02)**

Therefore, charge of coordination sphere/ complex ion has to be +2 **(02)**

Since oxidation state of Ti ion is +3, one Cl^- has to be coordinated to Ti in the complex. **(02)**

Since the complex has an octahedral geometry, six ligands (monodentate) need to be coordinated to Ti. **(02)**

Structure of **B** $[Ti(OH_2)_5Cl]Cl_2$ OR $[TiCl(OH_2)_5]Cl_2$ **(07)**

Note: H_2O / OH_2 are accepted.

(III) **A** – hexaaquatitanium(III) chloride **(03)**

B – pentaaquachloridotitanium(III) chloride **(03)**

10(a)(i) : 50 marks

(ii) **X**, **Y** and **Z** are coordination compounds of the metal ion **M(II)**. They have a square planar geometry. **X** is a neutral compound. On addition of $BaCl_2(aq)$ to an aqueous solution of **Y**, a white precipitate that is insoluble in dilute acids is obtained. **Z** gives three ions in aqueous solution.

Write the structural formulae of **X**, **Y** and **Z** selecting the appropriate species from the list given below.

K^+, NH_3, CN^-, SO_4^{2-}

X: $[M(CN)_2(NH_3)_2]$ OR $[M(NH_3)_2(CN)_2]$ **(08)**

Y: $[M(NH_3)_4]SO_4$ **(08)**

Z: $K_2[M(CN)_4]$ **OR** $2K^+[M(CN)_4]^{2-}$ **OR** $[M(NH_3)_4](CN)_2$

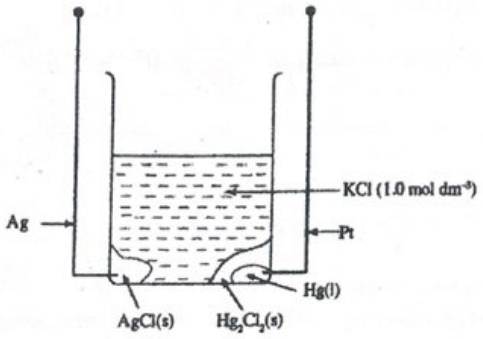
OR $[M(CN)(NH_3)_3]_2\,SO_4$ **OR** $[M(NH_3)_3\,(CN)]_2\,SO_4$

OR $K[M(CN)(NH_3)_3]\,SO_4$ **OR** $K[M(NH_3)_3\,(CN)]\,SO_4$ **(09)**

10(a)(ii) : 25 marks

10(a): 75 marks

(b)



An electrochemical cell is made as shown in the diagram above.

The following data are provided.

$Ag(s), AgCl(s) \mid Cl^-(aq)$ $\quad E^\circ = 0.22\,V$

$Hg(l) \mid Hg_2Cl_2(s) \mid Cl^-(aq)$ $\quad E^\circ = 0.27\,V$

(i) Write the reduction half reaction of the above cell.

Reduction half reaction

$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$ **(05)**

(ii) Write the oxidation half reaction of the above cell.

Oxidation half reaction

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

(iii) Construct the cell reaction.

Cell reaction

$Hg_2Cl_2(s) + 2Ag(s) \rightarrow 2AgCl(s) + 2Hg(l)$ **(10)**

(iv) Using the E^{o} values given, calculate the electromotive force of the cell.

Cell e.m.f

$E^{cell} = E^{0}_{Hg/Hg2Cl2} - E^{0}_{Ag/AgCl}$

$= 0.27V - 0.22V$ (04+01)

$= 0.05V$ (04+01)

(v) Give the standard cell notation of the above electrochemical cell.

Cell notation

$Ag(s)|AgCl(s)|Cl^{-}(aq, 1.0\ mol\ dm^{-3})||Hg_2Cl_2(s)|Hg(l)/Pt$ OR (10)

$Ag(s), AgCl(s)|Cl^{-}(aq, 1.0\ mol\ dm^{-3})||Hg_2Cl_2(s), Hg(l), Pt$

(Note: Do not deduct marks if Pt is written)

Note : For parts (i) to (v), Physical states are required

(vi) Does the electromotive force of the above electrochemical cell depend on the chloride ion concentration? Give reason/s for your answer.

The cell potential does not depend on the chloride ion concentration. Chloride ion concentration is not present in the cell reaction. (05 + 05)

no Cl^- in net reaction.

(vii) Calculate the change in the mass of Ag(s) + AgCl(s), when a current of 0.10A was drawn for a period of 60 minutes from the cell.

A current of 0.10A was drawn for 60 min.

The amount of charged passed through the cell = $0.10A \times 60\ min \times 60\ s\ min^{-1}$

$= 360\ c$ (04 + 01)

Electrode reaction in the left electrode $Ag(s) + Cl^{-}(aq) \rightarrow AgCl(s)$.

For every electron passed through the cell, one Ag atom combines with Cl^- to form AgCl(s).

Weight gain of Ag + AgCl = mass of Cl^- combined with Ag.

$= 35.5\ g\ mol^{-1}\ 360\ C/96500\ C\ mol^{-1}$ (04 + 01)

$= 0.132\ g$ (04 + 01)

(viii) What would be the chloride ion concentration in the solution after drawing the current in (vii) above?

Chloride ion concentration does not change (or) chloride ion concentration = $1.0\ mol\ dm^{-3}$.

(10)

10(b): 75 marks