Answers for MCQ

Chemistry I GCE A/L 2017

1 - 1
2 - 3 or 4
3 - 5
4 - 5
5 - 2
6 - 2or 3or 5
7 - 4
8 - 4
9 - 2
10 - 3

11 - 3
12 - 2
13 - 2
14 - 2
15 - 1 or 4
16 - 2
17 - 1
18 - 2
19 - 3
20 - 2

21 - 4
22 - 1
23 - 1
24 - 5
25 - 1
26 - 4
27 - 2
28 - 4
29 - 3
30 - 4

31 - 5
32 - 2
33 - 4
34 - 5
35 - 3
36 - 4
37 - 3
38 - 3
39 - 4
40 - 1 or 5

41 - 5
42 - 3
43 - 1
44 - 3
45 - 2 or 3
46 - 3
47 - 3
48 - 1
49 - 4
50 - all

PART A STRUCTURED ESSAY

1 (a)

Thinking process - : The charge of an atom in a Lewis structure is given by the following relation.

Charge = | No of valence electrons in the atom | - | No of electrons in lone pairs | - $\frac{1}{2}$ | No of electrons in bonding pairs around the atom

Answer - Q - $\boxed{N_A}$ - $\boxed{N_{LP}}$ - $\frac{1}{2}$ $\boxed{N_{BP}}$

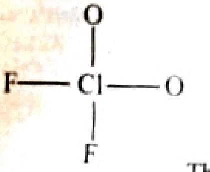
Thinking process -:

- You know that there are 6 valence electrons in the S atom. Then $N_A = 6$
- As per the given structure there is only one lone pair on the S atom. One lone pair means 2 electrons. Then $N_{LP} = 2$
- From the given structure you can understand that there are four bonds attached to S atom (3sygma and 1 π bonds).
- Each bond consists of two electrons and hence number of electrons in four bonds are $2 \times 4 = 8$.
- Then $N_{BP} = 8$

Answer = Q (sulfer) = $\boxed{6}$ - $\boxed{2}$ - ½ $\boxed{8}$

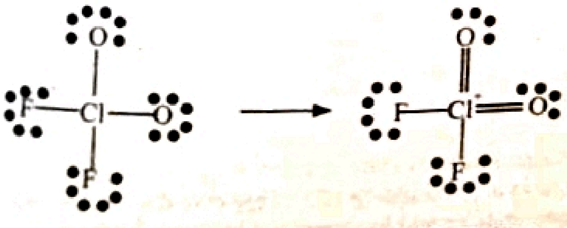
(ii) Thinking process -: [strategy for writing Lewis structure]

- First of all skeleton structure need to be drawn. Generally the atom which forms the largest number of bonds with other atoms is placed in the centre of skeleton structure.



Then add up the number of valence electrons . For neutral molecule, it is just the sum of the valence electrons of all the atoms present.

- In this case No of valance electrons = Cl (7) + F (7× 2) + O (6 × 2) = 33
- But the given structure has positive charge. Hence you have to subtract number of positive charges from number of valence electrons.
- Then the number of valence electrons = 33 – 1 = 32
- Then determine the number of bonded electrons (each bond contains two electrons). So bonded electrons = No. of bonds x 2 = 4 × 2 = 8.
- Subtract number of bonded electrons from the total sum of valence electrons In order to obtain remaining valence electrons = 32 – 8 = 24.
- Complete the octets of the atoms (initially most electro negative atoms) attached to the central atom by adding electrons in pairs. Place any remaining electrons on the central atom in pairs.
- In situation where each atom cannot be assigned an octet of electrons, form Double bonds. If necessary, form triple bonds to obtain stable Lewis structure.



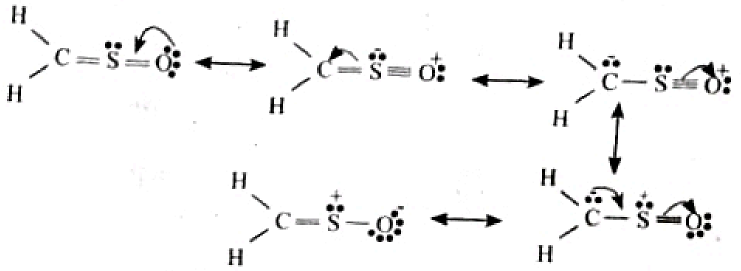
Answer = Lewis structure

(iii) Thinking process

Conditions for resonance

- The different contributing structures should have the same position of the constituent atoms, though they have different electronic arrangements.
- The number of unpaired electrons must be the same in each contributing structure.
- Sum of the lone pairs and bond pairs must be the same in each contributing structure.
- Those structures in which negative charge reside on the most electronegative atom and positive charge on the most electropositive atom.
- The contributing structures should be so written that unlike charges reside on neighbouring atoms. The contributing structures involving charge separation have little contribution to resonance hybrid.
- The compounds exhibiting resonance must be planar in nature.

Answer = Except the given Lewis structure, it is possible to draw 4 resonance structures. Although some of them are unstable, all possible structures are drawn below. You have to draw two structures out of 4.



(iv)

Answer -:

		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 shape or angular	Pyramidal
IV	hybridization	Sp	Sp^2	Sp^3	Sp^3

Thinking process

I
- VSEPR pairs of each atom is equal to sum of sigma bonds and lone pairs around the atom. Base on the given structure you can see there are only two sigma bonds around N_2 atom and hence VSEPR pairs around N_2 atom are 2.
- There are 3 sigma bonds around C_3 atom. Hence VSEPR pairs around C_3 atom are 3.
- There are 2 sigma bonds and 2 lone pairs around O_4 atom and therefore VSEPR pairs around O_4 atom are 4.
- There are 3 sigma bonds and one lone pair around N_5 atom. Hence VSEPR pairs around N_5 atom are 4.

II
- Electron pair geometry depends on the sum of sigma bonds and lone pairs around the atom. You can see from the Lewis structure N_2 has only two sygma bonds around the atom. Therefore electron pair geometry around N_2 atom is linear.
- C_3 has only three sigma bonds around the atom. Hence electron pair geometry around C_3 atom is trigonal planar.
- O_4 has 2 sygma bonds and 2 lone pairs around it while N_5 has 3 sygmabonds and one lone pair around it and hence electron pair geometry around each atom is tetrahedral.

III) • You must know that any atom surrounded by two sigma bonds, the shape around the central atom should be linear. Therefore, the shape around N_2 is linear.

- Any atom surrounded by three sigma bonds , the shape around the central atom should be trigonal planar. Hence, the shape around C_3 is trigonal planar.
- Any atom surrounded by 2 sygma bonds and one or two lone pairs, the shape around the central atom should be angular or V shape. Hence, shape Around O_4 atom is angula (or V shape).
- Any atom surrounded by three sigma bonds and one lone pair, the shape around the central atom should be pyramidal. Hence, shape around N_5 atom is pyramidal.

  Remember π bonds do not consider when determining the shape of molecule or ion.

IV) Hybridization of a given molecule could easily be determined by considerin the total number of repulsive units (VSEPR pairs) around the each atom.

N_2 has two repulsive pairs (2 sygma bond pairs). Hence hybridization = sp

C_3 has three repulsive pairs (3sygma bond pairs). Hence hybridization = sp^2

O_4 has four repulsive pairs (2sygma bond pairs and 2 lone pairs). Hence the Hybridization of O = sp^3.

N^5 also has four repulsive pairs (3 sygma bond pairs and one lone pais). Hence hybridization of N5 = sp^3 .

(v) Answer-:

I.

N^2 — C^3 N^2 __SP_ C^3 __SP^2
I I
O^4 — N^5 O^4 __SP^3 N^5 __SP^3
I I I
N^5 — H^6 N^5 __SP^3 H^6 __S_

IV. C^3 — O^7 C^3 __SP^2 O^7____SP^2 or 2P

(b) (i) Thinking process

- The value of 'l' depends on the value 'n' . For a given value of n, l can have values from zero to (n – 1) where n is the principal quantum number.
- Now, for n = 3, the values of l = 0,1 and 2
- You must know that
  l = 0 known as 's' sub-shell
  l= 1, known as 'p' sub-shell
  l=2, known as 'd' sub-shell
  l=3, known as 'f' sub-shell.
- Each sub-shell is composed of orbitals. Each orbital is designated by a
- Different value of m.
- The values of m range from –l to zero to +l and maximum values of m= 2l + 1.

for example-: when l = 0 (s sub-shell), m = 0
when l = 1 (p sub-shell), m = -1, 0, +1
when l = 2 (d sub-shell) m = -2, -1, 0, +1, +2

- The maximum number of electrons in an orbital is two. Now 's' sub-shell has only one orbital and hence it can occupied two electrons
  'p' sub-shell has three orbitals and hence it can occupied 6 (3x2) electrons.
  'd' sub-shell has five orbitals and hence it can occupied 10 (5x 2) electrons.

Now the answer-:

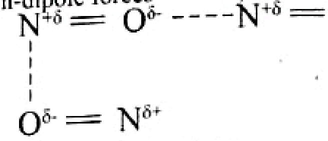
Sub- shell	Azimuthal quantum number (l)	Magnetic quantum number (ml)	Maximum number of electrons in each sub- shell
3s or s	0	0	2
3p or p	1	-1, 0, +1	6
3d or d	2	-1, 0, +1-1, 0, +1	10

(ii) I Answer -: Ar is a non-polar molecule. Hence intermolecular forces among molecules are solely London dispersionforces.

II Answer-: There is a electronegative difference between N and O. Hence NO molecule is polar compound. As a result intermolecular forces among NO molecules are mainly dipole-dipole and in addition to that London dispersion forces also present among NO molecules.

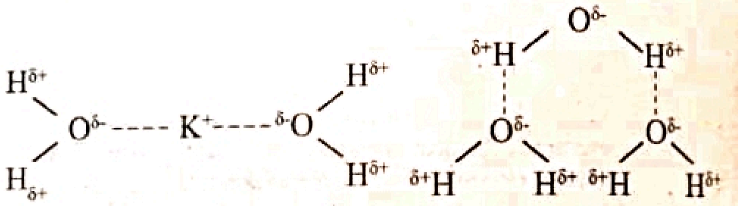
III Answer -: Cl- ions, K+ ions and polar water molecules are present in this solution. Hence there are two types of intermolecular forces exist in this solution. They are

a) Ion-dipole forces b) Hydrogen bonding



dipole -dipole forces

Hydrogen bond may be defined, as the electrostatic force attraction between hydrogen atom of one molecule and a highly electronegative element (such as N.O. or F) present within the same molecule or another molecule of the same or different compounds. Water is a polar molecule and therefore it can form hydrogen bonds between O atom of one molecule and H atom of another water molecule according to the following way



Ion - dipole forces Hydrogen bond

Note-: In your answer no need to give reason.

(iii) Answer-: Statement is true.

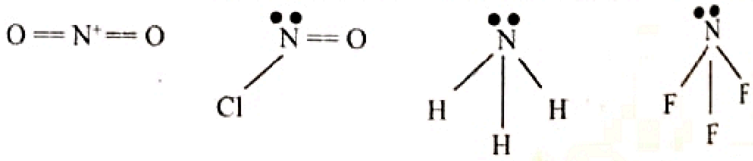
Reason -: n-butane and propane are non-polar molecules. Hence forces acting are London dispersion forces Since n-butane is greater in size than propane, London dispersion forces between n-butane molecules are greater than in propane molecules. Hence, boiling point of $C_4H_{10} > C_3H_8$

(iv) I Answer -: $K_2CO_3 > Na_2CO_3 > Li_2CO_3$.
(No need to give reason. However reason for this has given In MCQ number 44)

II Answer -: $NO_2^+ > NOCl > NH_3 > NF_3$.

Thinking process

The structures of given species are as follows.



- In NO_2^+ ion . N atom is sp hybridized. As a result ONO bond angle is 180^0 .
- In NOCl molecule, N atom is sp2hybride. Hence the Cl-N-O bond angle is approximately 120^0 . However due to lone pair on the N atom angle should be somewhat less than 120^0 .

N atom of both NH_3 and NF_3 is sp^3 hybridized. Hence Bond angles HNH and FNF are approximately 109^0 However bond angle of F-N-F is less than that of H-N-H (this has explain in MCQ number 36).

III Answer -: $CO_2 > HCN > COC_{l2} > CH_3Cl$

Thinking process

- Electronegativity is depends on the charge on the atom, oxidation state and the s character of the hybridized atom.
- Higher the positive charge , greater the electronegativity than neutral. Formal charge on the C atom in all the given compounds is zero. Hence we cannot decide the relative electronegativity of each C atom.
- We know that higher the oxidation state, greater the electronegativity.
- Oxidation state of C in given compounds except CH_3Cl is +4. But the oxidation state of the C in CH_3Cl is -2 and therefore it has lowest oxidation state. As a result C in CH_3Cl has least electronegativity.
- Other factor is that higher the s character of hybridization, higher the electronegativity. It is obvious that the s character of sp (50%) hybridization Is greater than that of sp2 (33%) which in turn greater than sp3 (25%).
- **Hybridization of each carbon atom in given compounds are as follows**

  CO_2 = sp, HCN = sp, $COCl_2 = sp^2$, $CH_3Cl = sp^3$

According to the explanation given above, C atom in CH_3Cl has least electronegativity. Although hybridizations of C in both compound CO_2 and HCN are identical, in CO_2 carbon has bonded with more electronegative Oxygen atom which withdraws the shared pair of electrons more towards It self. Hence, carbon atom in CO2 acquires some partial positive charge. On the other hand N is less electronegative than O and therefore intensity of Positive charge on the C atom in CO2 is greater than that of C in HCN. Hence, C in CO_2 has highest electronegative.

2]

(a) (i) **You must know that Br2 is the only non-metallic element which exist as a coloured liquid at room temperature. Hence, Y should be Br2 . If X,Y and Z are same group and they are in three successive periods respectively then X should be Cl2 and Z should be = I2 .**

Answer -: X = Cl , Y = Br , Z = I

(ii) I Thinking process

- As we move down a group in the periodic table, the atomic radii go on increasing. Down a group, the nuclear charge goes on increasing. The electrons get added in the new shells which screen the nucleus. The screening effect due to the addition of new shells goes on increasing. Thus, the attraction of the nucleus for the outer most electrons goes on decreasing. As a result, the atomic radii increase down the group.

Answer – : Atomic size - I > Br >Cl

II Thinking process

- Smaller the size of the atom, stronger is the attraction of its nucleus for the electron to be added.Thus, smaller the size of an atom , greater is the electron affinity.
- Greater the magnitude of nuclear charge of an element, stronger is the attraction of its nucleus for the electron to be added. So, greater will be the electron affinity.
- Down a group , there is simultaneous increase in atomic size and nuclear charge. However, the effect of increase in size is greater than the increase in nuclear charge. As a result , the incoming electron feels lesser attraction by the larger atom and hence the **electron affinity decreases.**

Answer -: electron affinity - Cl> Br > I

III Thinking process

- With the increase in nuclear charge, the force of attraction between the nucleus and valence electrons increases. Consequently, more energy is required to remove a valence electron. Hence, first ionization energy Increases with increase in nuclear charge.
- With increase in atomic size, the distance between the nucleus and the valence electrons increases. Thus, the force of attraction between the nucleus and the valence electrons decreases. Hence, energy required to remove a valence electron (or first I.E) decreases with increase in atomic size.
- The shells between the nucleus and the valence electrons reduce the force of attraction between nucleus and valence electrons. The reduction in force of attraction by the shell present in between the nucleus and valence electrons is called screening effect. Greater the number of shells in-between the nucleus and valence electrons , lesser will be the electron- nucleus attraction and lesser will be the ionization energy.
- As we move down the group, the nuclear charge goes on increasing. The electrons are added in the new shells. These shells screen the nucleus appreciably. The force of attraction between nucleus and outermost electron goes on decreasing. As a result , the first I.E. goes on decreasing.

Answer -: First ionization energy -: Cl> Br > I

(iii) Thinking process

- You must know that if you add AgNO3 solution into X,Y and Z solutions separately, X gives AgCl white precipitate while Y gives AgBr pale yellow precipitate and Z gives AgI dark yellow precipitate with $AgNO_3$.

Answer -: Reagent -:	$AgNO_3$ solution	
Observation :	X	: White precipitate
(for the anions)	Y	: Pale yellow precipitate
	Z	: Dark yellow precipitate.

Alternative answer-:

Reagent -:	Cl_2 and CCl_4 .	
Observation -:	X:	Colourless organic layer
(for the anions)	Y :	Red-orange organic layer
	Z :	Violet organic layer.

(iv) Answer -:

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

OR

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

OR

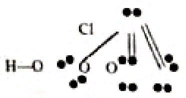
$3Cl_2(g) + 8NH_3(g) \longrightarrow N_2(g) + 6NH_4Cl(g)$

II $Cl_2(g) + 2NaOH(aq) \longrightarrow NOCl(aq) + NaCl(aq) + H_2O(l)$ = (v)

Answer -: You can draw any two of the following structures

(1)

(2)



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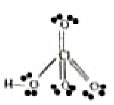
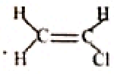


(4)

(vi) Answer – : Sea water / KCl (sylvine) / KCl $MgCl_2$ (Carnallite)

(vii) Answer -: I.  II. Polyvinyl chloride .

(b) (i) *Thinking process*

- **If colourless gas was evolved with HCl, then the gas may be CO_2,SO_2 or H_2S.**

Hence, anion containing in the solution Q may be CO_3^{2-} , SO_3^{2-} , $S_2O_3^{2-}$ or S2-.

- However the solution obtained by test I is clear and hence $S_2O_3^{2-}$ ions cannot be contained in the solution Q. Because it does not give clear solution with HCl due to precipitation of S.
- If the gas is H_2S, it gives black PbS precipitate with lead acetate.

$(CH_3COO)_2pb + H_2S \longrightarrow Pbs \underset{Black}{\downarrow} + 2CH_3COOH$

However evolved gas did not change the colour of filter paper moistened with lead acetate. Hence, the evolved gas cannot be H_2S and as a result S_2- ions cannot be contained in the Q solution.

- If the solution Q gives white precipitate with $BaCl_2$, the precipitate may be $BaSO_4$, $BaCO_3$, $BaSO_3$ or BaF_2
- However, BaSO4 and BaF2 do not dissolve in HCl and therefore the white precipitate should be either $BaCO_3$ or $BaSO_3$.
- $BaCO_3$ gives CO_2 gas with dilute HCl while BaSO3 gives SO_2 gas. However CO_2
  Does not reduce orange potassium dichromate into green chromium ions but SO_2 does. Therefore one of the anions in the solution Q should be SO_3^{2-}.
- If the solution Q does not give yellow precipitate with Conc HNO_3 and ammonium molybdate, PO_4^{3-} ions do not present in the solution.
- The gas NH_3 will turn the Nessler's reagent into brown colour and therefore the gas evolved in test (4) should be NH_3.
- Both NO_3^- and NO_2^- anions give NH_3 gas with Devarda's alloy (mixture of Al,Zn and Cu) in the presence of NaOH solution.
- However anion cannot be NO_2^- because if the said ion is present in the solution Q, it should give coloured gas (NO_2) with HCl in the test (1). Hence it is clear that one of the anions in the solution Q is NO_3^-.
- You must know that thaocianate (SCN-) ion gives blood red colour solution with $FeCl_3$.

$Fe^{+3} + SCN^- \; Fe(SCN)^{2+} \longrightarrow$ (blood red)

Answer -: SO_3^{2-}, NO_3^- and SCN- anions.

(ii) Answer-; $3SO_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$

3] (a) (i) Answer -: $Kb = \dfrac{[CH_3NH_3^+(aq)]\,[OH^-(aq)]}{[CH_3NH_2(aq)]}$

(ii) Descriptive answer

- It is given that the PH value of aqueous solution of methylamine is 11. You must know that, at 25C°, PH + POH = 14
  Hence POH of methylamine solution = 3
- Now POH = 3 = log $[OH^-]$, therefore $[OH^-] = 10^{-3}$ moldm^{-3}.
- According to the equation given below $[OH] = [CH_3NH_3^+] = 10^{-3}$ moldm^{-3}.

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

Initial concentration 0.2 moldm-3 0 0

Concentrations at equilibrium $0.2 - 10^{-3}$ 10^{-3} 10^{-3}

Hience, $K_b = \dfrac{10^{-3}\,moldm^{-3} \times 10^{-3}\,moldm^{-3}}{(0.2 - 10^{-3})moldm^{-3}}$

However, compared to the initial concentration of methylamine, 10-3 can be neglected. Hence, at the equilibrium
$[CH_3NH_2] = 0.2 - 10^{-3} = 0.2$ moldm^{-3}

Then $Kb = \dfrac{10^{-3}\,moldm^{-3} \times 10^{-3}\,moldm^{-3}}{(0.2)moldm^{-3}} = 5.0 \times 10^{-6}moldm^{-3}$.

(iii) Descriptive answer
Reaction of CH_3NH_2 with HCl is as follows
$CH_3NH_2(aq) + HCl(aq) \rightleftharpoons CH_3NH_3Cl(aq)$

- From the equation, you can see that molar ratio of
  $CH_3NH_2 : HCl : CH_3NH_3Cl = 1:1:1$
- According to the given data that the concentration of both CH_3NH_2 and HCl Is 0.2 moldm^{-3}.
- Therefore, at the equivalent point 25 cm^3 of CH_3NH_2 should be reacted completely with the same volume (25 cm^3) of HCl solution.

No. of moles HCl reacted $= \dfrac{0.2 \times 25 \text{ mol}}{103}$

No. of moles of CH_3NH_3Cl formed also should be $= 0.2 \times 25 / 10^3$mol

- CH_3NH_3Cl is completely ionized according to the following way
  $CH_3NH_3Cl \longrightarrow CH_3NH_3^+ + Cl^-$

Hence, the No. of moles of CH3NH3+ ion in the solution also should be $= 0.2 \times 25 / 10^3$mol
Now the total volume of the final solution is 50 cm^3
Hence, the concentration of $CH_3NH_3^+$
$= \dfrac{0.2 \times 25 \times 10^3}{10^3 \times 50} = 0.1$ moldm^{-3}.

$CH_3NH_3^+$ ion is partially ionized according to the following way and PH value at the equivalence point is determined by this reaction.

$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$

Initial concentration 0.2 0 0
Conc at the equilibrium $0.1 - x$ x x

Kaof the above reaction $= \dfrac{[CH_3NH_2(aq)]\,[H_3O^+(aq)]}{[CH_3NH_3^+(aq)]}$

Now $K_a \times K_b$

$\dfrac{[CH_3NH_2(aq)]\,[H_3O^+(aq)]}{[CH_3NH_3^+(aq)]} \qquad \dfrac{[CH_3NH_2(aq)]\,[H^+(aq)]}{[CH_3NH_2(aq)]}$

Therefore, $K_aK_b = [H_3O^+(aq)]\,[OH^-(aq)] = K_w = 10^{-14}$

Hence $K_a = K_w / K_b = 10^{-14}\,mol^2dm^{-6} / 5\times 10^{-6}moldm^{-3}$
$= 2 \times 10^{-9}$ moldm^{-3}

Now, as per the above equilibrium
$K_a = 2 \times 10^{-9} = \dfrac{x^2}{0.10 - x}$ = approximately $\dfrac{x^2}{0.10}$
Hence, $x^2 = 2 \times 10^{-10}$, then $x = 1.41 \times 10^{-5}$ moldm^{-3}

Now, PH value = log $[H_3O^+]$ = log x = log 1.41 × 10-5 = 4.85.

(b) (i) Answer -: There are three equilibria existing in the given solution.

$HX(aq) \longrightarrow H^+(aq) + X^-(aq)$

$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

(ii) Answer-:
Suppose Vdm^3 volume of 1.0moldm-3 $HNO_3$is added to the precipitate
MX. Then the reaction between HNO_3 and MX can be represented as
$MX(s) + HNO_3(aq) \longrightarrow M^+(aq) + NO_3^-(aq) + HX(aq)$

- No. of moles of HNO_3 reacted with MX = 1.0 moldm-3 x V dm^3 = V mol
- As per the above equation molar ratio of $HNO_3 : M^+ = 1 : 1$

Hence, No. of moles of M+ formed in the final solution = Vmol
Volume of the final solution = V dm^3.
Therefore, $[M^+]$ in the final solution = V mol × 1dm^3
= 1moldm^{-3} Vdm^3.

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

$$\text{Therefore}\quad [X^-(aq)] = \frac{3.6 \times 10\text{-}7\ mol^2\ dm^{-6}}{1.0\ moldm^{-3}} = 3.6 \times 10^{-7}\ moldm^{-3}\ .$$

(iii) Answer -:

- In an aqueous solution $[X^-(aq)]$ is determined only by K_{sp}
- The saturated aqueous solution of MX, the following equilibrium is established

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

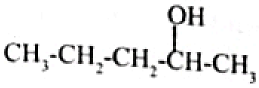
Now $KSP(MX) = [M^+(aq)][X^-(aq)] = 3.6 \times 10^{-7}\ mol^2dm^{-6}$.
From the above equation you can see that $[M \times (aq)] = [X^-(aq)]$
Hence $[X^-(aq)]^2 = 3.6 \times 10^{-7}\ mol^2\ dm^{-6}$.
Then $[X^-(aq)] = 6 \times 10^{-4} moldm^{-3}$.
Therefore, the value is higher than that in (ii).

4] (a) (i) Thinking process

- First of all we will draw all the possible structures of alcohol

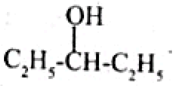
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$

(1)



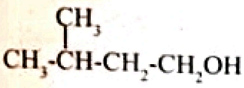
$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{OH}{C}H\text{-}CH_3$

(2)



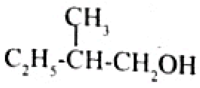
$C_2H_5\text{-}\overset{OH}{C}H\text{-}C_2H_5$

(3)



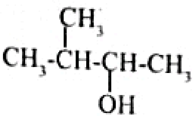
$CH_3\text{-}\overset{CH_3}{C}H\text{-}CH_2\text{-}CH_2OH$

(4)



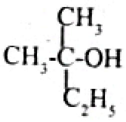
$C_2H_5\text{-}\overset{CH_3}{C}H\text{-}CH_2OH$

(5)



$CH_3\text{-}\overset{CH_3}{C}H\text{-}\underset{OH}{C}H\text{-}CH_3$

(6)

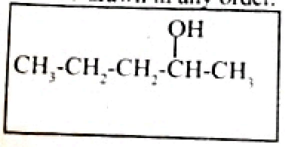


$CH_3\text{-}\overset{CH_3}{\underset{C_2H_5}{C}}\text{-}OH$

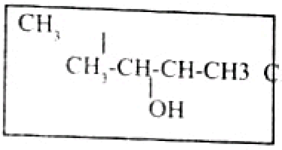
(7)

- To show optical isomerism , there should be asymmetric carbon atom in the molecule. You can see that structure 2,5 and 6 would show optical isomerism because those structures contain an asymmetric corbon atoms.
- Hence, structures 2,5 and 6 are the possible structures for A,B and C. But still we do not know which is which and therefore structures can be drawn in any order.

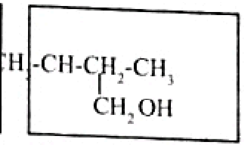
Answer-:



$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{OH}{C}H\text{-}CH_3$



$\overset{CH_3}{} \ CH_3\text{-}CH\text{-}\underset{OH}{C}H\text{-}CH3$

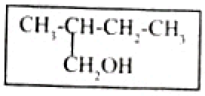


$CH_3\text{-}CH\text{-}\underset{CH_2OH}{C}H_2\text{-}CH_3$

(ii)Thinking process

- Primary alcohols are oxidized to aldehydes, which are, in turn, easily Oxidized to carboxylic acids by acidified $K_2Cr_2O_7$. But carboxylic acids Cannot be reduced back to alcohol by using $NaBH_4$.
- Secondary alcohols are oxidized only to ketones which can be converted back to alcohol by reacting with NaBH4 .
- Tertiary alcohols do not undergo oxidation with acidified K_2Cr_2O7 .
- Hence, B,C and D should be secondary alcohols.
- Out of structures A,B and C , two are secondary alcohols and therefore those twoshould be B and C. But still we do not know which is which. However remaining structure is a primery alcohol and it should be alcohol A.

Answer -:

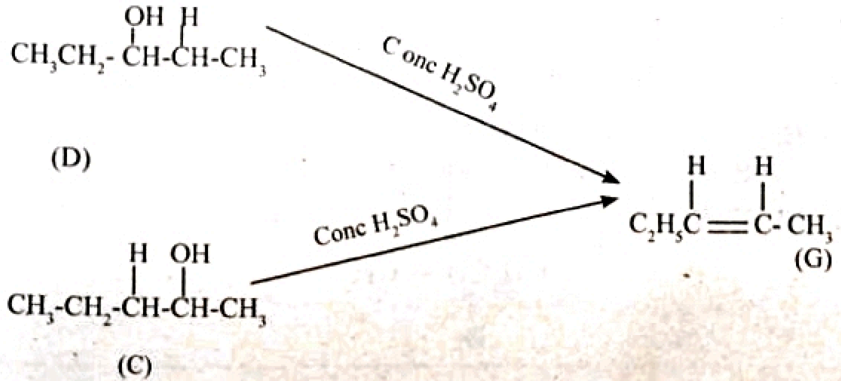


$CH_3\text{-}\underset{CH_2OH}{C}H\text{-}CH_2\text{-}CH_3$

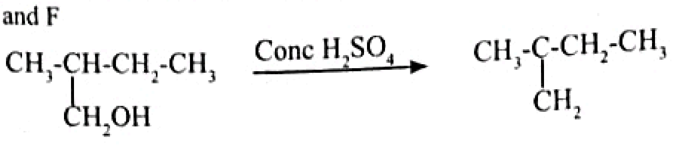
[A]

(iii)

- Apart from B and C the other secondary alcohol is structure (3) and hence, D should be structure (3).
- On heating with Conc: H_2SO_4, if both C and D gave same produc G then C Should be structure (2).

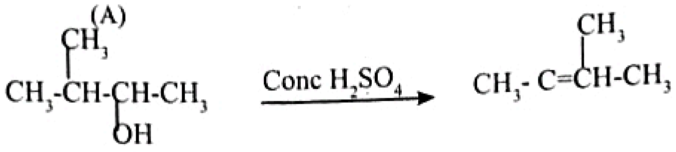


- Then, B should be structure No. (6). Now we have already been identified structures A, B, C and D.
- Now will see what are E and F



$$CH_3\text{-}\underset{CH_2OH}{\underset{|}{C}H}\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{Conc } H_2SO_4} CH_3\text{-}\underset{CH_2}{\underset{|}{C}}\text{-}CH_2\text{-}CH_3 \quad \text{(E)}$$

(A)

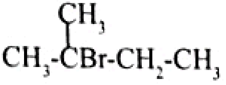


$$CH_3\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}\underset{OH}{\underset{|}{C}H}\text{-}CH_3 \xrightarrow{\text{Conc } H_2SO_4} CH_3\text{-}\ C{=}\overset{CH_3}{\overset{|}{C}H}\text{-}CH_3 \quad \text{(F)}$$

(B)

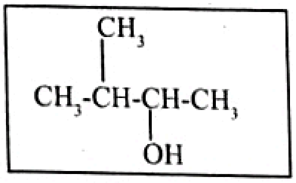
H

- You will realize the both E and F give the following bromide when reacts with HBr.



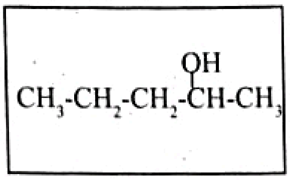
$$CH_3\text{-}\overset{CH_3}{\overset{|}{C}}Br\text{-}CH_2\text{-}CH_3$$

Answer -:



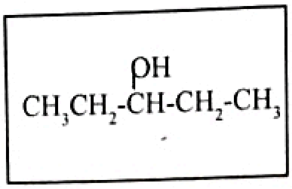
$$CH_3\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}\underset{OH}{\underset{|}{C}H}\text{-}CH_3$$

(B)



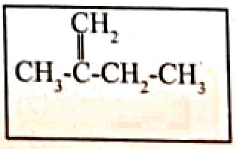
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_3$$

(C)



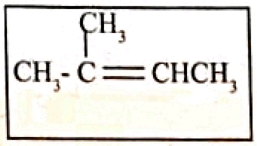
$$CH_3CH_2\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_2\text{-}CH_3$$

(D)



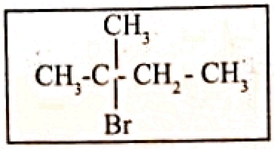
$$CH_3\text{-}\overset{CH_2}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_3$$

(E)



$$CH_3\text{-}\ \overset{CH_3}{\overset{|}{C}}{=}CHCH_3$$

(F)



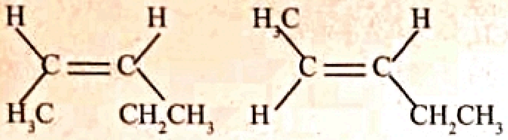
$$CH_3\text{-}\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{-}\ CH_2\text{-}\ CH_3$$

(G)

(iv)

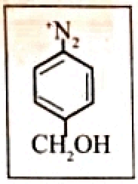
- G shows geometrical isomerism and you must know that geometrical isomers are diastereoisomers.

Answer -:

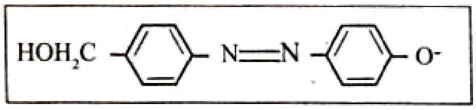


(b)

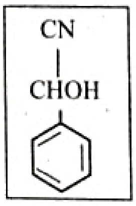
(i) Answer-:



(J)



(K)

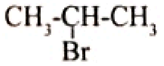


(L)

(ii) Answer -: V = NaOH or OH- , W = PCC

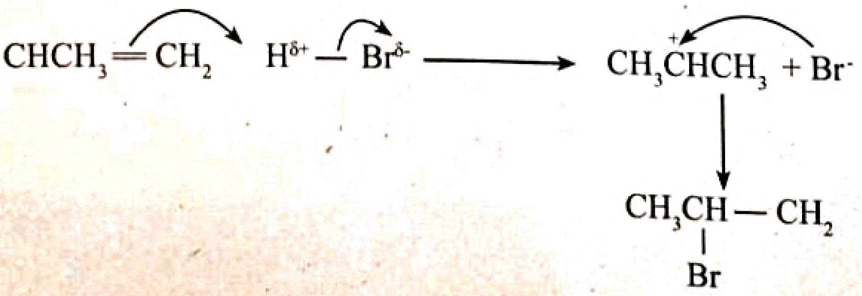
(iii) Answer -: Reaction 1 $\boxed{S_E}$, Reaction 2 $\boxed{S_N}$, Reaction 3 $\boxed{A_N}$

(c) (i) Answer-:



$$CH_3\text{-}\underset{Br}{\underset{|}{C}H}\text{-}CH_3$$

(ii) Answer -:



$$CHCH_3{=}CH_2 \quad H^{\delta+}\text{—}Br^{\delta-} \longrightarrow CH_3\overset{+}{C}HCH_3 + Br^- \;\Big\downarrow\; CH_3\underset{Br}{\underset{|}{C}H}\text{—}CH_2$$

Part B - Essay

(a) Answer-

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

System has CO_2 (g) and H_2O (g) as gaseous state. Suppose that total ber of moles and the total pressure in the system are n and P respecly. Assuming ideal behavior of gases, according to ideal gas equation

PV = nRT

Then $n = PV/RT = \dfrac{1.0 \times 10^6\ Pa \times 5.00 \times 10^{-3}\ m^3}{8.314\ JK^{-1}\ mol^{-1} \times 601K}$

is given that RT = 5000 Jmol-1 at 328K

Therefore $= \dfrac{1.0 \times 10^6\ Pa \times 5.00 \times 10^{-3}\ m^3}{5000\ Jmol^{-1}} = 1.0\ mol$

Now you can see that $n = n_{CO_2} + n_{H_2O}$

According to stoichiometry of the above equation $n_{CO_2} = n_{H_2O}$

Then, $n = 2n_{H_2O} = 1$, hence, $n_{H_2O} = 0.5\ mol$

) Answer -:

- Partial pressures of solid $NaHCO_3$ and Na_2CO_3 are constant and therefore their partial pressures are not appeared in the K_p equation.
- Suppose partial pressures of H_2O and CO_2 are P_{H_2O} and P_{CO_2} respectively.
- Then $K_p = P_{H_2O} \times P_{CO_2}$
- In the system total pressure $= P_{CO_2} + P_{H_2O} = 1.0 \times 10^6\ Pa$
- You must know that, at the constant temperature, pressure of the system directly proportional to number of moles of gaseous species
- Then $P \propto n$
- Number of moles of CO_2 and H_2O (g) in the system are equal each other

  Hence $P_{H_2O} = P_{CO_2} = 1.0 \times 10^6/2 = 5.0 \times 10^5\ Pa$
- Hence $K_p = (P_{CO_2})^2 = (5 \times 10^5)^2 = 2.5 \times 10^{11}\ Pa^2$.

  Now you must know that $K_p = K_c\,(RT)^n$

  n = No, of moles of gaseous products - No. moles of gaseous reacants = 2 -0 = 2

refore,

$$\frac{K_p}{(RT)^2} = \frac{2.5 \times 10^{11}\ Pa^2}{(8.314\ JK^{-1}\ mol^{-1} \times 601K)^2} = \frac{2.5 \times 10^{11}\ Pa^2}{(5000\ Jmol\text{-}1)^2}$$

$K_c = 1.0 \times 10^4\ mol^2\ m^{-6}$ or $(1.0 \times 10^{-2}\ mol^2\ dm^{-6})$

) Answer-:

- Suppose now patial pressure of H_2O (g) after adding extra amount of CO_2 = y Pa
- Then the partial pressure of CO_2 at the equilibrium = 4y Pa
- Now, $K_p = P_{H_2O(g)} \times P_{CO_2(g)} = y \times 4y = 4y^2$.

As the temperature is constant ,

$K_p = 2.5 \times 10^{11}\ Pa^2 = 4y^2$

Hence, $y^2 = \dfrac{2.5 \times 10^{11}\ Pa^2}{4} = \dfrac{25 \times 10^{10}\ Pa^2}{4}$.

Then $y = \dfrac{5 \times 10^5\ Pa}{2} = 2.5 \times 10^5\ Pa$

There fore $P_{H_2O(g)} = 2.5 \times 10^5\ Pa$.

$P_{CO_2(g)} = 4y = 4 \times 2.5 \times 10^5 = 1.0 \times 10^6\ Pa$.

(b) (i) Answer-:

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

The amount of heat absorbed during the reaction = mcΔt

$= 100g \times 4.0Jg^{-1}K^{-1} \times 5K = 2000J = 2Kj$

2kJ of hear absorbed when 0.08 moles of $NaHCO_3$ reacts with HCl

Hence heat absorbed per mole of $NaHCO_3$ = 2 Kj / 0.08 mol = 25

This reaction has taken place at the constant pressure

Hence, heat absorbed = enthalpy change $\Delta H = +25\ kJ\ mol^{-1}$.

Step II -: for the reaction with 0.04 moles of Na_2CO_3 (s)

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

Suppose heat energy evolved = Q = mcΔ t

$Q = 100g \times 4\ Jg^{-1}K^{-1} \times 3.5\ K = 1400\ J = 1.4\ kJ$

Hence, heat energy evolved for one mole $= \dfrac{1.4\ kJ}{0.04\ mol} = 35kJmol^{-1}$.

Now $Q = \Delta H = -35\ kJmol$

(ii) Answer-:

The reaction,

$2NsHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$ can be written with the help of following thermochemical cycle.

$$\begin{tikzcd}
2HCl(aq) + 2NaHCO_3(s) \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & Na_2CO_3(s) + CO_2(g) + H_2O(l) \arrow[dl, "\Delta H_3"] \\
& 2NaCl(aq) + CO_2(g) + H_2O(l) &
\end{tikzcd}$$

According to Hess's law, $\Delta H_1 + \Delta H_3 = \Delta H_2$

Hence, $\Delta H_1 = \Delta H_2 - \Delta H_3$

$H_1 = 25 \times 2 - (-35) = +85\ kJmol$

(iii) Answer -: At constant pressure

(iv) Answer -:
- A beaker is used instead of calorimeter. Hence, heat loss to environment is greater.
- Dissolution enthalpies of solids are different.

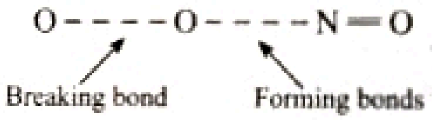
6] (a) (i) Answer -: Increase in concentration causes an increase in the number of molecules in unite volume and therefore increases the collision rate [number of collisions in unit time].

(ii) Answer-:
- The collision rate

  and
- The fraction of reacting molecules having energy greater than the activation energy increase with increasing temperature.

(iii) Answer -: Molecularity of an elementary reaction = order of reaction

(iv) Answer - :



(v) Answer -: • Suppose the reaction rate is R

Then, $R = k [A]^x [B]^y$.

or

You can write down rate as $-\frac{d[A]}{dt} = k [A]^x [B]^y$.

{Instead of d [A] and dt you can write down those as [A] and t Respectively}

(b) (i) Answer-:

Experiment (I)

No. of moles of A in 100 cm^3 of aqueous solution = 1.00×10^{-2} m

Initial concentration of A in the aqeous solution = $\frac{1.00 \times 10^{-2}}{100} \times 1000$

$= 0.1\ moldm^{-3}$.

Experiment (II)

Now there are two layers and therefore certain amount of A in the aqueous layer is extracted into the organic layer.

Suppose the amount of A in the aqueous layer is y mol

Then amount of A in the organic layer = $(1.25 \times 10^{-1} - y)$ mol

Now [A] in the aqueous layer = $\frac{y \times 10^3\ moldm^{-3}}{100}$

Likewise [A] in the organic layer = $moldm^{-3}$.

Now $K_D = \frac{[A(org)]}{[A(aq)]} = \frac{(1.25 \times 10^{-1} - y)\, 10^3 / 100}{y \times 10^3 / 100} = 4$

Therefore, $1.25 \times 10^{-1} - y = 4y$, then $y = 2.5 \times 10^{-2}$ mol

Hence, [A] in the aqueous layer

$= \frac{(1.25 \times 10^{-1} - y)}{100} \times 10^3 = 2.5 \times 10^{-1}\ moldm^{-3}$

Experiment (III)

Let p mol be the amount of A in the aqueous layer, then

[A] in the aqueous layer = $\frac{p \times 1000}{50}$ = $20p\ moldm^{-3}$.

Now No. of moles of A in the organic layer = $(6.25 \times 10^{-2} - p)$ mol

Hence, [A] in the organic layer = $\frac{(6.25 \times 10^{-2} - p)\, 1000}{50}\ moldm^{-3}$

$= (6.25 \times 10^{-2} - p)\, 20\ moldm^{-3}$.

According to Nernst's law $\frac{(6.25 \times 10^{-2} - p)\, 20}{20p} = 4$

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

Therefore, p $= 1.25 \times 10^{-2}$ mol

Hence, [A] in the aqueous layer

$= \frac{1.25 \times 10^{-2} \times 10^3}{50} = 2.5 \times 10^{-1}\ moldm^{-3}$

(ii) Answer -: In experiments (I) and (II), the concentration of B in the aqueous laye is the same.

[B] in the aqueous layer in experiments (I) and (II) = $\frac{1.00 \times 10^{-2} \times 10^3}{100}$

" " = $0.1\ moldm^{-3}$

Now Rate = $k[A]^x[B]^y$.

From experiment (I)

$1.2 \times 10^{-5}\ moldm^{-3} s^{-1} = k\,[0.1 moldm^{-3}]^x\,[0.1 moldm^{-3}]^y$ ------(1)

From experiment (II)

$7.5 \times 10^{-5}\ moldm^{-3} s^{-1} = k\,[0.25 moldm\text{-}3]^x\,[0.1 moldm\text{-}3]^y$ ------(2)

From experiment (III)

$1.5 \times 10^{-3}\ moldm^{-3} s^{-1} = k\,[0.25\ moldm^{-3}]^x\,[0.2\ moldm^{-3}]^y$ ----(3)

Now, (2)/(1) $= \frac{7.5 \times 10^{-5}}{1.2 \times 10^{-5}} = \left(\frac{0.25}{0.1}\right)^x$

$6.25 = (2.5/1)^x$

$2.5^2 = 2.5^x$. therefore , x = 2

(iii) Answer-: You can see that in experiments II and III, the concentration of A in the aqueous layer is the same.

(3)/ (2) $\frac{1.5 \times 10^{-3}}{7.5 \times 10^{-5}} = (0.2/0.1)^y$

20/1 = (2/1)y, hence, log20 = ylog2

1.3010 = y × 0.3010

Then y = 4.32 = 4

(iv) Answer -: Using data in experiment I [however you can use data in any experiment]

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

[If you want 4.32 can be used instead of 4]

$k = \frac{1.20 \times 10^{-5}\ moldm^{-3} s^{-1}}{(1.00 \times 10^{-1}\ moldm^{-3})^2\,(1.00 \times 10^{-1}\ moldm^{-3})^4}$

Therefore $k = 1.2 \times 10\ mol^{-5} dm^{15} s^{-1}$.

(v) Answer -: The rate of the reaction depends on the concentration of A in the aqueous layer. Even if you removed 10 cm^3 volume from the organic layer, the concentration of A in the aqueous layer does not change. Consequently the initial rate of the reaction will not change.

(c) Answer-: For the first condition suppose molar fractions of X and Y in the liquid Phase is X_x and Y_y respectively.

Then $X_x = \frac{1.2mol}{(1.2 + 2.8)mol} = 0.3$

Therefore, $Y_y = 1 - 0.3 = 0.7$

Suppose the partial pressures of X and Y in t Phe vapour phase are P_X and PY respectively and the saturated vapour pressures of X and Y liquids at the given temperature are P^0_X and P^0_Y respectively.

According to Rault's law

$P_X = 0.3 \times P^0_X$ ------ (1)

Likewise $P_Y - 0.7 \times P^0_Y$ ------- (2)

Now total pressure in the vapour phase = $P_X + P_Y$

Therefore $3.4 \times 10^4\ Pa = 0.3P^0_X + 0.7P^0_Y$ -------(3)

Similarly, for the second condition

$X_x = \frac{1.2\ mol}{(1.2 + 4.8)mol} = 0.2$, then $Y_y = 1 - 0.2 = 0.8$

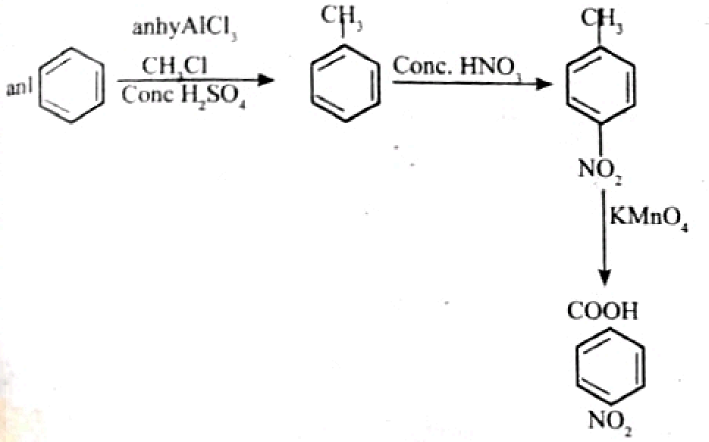
$P_X = 0.2 \times P^0_X$ ----(4) and $P_Y = 0.8\ P^0_Y$.-------(5)

Therefore, $3.6 \times 10^4\ Pa = 0.2P^0_X + 0.8P^0_Y$ -----------(6)

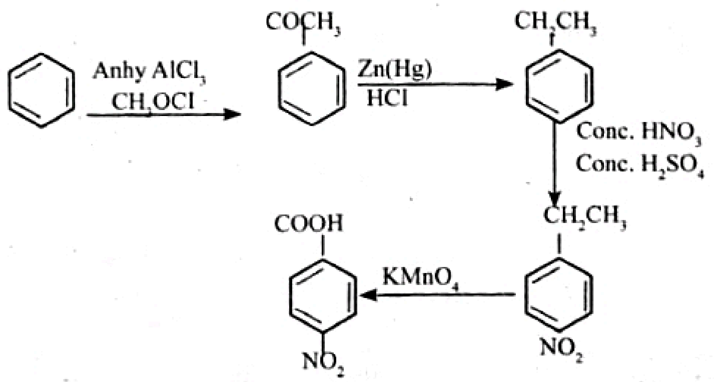
By solving two simultaneous equations (3) and (6) you can obtain the values of P^0_X and P^0_Y

$P^0_X = 2.0 \times 10^4$ Pa and $P^0_Y = 4.0 X 10^4$ Pa

7) Answer-:

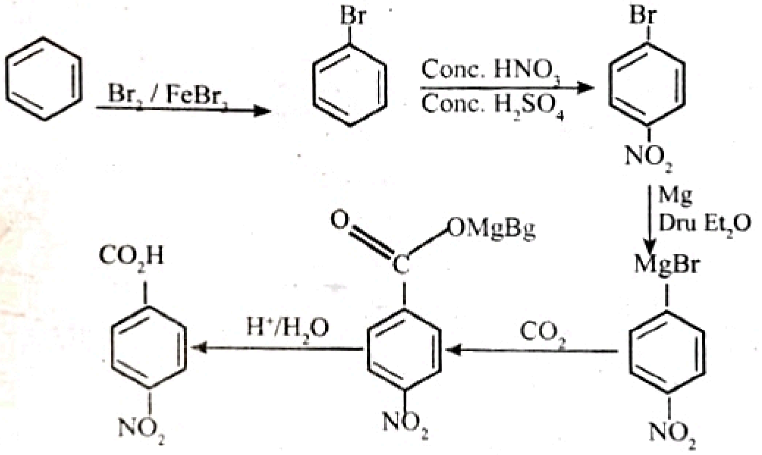


Alternative answer (1)

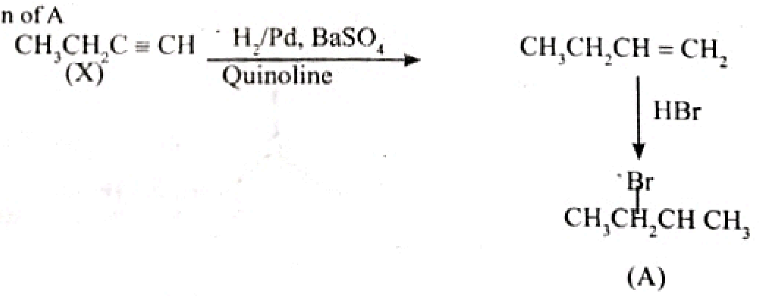


[Instead of CH_3Cl any other appropriate alkyl halide can be written]

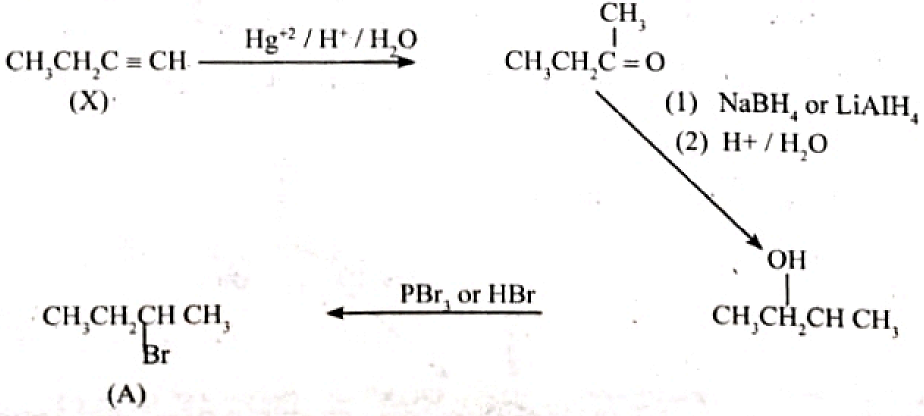
Alternative Answer (2)



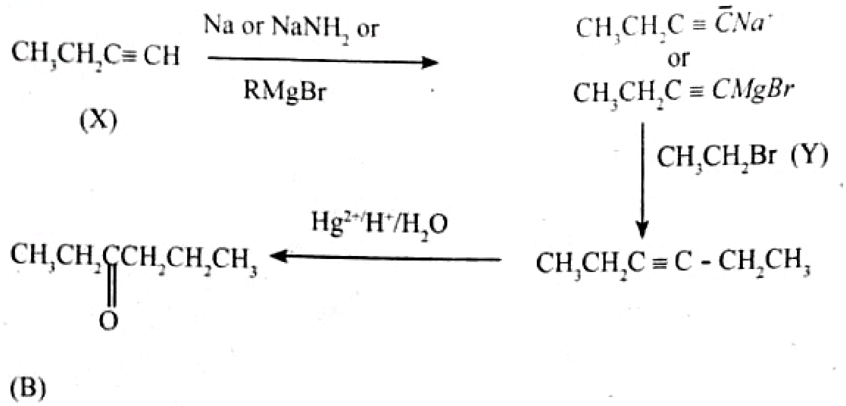
(b) (i) Preparation of A

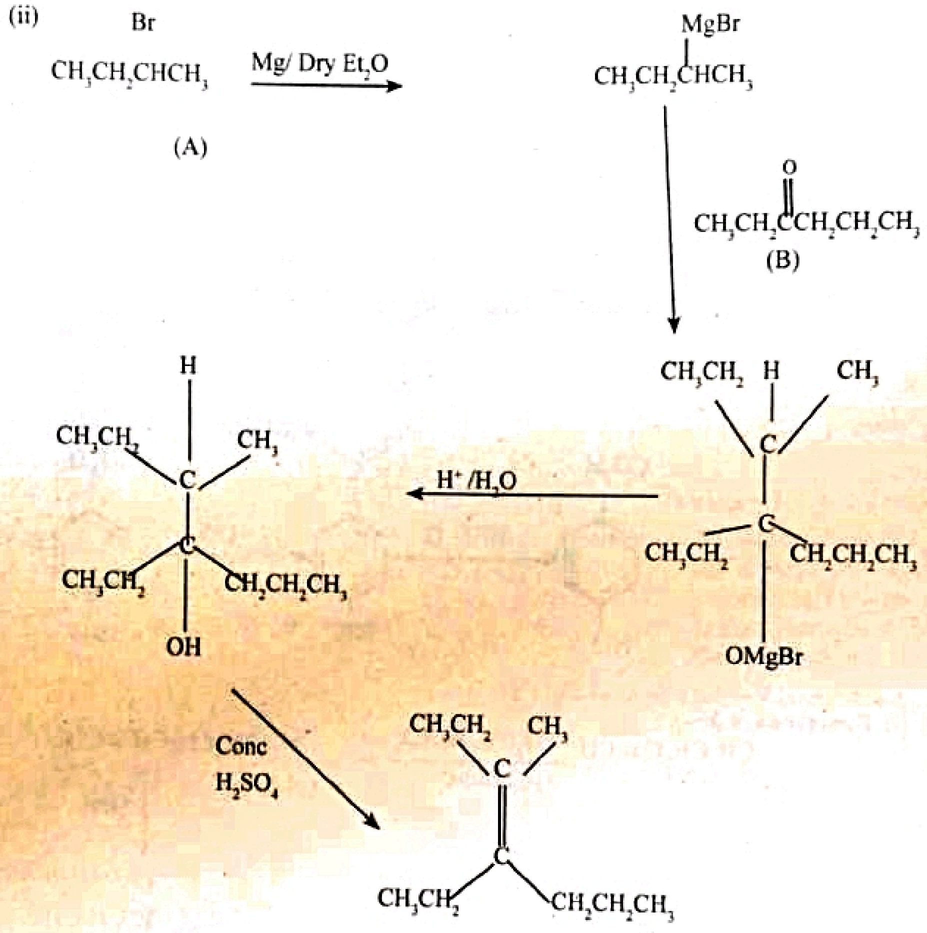


Alternative answer.

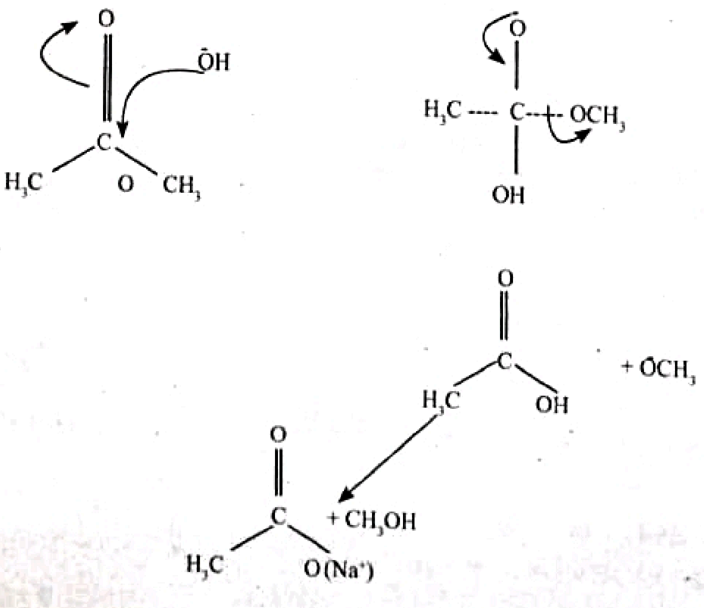


Preparation of B





(c) Answer-:



[illegible]

[illegible] gives white precipitate (P_1) with dil HCl, P_1 may con- [illegible] Hg_2Cl_2 or $PbCl_2$. Hence, solution Y may consist one [illegible] Ag^+, Pb^{2+} and Hg_2^{2+} (cations of first group present)

[illegible] removing P_1, if the filtrate gives black precipitate (P_2) with [illegible] P_2 may consist of HgS, PbS, Bi_2S_3 and CuS. Hence, Y may [illegible] or more of Hg^{2+}, Pb^{2+}, Bi^{3+} and Cu^{2+} cations (cations [illegible] second group present).

- The filtrate of P_2 did not give any precipitate with NH_4OH /NH_4Cl. It means that there is no cations of third group in Y, i.e. Al^{3+}, Fe^{3+} or Cr^{3+}.

- Now the filtrate of P_2 become basic due to adding of NH_4OH. This basic solution has given black precipitate (P_3) with H_2S and therefore the P_3 may consist of NiS or CoS or both. Hence, solution Y may consist of Ni^{2+} or Co^{2+} or both cations (cations of group IV present).

i)

ecipitate P_1

- $PbCl_2$ is soluble in hot water while AgCl and Hg_2Cl_2 are insoluble. Part of P_1 has dissolved in hot water and there fore dissolved part should be $PbCl_2$

- The filtrate F_1 has given white precipitate with dilute H_2SO_4 and therefore the solution Y should contain Pb^{2+}.

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4\downarrow} + 2HCl$$

- AgCl is dissolved in NH_4OH while Hg_2Cl_2 is not soluble. Now residue R should contain AgCl.

$$AgCl + NH_4OH \longrightarrow \underset{\text{(soluble)}}{Ag(NH_3)_2Cl + 2H_2O}$$

- You must know that the above solution gives AgI dark yellow precipitate with KI (AgI is insoluble in NH_4OH).

$$Ag(NH_3)_2Cl + KI + H_2O \longrightarrow \underset{\text{Dark yellow}}{AgI\downarrow} + KCl + 2\,NH_4OH$$

- Hence, it is confirmed that the solution Y should contain Ag^+ cation.

cipitate P_2

- If precipitate P_2 has dissolved in warm dil HNO_3 and therefore it cannot be HgS as it does not dissolve in warm dil HNO_3.
- Therefore P_2 may consist one or more of CuS,PbS and Bi_2S_3.
- But only Pb^{2+} ions gives yellow $PbCrO_4$ precipitate with K_2CrO_4

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow}}{PbCrO_4\downarrow} + 2KNO_3$$

- Hence, it is confirmed that Pb^{2+} cations should in the solution Y.

cipitate P_3

- If P_3 gives pink colour solution with warm conc HNO_3 it should be CoS. Because Co^{2+} ions in the aqueous solution gives pink colour.
- Co^{2+} ions reacts with conc HCl to give blue solution of $[CoCl_4]^{2-}$.
- Further to that Co^{2+} ions reacts with ammonia solution to give Yellow – brown complex ion of $[Co(NH_3)_6]^{2+}$.

(i) Answer -: Pb^{2+}, Co^{2+}, Ag^+.

(ii) I Answer -: P_1 = $PbCl_2$ and AgCl , P_2 = PbS , P_3 = CoS

II Answer-: Solution 1 = Co^{2+} OR $[Co(H_2O)_6]^{2+}$ OR $Co(NO_3)_2$.
Solution 2 = $[CoCl_4]^{2-}$.
Solution 3 = $[Co(NH_3)_6]^{2+}$.

(iii) Answer-:

- For cations to precipitate from solution as sulfides
  $[M^{2+}][S^{2-}] > K_{sp}$ (solubility product)
- H_2S partially ionized in the aqueous medium as follows
  $H_2S \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$
  In acidic medium $[S^{2-}]$ is reduced due to common ion effect.
- K_{sp} of sulfides of Group IV cations (Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}) are greater than that of Group II cations. Therefore, as $[S^{2-}]$ is reduced in acidic medium, it is not sufficient to precipitate the group IV cations as sulfide. Hence, they remain in solution.

b) (i) Answer -: Ammonia gas (NH_3)

(ii) Answer -: Ammonia gas (NH_3).

(iii) Reactions in procedure I

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O \text{ ----(1)}$$
$$NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O \text{ -------(2)}$$

Reactions in procedure II

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O \text{ ---(3)}$$
$$NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O \text{ -----(4)}$$
$$5NaOH + 3NaNO_3 + 2H_2O + 8Al \longrightarrow 8NaAlO_2 + 3NH_3 \text{ ---(5)}$$

OR

$$5OH^- + 3NO_3^- + 2H_2O + 8Al \longrightarrow 8AlO_2^- + 3NH_3$$

(iv) Suppose mass of $(NH_4)_2SO_4$ in sample is xg while mass of NH_4NO_3 is yg. Molar masses of $(NH_4)_2SO4$ and NH_4NO_3 are 132 and 80 respectively.

Therefore, No. of moles of $(NH_4)_2SO_4$ = x/132
No. of moles of NH_4NO_3 = y/80

For procedure I

Moles of NaOH used to neutralized excess of HCl = $\dfrac{0.1 \times 10.2 \text{ mol}}{1000}$

The reaction between NaOH and HCl as follows
$HCl + NaOH \longrightarrow NaCl + H_2O$
As molar ration between HCl and NaOH is 1 : 1, moles of HCl reacted With NaOH is also
$= \dfrac{0.1 \times 10.2 \text{ mol}}{1000}$

Reaction between NH_3 and HCl is given below.
$NH_3 + HCl \longrightarrow NH_4Cl$

Now the moles of HCl reacted with NH_3 = $\dfrac{0.10 \times 30.0}{1000} - \dfrac{0.10 \times 10.20}{1000}$

" " = $\dfrac{0.10 \times 19.80}{1000}$

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

Now, No. of moles of $(NH_4)_2SO_4$ in 50 cm³ of the solution S
= $\dfrac{x\,(50)}{132 \times 250}$

" " = $\dfrac{x}{132 \times 5}$

Similarly moles of NH_4NO_3 in 50 cm³
= $\dfrac{y \times 50}{80 \times 250}$ = $\dfrac{y}{80 \times 5}$

According to equation (1) and (2), one mole of $(NH_4)_2SO_4$ gives two moles of NH_3 while one mole of NH_4NO_3 gives one mole of NH_3 with NaOH.

Hence, moles of NH_3 given out by 50 cm³ of solution $= \frac{2(x)}{132 \times 5} + \frac{y}{80 \times 5}$

Now $\frac{2(x)}{132 \times 5} + \frac{y}{80 \times 5} = \frac{0.10 \times 19.8}{1000}$ ---------(6)

Similarly for procedure 2

Moles of NaOH $= \frac{0.10 \times 15}{1000}$

Therefore, moles of HCl reacted with NaOH $= \frac{0.10 \times 15}{1000}$

Therefore, moles of HCl reacted with NH_3 $= \frac{0.10 \times 30}{1000} - \frac{0.10 \times 15}{1000}$

" " $= \frac{0.10 \times 15}{1000}$

Hence, moles of $NH_3(g)$ liberated $= \frac{0.10 \times 15}{1000}$

Moles of $(NH_4)_2SO_4$ in 25 cm³ $= \frac{(x)\,25}{132 \times 250} = \frac{x}{132 \times 10}$

Moles of NH_4NO_3 in 25 cm³ $= \frac{y \times 25}{80 \times 250} = \frac{y}{80 \times 10}$

Now according to the equations (3), (4) and (5) total amount of NH_3 given out by 25.0 cm³ solution of S

$$= \frac{2(x)}{132 \times 10} + \frac{y}{80 \times 10} + \frac{y}{80 \times 10}$$

Hence, $\frac{2(x)}{132 \times 10} + \frac{y}{80 \times 10} + \frac{y}{80 \times 10} = \frac{0.10 \times 15}{1000}$

After simplifying the above we can obtain the following equation

$$\frac{x}{132 \times 5} + \frac{y}{80 \times 5} = \frac{0.1 \times 15}{1000} \quad \text{-------- (7)}$$

Throughout the equation (6) divided by 2

$$\frac{x}{132 \times 5} + \frac{y}{80 \times 10} = \frac{0.10 \times 19.8}{1000 \times 2} \quad \text{---------(6)}$$

Now eq (7) – (6) $\frac{y}{80 \times 10} = \frac{0.1 \times 15}{1000} - \frac{0.1 \times 9.9}{1000}$

$$y = \frac{0.1 \times 5.1 \times 800}{1000} = 0.408$$

Now, substituting the value of y in equation (7) $\frac{x}{132 \times 5} + \frac{0.408}{80 \times 5} = \frac{0.1 \times 15}{1000}$

Then $\frac{x}{660} = \frac{0.1 \times 15}{1000} - \frac{0.408}{400} = \frac{6 - 4.08}{4000}$

Therefore x $= 0.317$.

Now % of $(NH_4)_2SO_4$ $= \frac{0.317 \times 100}{1.0} = \underline{31.7\,\%}$

% of NH_4NO_3 $= \frac{0.408 \times 100}{1.0} = \underline{40.8\%}$

Answer

(i) Bleaching powder -: $CaCO_3$ (lime stone), CaO (quicklime), $Ca(OH)_2$ (slaked lime) and Cl_2.

(ii) Calcium carbide -: CaO (quicklime), $CaCO_3$ (lime stone) and C (coke).

(iii) Urea -: NH_3 (l or gas) and CO_2 (l or gas)

(iv) Sulphuric acid -: sulfur (S) , FeS_2 (iron pyrite), air and H_2O.

Answer

(i) Bleaching powder

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

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

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

(ii) Calcium carbide

$$CaO(s) + 3C(s) \xrightarrow{2000^0C} CaC_2(s) + CO(g)$$

OR

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

OR

$$CaCO_3(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g) + CO_2(g)$$

(iii) Urea

$$2NH_3(l\ or\ g) + CO_2(l\ or\ g) \xrightarrow[150\ atm]{180-200\ ^0C} NH_2COONH_4(s)$$

$$NH_2COONH_4(s) \xrightarrow[low\ pressure]{Decompose\ at} CO(NH_2)_2\ (solution) + H_2O$$

$$CO(NH_2)_2\ (solution) \xrightarrow[Evaporation]{concentrated\ by} CO(NH_2)_2(s)$$

(iv) Sulphuric acid

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

OR

$$4FeS_2 + 11O_2 \longrightarrow 8SO_2(g) + 2Fe_2O_3 .$$

$$2SO_2(g) + O_2(g) \xrightarrow[450^0C,\ 1\ atm]{V_2O_5} 2SO_3(g)$$

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

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

Uses

Bleaching powder

- Bleaching agent
- Disinfects water

Calcium carbide

Any two of the following

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

Urea

- To manufacture nitrogen rich fertilizers.
- Manufacturing of urea – formaldehyde polymer.

Sulphuric acid

Any two of the following

- Manufacturing of phosphate fertilizer.
- Manufacturing of $(NH_4)_2SO_4$.
- Manufacturing of rayon and plastics.
- Manufacturing of dyes.
- Manufacturing of explosives
- Manufacturing of drugs.
- As a battery acid.
- To dry gases (eg. Cl_2 gas)

(i) Answer-:

I

- Atmosphere - CO_2
- Planta - glucose / starch / cellulose / lignin (any one of these)
- Water - HCO_3^- / CO_3^{2-} [CO_2 (aq)]
- Earth's crust - $CaCO_3$ / $CaCO_3.MgCO_3$ / fossil fuel / graphite

II

Removed via

- Industrial fixation (Haber process) / high temperature combustion.
- Biological fixation (nitrogen fixing bacteria)
- Atmosphere fixation (by lightining)

Replenished via

- Denitrifying bacteria that converts NO_3^- to N_2 gas

III

Under aerobic conditions carbon compounds in soil are converted to CO_2 whereas, under anaerobic conditions they are converted to CH_4 and CO.

(ii) Two main nitrogen containing compounds present in the atmosphere that contribute to acid rain are NO and NO_2 .

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

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

OR

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

HNO_3 is a strong acid which gives $H^+ + NO_3^-$

(iii)

Ozone layer depletion

- Air – conditioning industry[chemical liberated -: CFC/HCFC/aerosol]
- Refrigerator industry [CFC / HCFC]
- Aircraft industry of supersonic jets [NO_2]
- Agrochemical industry [CH_3Br weedicide , fumigant]
- Fire extinguisher industry using or releasing Cl_2 .

Global warming

- Agriculture [CH_4, N_2O]
- Air- conditioners [CFC/ HCFC]
- Refrigerator industry [CFC / HCFC]
- Poultry farming [CH_4]
- Coal power plant [CO_2]
- Halons in fire extinguishers
- Any industry producing/ using chlorine gas.
- Aerosol / spraying agent.

Acid rain

- Burning fossil fuels in transportation [NO and NO_2]
- Burning of fossil in coal power plants [SO_2]
- High temperature combustion [NO, NO_2]

(iv)

- I Manufacturing of NH_3 by Haber process.
- NH_3 can be converted to HNO_3 acid by Ostwald process.

$$NH_3 \longrightarrow HNO_3 .$$

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

OR

II Liquid NH_3 is directly used as a fertilizer.

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

V As a result of unregulated disposal of solid waste, large amounts of methane (CH_4) are produced, between the layers of solid waste, due to the action of bacteria under anaerobic conditions. This methane is a greenhouse gas and contributes to global warming.

10] (a) (i) (I) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^1$ OR $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$.
[oxidation state of Ti in both A and B is the same]
(II) Structure of A

- White precipitate is AgCl and its relative molecular mass is 143.5.
- Number of moles of A in solution $= \frac{0.2 \times 50.00}{1000} = 0.010$
- Number of moles of AgCl in 4.305 g of precipitate $= \frac{4.305}{143.5} = 0.03$
- Therefore, A contains three ionic chlorides ($3Cl^-$)
- Therefore, charge of coordination sphere/ complex ion has to be +3.
- However oxidation state of Ti is +3. Therefore, only neutral ligands
- Could be coordinated to Ti. Since the complex has an octahedral Geometry, six ligands need to be coordinated to Ti.
  Therefore, structure A = $[\,Ti\,(H_2O)_6]Cl_3$.

Structure B

- Number of moles of B solution $= \frac{0.30 \times 50.00}{1000} = 0.015$
- Number of moles of AgCl in 4.305 g of precipitate $= \frac{4.305}{143.5} = 0.03$
- Therefore, B contains two ionic chlorides ($2Cl^-$)
- Therefore, charge of coordination sphere has to be +2
- Since oxidation state of Ti ion is +3, one Cl- has to be coordinated to Ti in the complex. Since the complex has an octahedral geometry, six ligands need to be coordinated to Ti.

Hence, structure of B = $[\,Ti(H_2O)_5Cl]Cl_2$

(III) A -: hexaaquatitanium (III) chloride.

B - : pentaaquachlorotitanium (III) chloride.

(ii) Answer-: X = $[M(NH_1)_2(CN)_2]$. Y = $[M(NH_3)_4]SO_4$

Z = $K_2[M(CN)_4]$ OR $[M(NH_1)_4](CN)_2$ OR $[M(CN)(NH_1)_3]_2SO_4$
OR $K[M(CN)(NH_3)_3]\,SO_4$

(b) (i) Reduction half reaction of the given cell
$Hg_2Cl_2\,(s) + 2e \longrightarrow 2Hg(l) + 2Cl^-(aq)$

(ii) oxidation half reaction
$Ag\,(s) + Cl\text{-}\,(aq) \longrightarrow AgCl\,(s) + e$

(iii) Cell reaction
$Hg_2Cl_2\,(s) + 2Ag\,(s) \longrightarrow 2AgCl(s) + 2Hg(l)$

(iv) $E_{cell} = E^0_{Hg/Hg2Cl2} - E^0_{Ag/AgCl}$.
$= 0.27 - 0.22 = 0.05V$
Hence, e.m.f of the cell = 0.05 V

(v) $Ag(s)\ \ AgCl\,(s)\ \ Cl^-\,(\,aq,\ 1.0moldm^{-3}\,)\ \ Hg_2Cl_2\,(s)\ \ Hg(l)$

(vi) Chloride ion concentration is not present in the cell reaction. Hence, The cell potential does not depend on the chloride ion concentration.

(vii) A current of 0.10A was drawn for 60 min.
The amount of charge passed through the cell
$= 0.1A \times (60 \times 60)s$
" " " $= 360\ C$

Electrode reaction in the left electrode
$Ag(s) + Cl^-\,(aq) \longrightarrow AgCl(s)$

For every electron passed through the cell , one Ag atom combines with Cl^- to form AgCl (s).
. Now, weight gain of Ag + AgCl = mass of Cl^- combined with Ag

$= 35.5\ gmol^{-1} \times 360C\ /\ 96500Cmol^{-1} = 0.132\ g$

(viii) Chloride ion concentration does not change.