Answers for MCQ

Chemistry I GCE A/L 2015

1 - 2	11 - 1	21 - 3	31 - 5	41 - 1
2 - 3	12 - 2	22 - 4	32 - 2	42 - 4
3 - 2	13 - 1	23 - 4	33 - 2	43 - 4
4 - 3	14 - 5	24 - 2	34 - 5	44 - 1
5 - 1	15 - 1	25 - 1	35 - 4/5	45 - 3
6 - 2	16 - 1	26 - 2	36 - 1	46 - 5
7 - 4	17 - 5	27 - 3	37 - 3	47 - 5
8 - 3	18 - 4	28 - 3	38 - 5	48 - 2
9 - 3	19 - 2	29 - 3	39 - 5	49 - 1
10 - 3	20 - 4	30 - 1	40 - 1	50 - 4

fter the discovery of electrons and protons , J.J Thomson tried to explain the arrangement of electrons and pro
e proposed a model having negatively charged particles (electrons) embedded in a sphere of positively charged
om. This is often called " The plum pudding model".

Answers

Chemistry II GCE A/L 2015

Part A -

STRUCTURED ESSAY

(a) i) Answer -: Na_2SO_4 .

Thinking process -:

- We know that Na_2SO_4 is a salt which has ionic bond between Na^+ ions and SO_4^{2-} ions. Further, sulphate ion itself has covalent bonds between oxygen and sulfur. Now the answer is clear. Alternatively, we know that covalent bonds are formed between two similar or dissimilar non – metals. You can see all the atoms in the given species, except Na_2SO_4 , are non-metals. As such ionic (may be polar) bonds cannot be formed among those. (however there are exceptions)

ii) Answer -: NO_3^- .

Thinking process -:

- Atomic numbers of B and F are 5 and 9 respectively. Therefore there are 32 electrons in BF_3 molecule (5 + 9x3). Now you know that atomic number of Xe itself is greater than 32. As such XeF_2 cannot be isoelectronic with BF_3.
- Atomic number of S is three times as greater as that of B and there are five F atoms attached to S atom in SF_5^- ion. Its mean that number of electrons in SF_5^- ion is much greater than that of BF_3. Similarly SO_3 and Na_2SO_4 also will be rejected.
- Without any calculations you can reject HF because number of electrons in HF molecule are very much less than 32. Now the answer is clear. Number of electrons in NO_3^- ion is 7 + 8 x3 + 1 additional electron due to negative charge = 32

iii) Answer -: SF_5^- .

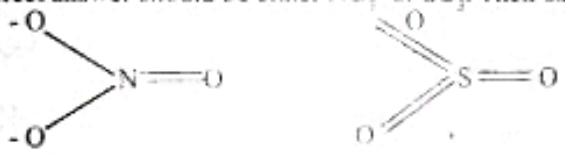
Thinking process -:

- If there are five atoms bonded with central atom and one lone pair of electrons on the central atom, the molecule will adopt square Pyramidal geometry in order to have minimum inter-electron pair repulsion. Out of given species only SF_5^- ion is fulfilled said requirements.

iv) Answer -: SO_3 .

Thinking process -:

- Each bond contains two electrons. But each F atom contains 7 electrons in its valence shell and Xe has 8 electrons in its valence shell. XeF_2 molecule has only two bonds, i.e, number of bonding electrons are 4. But you can see non – bonding electrons are much more than bonding electrons.
- Only 10 bonding electrons (5 bonds) are in SF_5^- ion but there are 7 valence electrons in each F atom. As such non-bonding electrons are much more. Similarly Na_2SO_4 also can be rejected.
- HF has two bonding electrons (It has only one bond) but F itself has 7 valence electrons.
- Now the correct answer should be either NO_3^- or SO_3. Their stable Lewis structures are as follows.



Bonding electrons ⟶	2 x 4 = 8	2 x 6 = 12
No of valence electrons	3 x 6 + 5 + 1 due to charge = 24	3 x 6 + 6 = 24
No of non-bonding electrons ⟶	24 - 8 = 16	24 -12 =12

Now the answer is clear.

v) Answer -: HF

Thinking process -:

- The covalent bond is formed due to the interaction of valence electrons as the atoms approach each other. Among the given atoms only hydrogen has 1s orbital in its valence shell. Now

The answer is clear.

vi) Answer -: XeF_2 .

Thinking process -:

- Molecules or ions made up of three or more atoms, the angle Between the two covalent bonds made by the same central atom Is known as bond angle.
- According to the definition you can disregard HF because it has only two atoms.
- You know that SO_3 and NO_3^- both have trigonal planer geometry whereas SO_4^{-2} ion in Na_2SO_4 has tetrahedral shape and you have already been identified that the SF_5^- ion has square pyramidal shape. None of these contain a bond angle of 180°. Now the answer is clear.
- In case of molecules or ions, where the central atom is surrounded by two pairs of bonding electrons as well as three unshared

pairs of electrons, the shape is linear.

- In XaF_2 molecule there are two F atoms bonded to Xe atom and there are three lone pairs of electrons around the central Xe atom.

[1 (a) - 4 X 6 = 24 Marks]

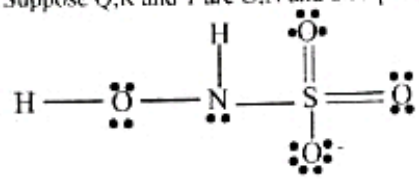
Note -: If more than one answer is given for a question, award zero marks for that question.

b) i) Answer -: Q =O , R = N, T = S or Q = N , R = C, T = S [02 + 02 + 02]marks

Thinking process -:

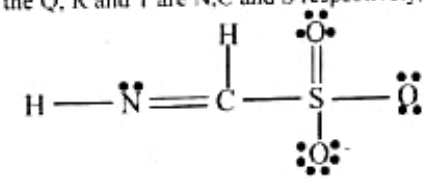
- Electronegativies of Q,R and T are greater than 2 and Q and R belong to the second period. If so Q and R could be that of C,N,O or F.
- If T is belongs to third period it may be P,S or Cl. According to the given skeleton structure T supposed to be central atom.
- Generally, less electronegative atom constitutes the central atom. Hence Cl can be disregarded
- There are three oxygen atoms bonded to T and one oxygen atom Carries negative charge and therefore, said oxygen atom must be bonded to T with single bond. Other two oxygen atoms around the T must be bonded to T with double bonds. As such there are six bonds around the T. Hence T should be S.
- Given skeleton structure shows that there are three atoms bonded to R whereas Q bonded to two atoms. Hence Q or R cannot be F because F can form only one bond. Further, R cannot be oxygen and therefore R must be N or C.
- Suppose that R is N then, Q cannot be C. Because if Q is carbon there Should be triple bond between Q and N to satisfy the valence of C. Then, there will be five bonds around N. This cannot be happened. Therefore Q must be oxygen.
- Suppose R is C, then, there should be double bond between Q and C in Order to fulfill the valence of carbon. Then there will be three bonds around Q. As a result Q cannot be O. Then Q should be N. Therefore given two answers are clear.

ii) Answer -: Suppose Q,R and T are O,N and S respectively, then the Lewis structure is given below.



[08 marks]

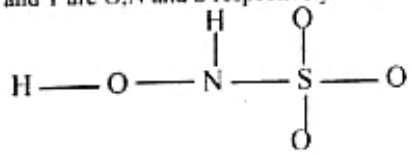
Alternative answer -: If the Q, R and T are N,C and S respectively, then the Lewis structure Is given below.



[08 marks]

Thinking process -:

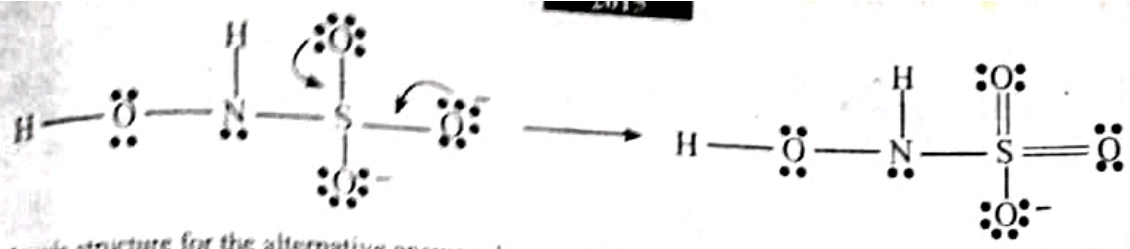
- Suppose Q,R and T are O,N and S respectively. Then first of all skeleton structure need to be drawn.



- Then add up the number of valence electrons. For neutral molecules, it is just the sum of the valence electrons of all the atoms present. In case of negatively charged ions, add the number of charges to the number of valence electrons of atoms and subtract the number of charges in case of positively charged ions.
- In this structure

No of valence electrons = O (6 x 4) + S(6) + N(5) + H(1 x 2) + negative charge(1) = 38

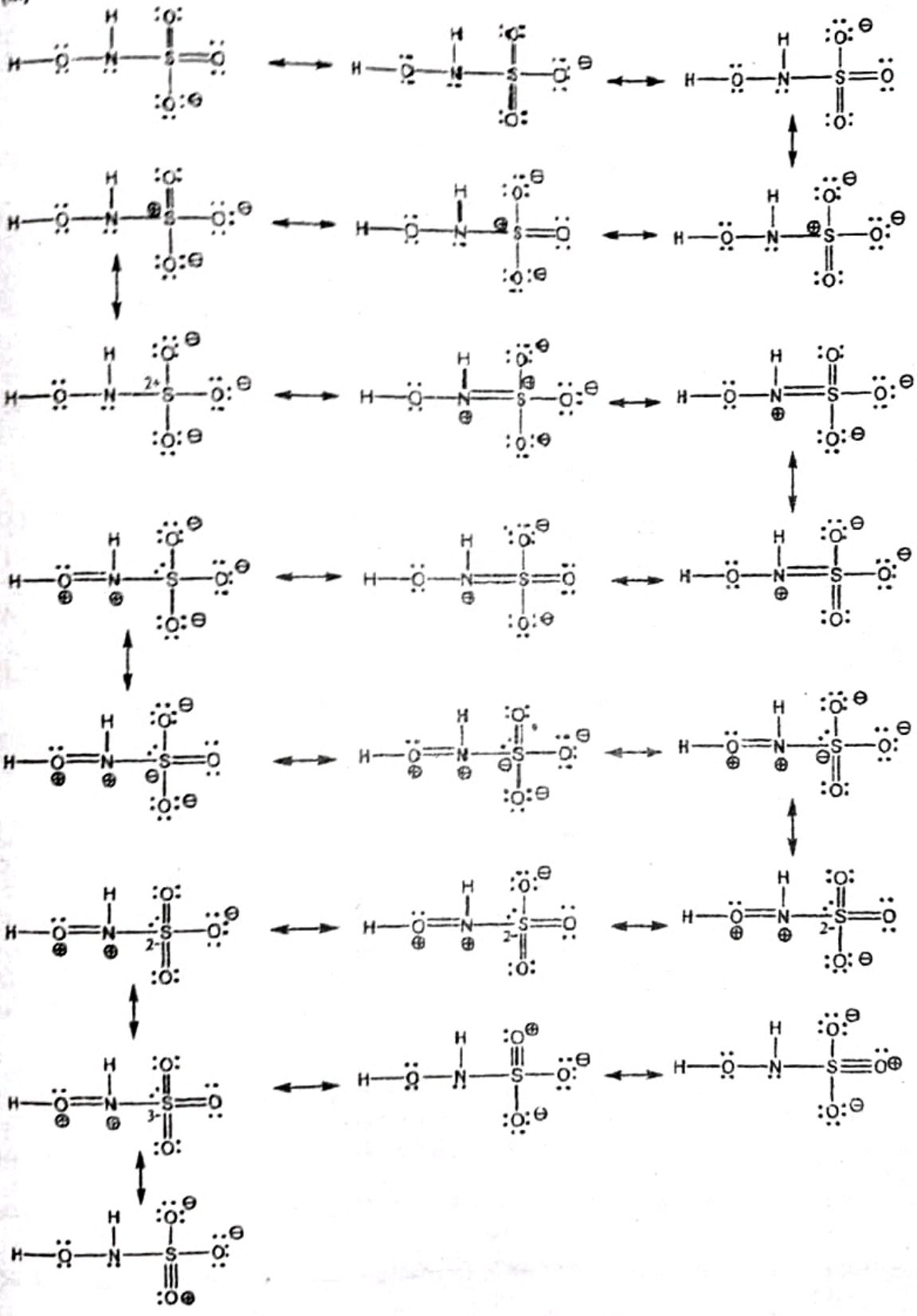
- Determine the number of bonded electrons (each bond contains two electrons). So bonded electrons = number of bonds x 2 = 7 x 2 = 14
- subtract number of bonded electrons from the total sum of valence electrons in order to obtain remaining valence electrons 38 - 14 = 24
- Complete the octets of the atoms (initially most elector negative atoms) attached to the central atom by adding electrons as 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 most stable Lewis structure.



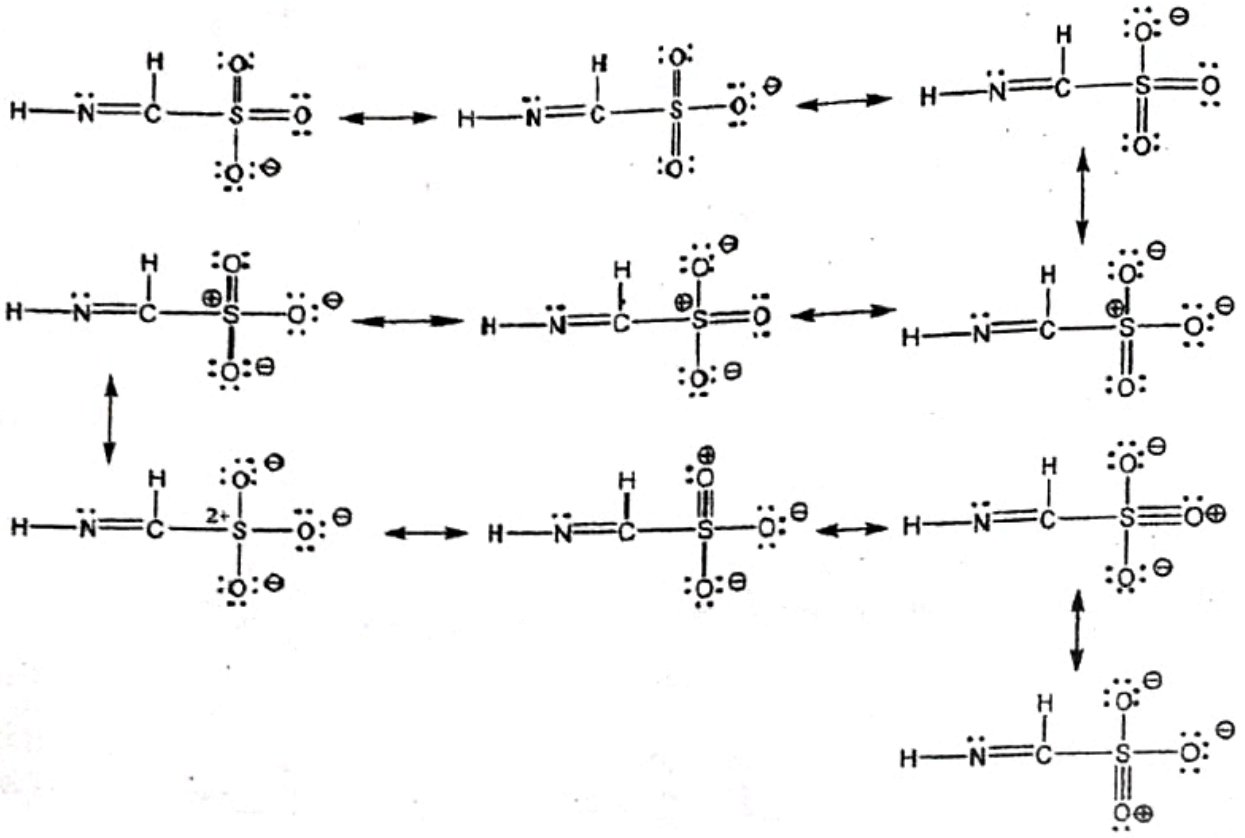
- Lewis structure for the alternative answer also can be drawn accordingly.

(ii) Answer -: If the Q,R and T are O,N and S, it is possible to draw 22 resonance structures. Although some of them are unstable, all possible resonance structures are drawn below. You have to draw only six structures out of 22.

(iii)



Alternative answer for b(iii) -: If the Q,R and T are N,C and S, it is possible to draw 10 Resonance structures. Although some of these are unstable, all possible resonance structures are drawn below. Out of those you have to draw only 6



iv) Answer -: If the Q,R and T are O,N and S respectively

		Q	R	T
I	Electron pair geometry	Tetrahedral	Tetrahedral	Tetrahedral
II	Shape	Angular/V	Pyramidal	Tetrahedral
III	Hybridization	SP^3	SP^3	SP^3
IV	Bond angle	$103 - 105^0$	$106 - 108^0$	108 - 110

(01 x 12 = 12 marks)

Thinking process -: (I)

- Electron pair geometry depends on the total sum of sigma bonds and lone pairs around the atom.
- You can see there are two sigma bonds and two lone pairs around Q whereas rhas three sigma bonds and one lone pair. There are four sigma bonds around T. Its mean that total sum of sigma bonds and lone pairs around each atom (Q,R and T) is 4. Hence electron pair geometry around each given atom is tetrahedral.

(II)
- There are two sigma bonds and two lone pairs around Q. You must know that any atom surrounded by two sigma bonds and one or two lone pairs, the shape around the central atom should be angular or V shape.
- Atom R surrounded by three sigma bonds and one lone pair and therefore, shape around R should be pyramidal.
- Atom T surrounded by four sigma bonds. Hence the shape around T atom must be tetrahedral (π bonds do not consider when determining the shape of a molecule or ion).

(III)
- Hybridization of a given molecule could easily be determined by considering the total number of repulsive units around the middle atom. Here the total repulsion units represent the sum of number of lone pairs and number of bond pairs (sigma)
- Q has four repulsion units (two bond pairs and two lone pairs). Therefore its orbital distribution is tetrahedral. Hence the Hybridization of Q is SP^3.
- Likewise both R and T surrounded by four repulsion units (remember Π bonds do not consider) and therefore, hybridization of both must be SP^3.

(IV)
- Bond angle of angular shape molecule is around 104.5^0. Depending of on the nature of surrounding atoms, angle can be varied from 103^0 to 105^0 .

- Bond angle of pyramidal shape molecule is around 107° and depending on the nature of surrounding atoms, bond angle can be varied from 106° to 108°. Likewise the bond angle of tetrahedral shape can be varied from 108° to 110°.

Alternative answer for b (iv) -: If the Q,R and T are N,C and S respectively

		Q	R	T
I	Electron pair geometry	Trigonal planer	Trigonal planar	Tetrahedral
II	Shape	Angular/V	Trigonal planar	Tetrahedral
III	Hybridization	SP^2	SP^2	SP^3
IV	Bond angle	$119 - 121^0$	$119 - 121^0$	$108 - 110^0$

[01 x 12 = 12 marks]

Thinking process -: According to the explanations I have given in the preceding answer, you must be able to predict the above properties in the lewis structure.

v) Answer -: If the Q,R and T are O,N and S

I) Q——R ⟶ Q sp^3 (hybridized orbital) R sp^3 (hybridized orbital)
II) R——T ⟶ R sp^3 (hybridized orbital) T sp^3 (hybridized orbital)
III) T——O ⟶ T sp^3 (hybridized orbital) O 2p atomic orbital or sp^3 (h o)

(01 x 6 = 06 marks)

Alternative answer -: If Q,R and T are N,C and S respectively.

I) Q——R ⟶ Q sp^2 (hybridized orbital) R sp^2 (hybridized orbital)
II) R——T ⟶ R sp^2 (hybridized orbital) T sp^3 (hybridized orbital)
III) T——O ⟶ sp^3 (h. o) O 2p (a.o) or sp^3 (h.o) [01 x 6 = 06 marks]

b vi) I) Answer -:
1) Distribution of valence electrons (as bond pairs and lone pairs)
2) charges on atoms
Can be directly obtained from a Lewis structure.

[02 + 01 =03 marks]

II) Following information is not directly provided by a Lewis structure.
1) bond angles
2) shape around central atom/s
3) Hybridization
4) what orbitals overlap to form bonds.
5) nature of orbitals occupied by lone pairs.

Any two [02 + 01 = 03 marks]

[1(b) : 56 marks]

c) i) Answer -: True [04 marks]

Reason -: Electronegativity is depends on the charge on the atom, oxidation Number and the s character of the hybridized atom.

	NO_2F	NO_4^{3-}	NH_3
Charge on N	+1	+1	0
Oxidation state of N	+5	+5	-3
Hybridization of N	SP^2	SP^3	SP^3

Higher the positive charge, greater the electronegativity than neutral. Formal charges On the N in NO_2F and NO_4^{3-} species are +1 whereas charge on the N in NH_3 molecule is Zero. Hence N in ammonia molecule has least electronegativity.

We know that higher the oxidation state, greater the electronegativity. However it is not possible to differentiate remaining two species by oxidation state, because oxidation state of both is the same (+5).

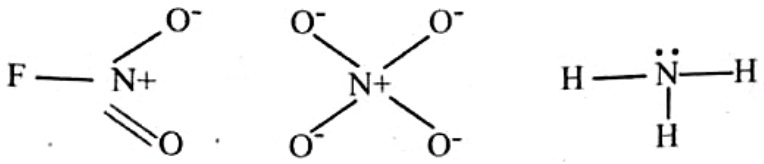
Other factor is that higher the s characters of hybridization, higher the electronegativity It is obvious that the s character of sp^2(33%) hybridization is greater than that of sp^3(25%). Hence most electronegative N atom must be in NO_2F molecule. Therefore decreasing order of electronegativity of N in given species is as follows

$NO_2F > NO_4^{3-} > NH_3$. [06 marks]

[No need to give this type of comprehensive answers for the structured type questions. But the reasons need to be pointed out briefly.]

Thinking process -:

- Stable Lewis structures of species are as follows. Suppose oxidation state of N is y.



Oxidation number of N -1 +y + (-2x2) =0 , y + (-2x4) = -3 , 1x3 + y =0

Y = +5 y = +5 y = -3

Formal charge on a atom = | No. of valence electrons In the free atom | - | total No. of lone pairs electrons | - $\frac{1}{2}$ | Total No. of bonding electrons

then the charge on N 5 – 0 – ½(8)= +1 , 5 – 0 – ½(8) = +1, 5 – 2 -1/2 (6) = 0

- As I said earlier nature of the hybridization is depending on the total sum of the number of sigma bonds and number of l pairs around the hybridized atom.
  Now N in NO_2F molecule has only three sigma bonds. Therefore its hybridization is sp^2.
  N in NO_4^{3-} ion has only four sigma bonds around it. Hence, its hybridization is sp^3.
  N in NH_3 has three sigma bonds and one lone pare and therefore its hybridization is also sp^3.

c (ii) Answer -: False [04 mar

Reason -:

- Cation of the given compound is the same. Although charge of the anions is same their size increases from F- to I-.Polarizabi of the anion increases with an increase in size of the anion. Therefore polarizability decreases from I- to F-.i,e. I-> Br-> C F-.

- Therefore ionic character of given compounds decreases according to the following way.
  LiF > LiCl > Li Br > Li I

- Higher the ionic character, higher the melting point. Hence ascending order of melting points must be as follows
  LiI < LiBr < LiCl < LiF
  Therefore given sequence is incorrect. [06 mark

Alternative answer for c (ii) -: False

Reason -:

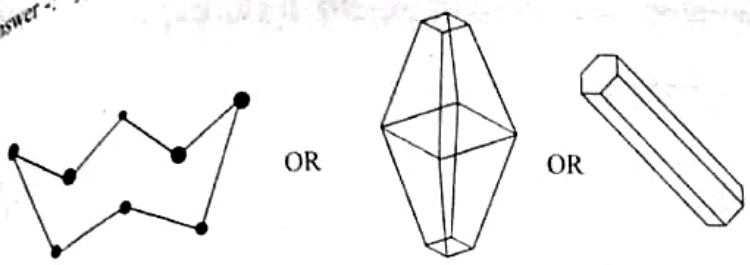
- Cation is the same and electronegativity of anions (halides) decreases from F- to I-, i.e, F->Cl-> Br-> I-.
- Therefore electronegativity difference of the given compound Increases from LiI to LF, i.e, LI <LBr<LiCl<LiF .
- Therefore, ionic character increases from LiI to Li F and therefore, melting point increases from LiI to LiF, i.e, LiI < LiBr < LiCl < LiF

Another alternative answer for c(ii) -: False

Reason -:

- Lattice energy of ionic compound is proportional to $\frac{\text{charge of cation} \times \text{charge of anion}}{\text{redius of cation} + \text{radius of anion}}$
- Charges of both cation and the anions are the same. Further, size of the cation is the same. But size of the anions decrea from I- to F-.
- Hence the lattice energy of the given compounds increases from LiI to LiF, i.e, LiI<LiBr<LiCl<LiF .
- Therefore ionic character increases – LiI<LiBr<LiCl<LiF .
- Consequently, ascending order of their melting poins must be Li I< Li Br <Li Cl < LF. [1 c : 20 mark

(i) Answer -: X is -: S (Sulphur) [04 marks]



OR OR

STRUCTURE OF X [04 marks]

(ii) Electronic configuration of X -: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$. [04 marks]

(iii) Positive oxidation states of X -: +2, +4, +6 or + II, +IV , +VI Any two [02 + 02] marks

(iv) Answer -: $X_1 = SO_2$, $X_2 = BaSO_3$, $X_3 = H_2SO_3$, $X_4 = SO_3$, $X_5 = H_2SO_4$.

[04 X 5 = 20 marks]

Working process -:

- If X is belongs to p-block element with atomic number less than 20, It cannot be (I) or (II) group element.
- If it gives colourless gas X_1 when burning in air, the gas may be either CO_2 or SO_2. But gas has a pungent smell, then the gas X_1 must be SO_2. Hence X must be sulphur (S).
- We know that SO2 is readily soluble in water and give H_2SO_3 weak acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3.$$

When solution of Ba Cl_2 is added to this weak acid solution, react each other to form $BaSO_3$ white precipitate. Therefore X_2 must be BaSO3 .

$$BaCl_2 + H_2SO_3 \longrightarrow BaSO_3 \downarrow + 2HCl$$

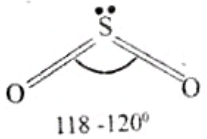
White

- $BaSO_3$ reacts with dil. HCl acid to give SO_2 and this gas itself dissolve in the dilute solution to give weak acid H_2SO_3. Therefore X_3 must be H_2SO_3 .
- We know that SO_2 acts as a reducing agent and reduces MnO_4^- ions into Mn^{+2} ions in the acidified medium. SO_2 can be oxidized to SO_3 , when allowed to react with O_2. Therefore X_4 must be SO_3 .

$$2SO_2 + O_2 \xrightarrow[1\ atm]{V_2O_5\ /\ 450^0C} 2SO_3.$$

- You know that in " Contact Process" SO_3 gas used to manufacture strong H_2SO_4 acid.Therefore, X_5 must be suphuric acid.

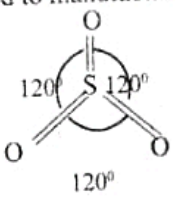
(v) Answer - :



118 -120^0

X_1

[sketch must show V or angular arrangement]



120^0

X_2

[sketch must show trigonal planar arrangement]

Sketch (02 + 01) + (02 + 01); angle (01) + (01) = 08 marks

Note – Lone pairs of electrons on oxygen are not required.

(vi) Answer -:

$$5\,(SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e\,) \quad \text{----- (1)}$$
$$2(MnO_4^- + 8H+ + 5e \longrightarrow Mn^{2+} + 4H_2O\,) \quad \text{------ (2)}$$

(1) + (2) $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H+$

OR

$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow 2MnSO_4 + K_2SO_4 + 2H_2SO_4$

OR

$5(SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e)$ ------ (1)

$2(MnO_4^- + 8H+ + 5e \longrightarrow Mn_2+ + 4H_2O)$ ------(2)

(1) + (2) $2MnO_4^- + 5SO_3^{2-} + 6H+ \longrightarrow 2Mn^{2+} + SO_4^{2-} + 3H_2O$

Out of three any balanced equation (06 marks)

(If only half reactions are given, you will get 02 marks for each) [2(a): 50 marks]

b) i) Answer -: A = $NaHCO_3$, B = $(NH_4)_2CO_3$ C = $(NH_4)_2SO_4$ D) $Mg(NO_3)_2$

E = NH_4NO_3 [05 X5 = 25marks]

ii) A -: $2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$

B -: $(NH_4)_2CO_3(s) \xrightarrow{\Delta} 2NH_3(g) + CO_2(g) + H_2O(g)$

C -: $(NH_4)_2SO_4(s) \xrightarrow{\Delta} 2NH_3(g) + H_2SO_4$

D -: $2Mg(NO_3)_2(g) \xrightarrow{\Delta} 2MgO(s) + 4NO_2(g) + O_2(g)$

C -: $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$

[05 x 5 = 25 marks]

[2(b) : 50 marks]

Thinking process -:

- If the colourless gas that turns lime water creamy then, the gas must be CO_2. Therefore A must be either $NaHCO_3$ or $(NH_4)_2CO_3$. Bu only $NaHCO_3$ gives basic white powder (Na_2CO_3) when heated. Hence A must be $NaHCO_3$.
- Only $(NH_4)_2CO_3$ gives three gaseous products on heating(see above reaction). Hence B must be $(NH_4)_2CO_3$
- Only NH_3 gives brown precipitate or colouration with Nessler's reagent. Then C must beAmmonium compound (however certain ammonium compound do not liberate NH_3 on heating). If it gives strong acid (H_2SO_4) then, C must be $(NH_4)_2SO_4$.
- In the periodic table, nitrate of second group elements give red- brown NO_2, colourless diatomic O_2 and its white oxide on heating. Hence D must be $Mg(NO_3)_2$.
- Now the remaining compound is NH_4NO_3. It gives water vapour and non-toxic N_2O gas on heating.

3] (a) (i) Answer -:

Expt	[A]0/moldm^{-3}	[B]0 / moldm^{-3}	[C]0 / moldm^{-3}	[A]0 / moldm^{-3}	t/s	Initial rate (R) / Moldm^{-3} s^{-1}
1	0.2	0.2	0.2	0.040	50	$R_1 = 8.0 \times 10^{-4}$
2	0.4	0.2	0.2	0.096	60	$R_2 = 1.60 \times 10^{-3}$
3	0.4	0.4	0.2	0.128	40	$R_3 = 3.2 \times 10^{-3}$
4	0.2	0.2	0.4	0.080	25	$R_4 = 3.2 \times 10$-3

Thinking process-:

- Initial rate R is = $\frac{\text{change in concentration of A during (0-t) time}}{\text{Time elapsed (t)}}$
- Therefore R_1 = $\frac{\Delta [A]0 \text{ moldm}^{-3}}{t \text{ s}}$ = $\frac{0.040 \text{ moldm}^{-3}}{50\text{s}}$ = 8×10^{-4} moldm^{-3} s^{-1}

Similarly R_2 = $\frac{0.096\ moldm^{-3}}{60\ s}$ = $1.6 \times 10^{-3}\ moldm^{-3}\ s^{-1}$

Likewise you must be able to determine R3 and R4.

[05 x 4 = 20 marks]

(ii) Answer -: Suppose that the rate of the reaction = $k\ [A]^a\ [B]^b\ [C]^c$.
[k is rate constant]
Now from experiment 1

$R_1 = 8.0 \times 10^{-4}\ moldm^{-3}\ s^{-1} = k\ [0.2\ moldm^{-3}]^a\ [0.2\ moldm^{-3}]^b\ [0.2\ moldm^{-3}]^c$ ---- (1)

From experiment 2
$R_2 = 16.0 \times 10^{-4}\ moldm^{-3}\ s^{-1} = k\ [0.4\ moldm^{-3}]^a\ [0.2\ moldm^{-3}\ s^{-1}]^b\ [0.2\ moldm^{-3}]^c$ ---- (2)
From experiment 3
$R_3 = 32 \times 10^{-4}\ moldm^{-3}\ s^{-1} = k\ [0.4\ moldm^{-3}]^a\ [0.4\ moldm^{-3}]^b\ [0.2\ moldm^{-3}]^c$ ---- (3)
From experiment 4
$R_4 = 32 \times 10^{-4}\ moldm^{-3}\ s^{-1} = k\ [0.2\ moldm^{-3}]^a\ [0.2\ moldm^{-3}]^b\ [0.4\ moldm^{-3}]^c$ ----(4)
From (1) / (2) we get $\frac{1}{2} = (1/2)^a$, then a = 1
From eq (2) / (3), we gat $\frac{1}{2} = (1/2)^b$, then b = 1
From (1)/ (4), we gat $\frac{1}{4} = (1/2)^c$, then c = 2
Therefore rate = $[A]\ [B]\ [C]^2$.

[2.5 x 4 + 05 x 4 = 30 marks]

(iii) Answer - : The overall order of the reaction is the sum of the powers to which the concentration raised in the experimentally determined rate equation.
Hence the overall order of the given reaction = 1+1+2 = 4

[05 marks]

(iv) By using any one of the equation, it is possible to determine the rate constant k,
from equation (1)

$K = \frac{8.0 \times 10^{-4}\ moldm^{-3}\ s^{-1}}{(0.2)\ (0.2)\ (0.2)^2\ mol^4\ dm^{-12}}$ = 0.5 mol-3 $dm^9\ s^{-1}$

[05 + 04 + 01 = 10 marks]

(b): (i) (I) Answer -: Now we know rate [R] = k [A] [B] $[C]^2$
You can see that the concentrations of [B] and [C] are considerably higher when compared to the concentration of [A]. Hence the concentrations of B and C can be taken as constant.
Then k [B][C]2 = another constant = k'.
When substitute this into initial rate expression, we get
Rate = k' [A] [or Rate = $k' [A]^a$.

[05 marks]

(II) Answer -: We assumed that [B] and [C] do not change during the experiment.

[05 marks]

(ii) Answer -: Now $2.303 \log [A] = -k' t + 2.303 \log [A]_0$ is given
Half-life is defined as the time required when half the concentration of a reactant is consumed. Therefore.
When $t = t_{1/2}$, $[A] = [A]_0/2$

[05 marks]

When substitute both into the given equation
$2.303 \log [A]_0/2 = -k' t_{1/2} + 2.303 \log [A]_0$
Therefore $k' t_{1/2} = 2.303 \log [A]_0 - 2.303 \log [A]_0/2$

[05 marks]

$t_{½} = \frac{\log 2}{k'} = 0.693/k'$

But $k' = k [B] [C]^2$ and therefore $k' = 0.5$ mol-3$dm^9\ s^{-1} \times (1 moldm^{-3}) (2 moldm^{-3})^2$.

Then $k' = 2s^{-1}$

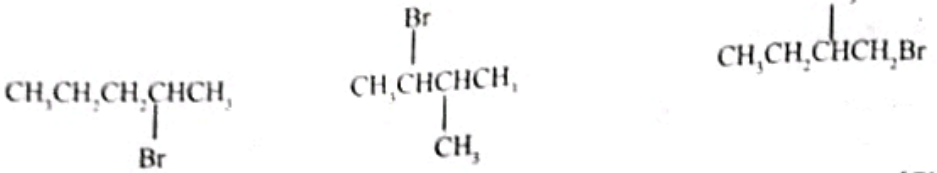
[05 marks]

Therefore $t ½ = 0.693/2s^{-1} = 0.347$ s (or 0.35)

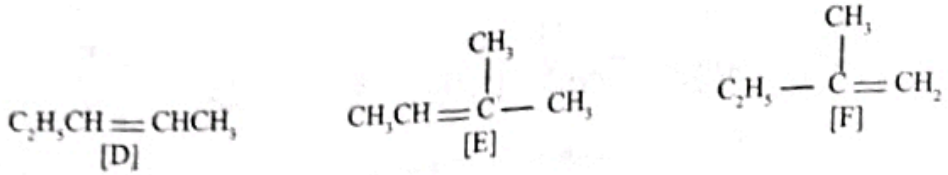
[05 marks]

[3(b) : 30 marks]

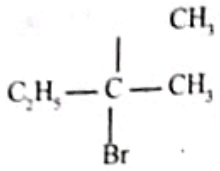
4 (a) Answer -:



[A] [B] [C]



[D] [E] [F]



[G]

[07 x 7 = 49 marks]

[B and C can be interchanged. If so, E and F should also be interchanged]

Thinking process -:

- We can draw number of structures with the formula of $C_5H_{11}Br$.

$CH_3CH_2CH_2CH_2CH_2Br$ [1] $CH_3CH_2CH_2CH(Br)CH_3$ [2] $CH_3CH_2CH(Br)CH_2CH_3$ [3]

$CH_3CH_2CH(CH_3)CH_2Br$ [4] $CH_3CH(CH_3)CH_2CH_2Br$ [5] $CH_3CH_2C(CH_3)BrCH_3$ [6]

$(CH_3)_2CCH_2Br$ [7] $CH_3CHBrCH(CH_3)_2$ [8] $CH_3CH(CH_3)CHBrCH_3$ [9]

- If A,B and C are optical isomers, then there must have asymmetrical carbon atom therefore, structures 1,3,5,6,7 and 8 can be disregarded.Hence A,B and C must be 2,4 and 9 (not in order).
- Alkyl halides when treated with alcoholic KOH, undergo elimination reaction to form alkenes. Therefore

Major product from structure (2) $— C_2H_5CH = CHCH_3$

Major product from structure (4) $— C_2H_5 — \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2$

Major product from structure (9) $— CH_3CH = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} — CH_3$

- Two requirements need to be fulfilled to exist geometrical isomerism.
  a) Compound should contain double bond.
  b) Each double bonded carbon atom must have different groups attached to it.
- According to these requirements only structure (10) exhibit geometrical isomerism. Hence Structure (10) must be D
- D gave from A , therefore A must be structure (2) . Now B and C must be 4 and 9 vice versa.
  Further E and F must be 11 and 12 vice versa.
- When E and F allowed to react with HBr, according to the Markovnokov rule, the positive part (H) of the HBr goes to the double bonded carbon that already has the greatest number of hydrogen atoms. Therefore, both E and F give the same structure G which does not exhibit geometrical isomerism.

cold alkaline $KMnO_4$ or cold $KMnO_4$ (04)

(H)

KI (03)

(I)

$H_2/Pd/BaSO_4$ / Quinoline or H_2/ Lindlar catalyst (04)

(J)

$NaBH_4$ (03)

(K)

$KMnO_4$ or $H^+/KMnO_4$ Or $H^+/K_2Cr_2O_7$ or H+ / CrO_3 (04)

(L)

Anhydrous Al_2O_3 / Δ or Conc H_2SO_4 or P_2O_5 (04)

(M)

NH_3/Cu_2Cl_2 Or NH_3 /CuCl or Ammoniacal Cu Cl or NH_4OH/Cu_2Cl_2 (03)

(N)

PCl_5 or PCl_3 (03)

(O)

$LiAlH_4$ (03)

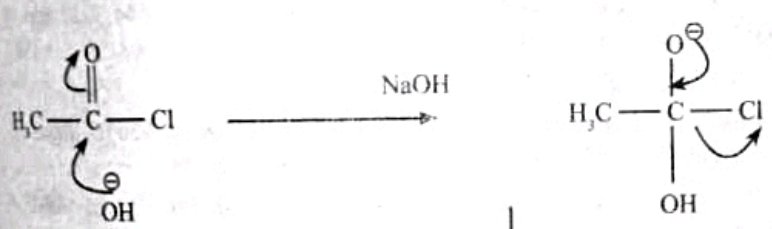
(P)

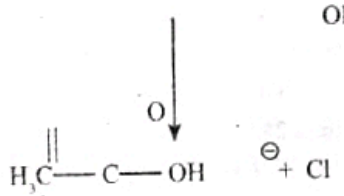
CH_3COCl Anhydrous $AlCl_3$ (04)

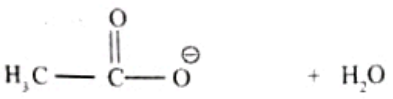
(Q)

[4(b): 35 marks]

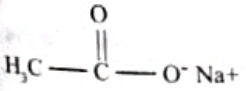
Answer -:







OR



(Note :- Lone pair need not be included for the award of marks)

[4c 16 marks]

Answers

Chemistry II GCE A/L 2015

Part B - ESSAY

$AB(s) \longrightarrow C(g) + D(g)$

a) i) First of all will find the enthalpy change (ΔH^0_m) of the above reaction.

Now we know $\Delta H^0_m = \Delta H^0_{products} - \Delta H^0_{reactants}$ [01]

$\Delta H^0_m = \Delta H^0_f(C) + \Delta H^0_f(D) - \Delta H^0_f(AB)$ [04]

Then $= [(-600) + (-500) - (-1208)]$ kjmol^{-1}

$= 108$ kjmol^{-1} [04 + 01]

Now will calculate the entropy change (ΔS^0_m) of the above reaction.

We know $\Delta S^0_m = \Delta S^0_{products} - \Delta S^0_{reactants}$ [01]

Then $\Delta S^0_m = \Delta S^0_f(C) + \Delta S^0_f(D) -- \Delta S^0_f(AB)$ [04]

$= (50) + (170) -- (100)]$ JK^{-1} mol^{-1}

$= 120$ JK-1mol-1

$= 120$ JK^{-1} mol^{-1} x $10^{-3} = 0.120$ kJ K^{-1} mol^{-1} [04 + 01]

Now $\Delta G^0_m = \Delta H^0_m -- T\,\Delta S^0_m$ [05]

Then $= 108$ kjmol^{-1} - 298K x 0.120 kjK^{-1}mol^{-1}

$= 72.2$ kjmol^{-1} [04 + 01]

Now it is clear that ΔG^0_m is positive quantity, i.e, $\Delta G^0_m > 0$ [05]

Therefore reaction is non-spontaneous at 298 K (25 ^{0}C)

ii) It is given that the reaction is spontaneous ($\Delta G^0_m < 0$) when the temperature is greater than T ^{0}C and the reaction is non – spontaneous ($\Delta G^0_m > 0$) when the temperature is less than T ^{0}C . Then at the temperature T ^{0}C the value of ΔG^0_m should be zero.

If $\Delta G^0_m = 0$

Then $\Delta H^0_m -- (T + 273)\ \Delta S^0_m = 0$ [05]

Then $(T + 273) = \dfrac{\Delta H^0_m}{\Delta S^0_m}$

$= 108$ kjmol-1 / 120 x 10-3 kJ K-1 mol-1 $= 900$ K

Then $T = 900 - 273 = 627\ ^0$C [05]

iii) ΔH^0_m and ΔS^0_m are assumed to be temperature independent. [05]

[5(a): 50 marks]

b) i) $AB(s) \rightleftharpoons C(s) + D(g)$

In this equilibrium system, you can see that the both AB and C are in solid state.
Hence those terms are not appeared in the Kp expression.
Suppose that the partial pressure of D (g) is P_D
Then, assuming ideal behavior of gas $Kp = P_D$ [05]
Now you can see that the system has only D(g) as gaseous spacies.
Therefore $K_P = P_D$ = Pressure of the container = 4.0×10^5 Pa [01 + 04]

We know that $K_P = K_C (RT)^{\Delta n}$. [05]
According to the system $\Delta n = 1 - 0 = 1$ [05]
Hence $K_P = K_C (RT)$
Then $K_C = K_P / RT = 4 \times 10^5$ Pa / 8.314 JK^{-1} mol^{-1} x 1203 K

$K_C = 4 \times 10^5$ Pa / 10000 Jmol^{-1} = 40 mol m^{-3} or (4×10^{-2} moldm^{-3}) [04 + 01]

[You will get the same marks (15), even if you calculated K_C by another correct method]

ii) Now the partial pressure of the D(g) in the equilibrium system is given as 7.5×10^5 Pa .

Suppose number of moles of D(g) in the equilibrium system is n_D, by using PV = nRT for D(g)

n_D = $P_D V / RT$ = 7.5×10^5 Pa x 2.00×10^{-3} m^3 / 8.314 JK^{-1} mol^{-1} x 1203 K
= 7.5×10^5 Pa x 2.00×10^{-3} m^3 / 10000 $Jmol^{-1}$
= 7.5×10^5 Jm-3 x 2.00×10^{-3} m^3 / 10000 $Jmol^{-1}$
= 0.15 mol

According to the stoichiometry of the equilibrium system, it is clear that
0.15/2 mol of X(g) need to be reacted to form 0.15 mol of D (g) [X : D = 1:2].

$$AB(s) + X(g) \rightleftharpoons C(s) + 2D(g)$$

Initial amount of gaseous species	=	0.225 mol	
Amount dissociated	=	0.15/2mol	
Amount produced	=	0.15 mol	
Amount of gaseous species at the equilibrium	=	(0.225 – 0.075)mol	0.15 mol
	=	0.15 mol	0.15 mol

Total amount at the equilibrium = 0.15 + 0.15 = 0.3 mol
Now mole fraction of D = x_D = 0.15 mol / 0.3 mol = ½

Similarly mole fraction of X = x_X = ½ [05 + 05 + 05]

We know P_D = Total pressure of the system (P_T) x mole fraction of D (x_D)

Therefore $P_T = P_D / x_D$ = 7.5×10^5 x 2Pa = 15×10^5 Pa
Then P_X = 15×10^5 x ½ Pa = 7.5×10^5 Pa

Now the K_p of the given reaction = $(P_D)^2 / P_X$

K_p = (7.5×10^5 Pa)2 / 7.5×10^5 Pa = 7.5×10^5 Pa

Now $K_p = K_C (RT)^{\Delta n}$
In this system $\Delta n = 2 - 1 = 1$

Therefore $K_p = K_C (RT)$
Then $K_C = K_p / RT$

K_C = 7.5×10^5 Pa / 8.314 JK^{-1} mol^{-1} x 1203 K
= 7.5×10^5 Pa / 10000 $Jmol^{-1}$
= 75 $molm^{-3}$ or ($7\text{-}5 \times 10^{-2}$ mol dm^{-3})

[even if you calculated K_C by another correct method you will get the same marks]

(iii) (I) In the given system C is in a solid state and therefore its concentration does not change even if some amount of C is removed from the system. As such it does not effect to the equilibrium of the system. [05+05]

(II) As the amount of D decreases, according to the Le Chatlier principal the equilibrium of the system shifts to the right. [05 + 05]

6) (i) Let us suppose that the solubility of the sparingly soluble salt XA is S $moldm^{-3}$, then we have [5(b) : 100 marks]

$$XA(s) \rightleftharpoons X^+(aq) + A^-(aq)$$
S $moldm^{-3}$ S $moldm^{-3}$

But the solubility is given in $mgdm^{-3}$ and therefore it is need to be converted it into $moldm^{-3}$.

Now given solubility = 2.01 $mgdm^{-3}$ = 2.01×10^{-3} gdm^{-3} = 2.01×10^{-3} /150 $moldm^{-3}$
Now molar mass of XA is 150 $gmol^{-1}$

Therefore solubility of XA = $2{,}01 \times 10^{-3}$ / 150 $moldm^{-3}$ = 1.34 x 10-5 $moldm^{-3}$

Hence S = 1.34×10^{-5} $moldm^{-3}$.

Now K_{sp} of XA = $[X^+(aq)][A^-(aq)]$ = (1.34×10^{-5} $moldm^{-3}$) (1.34×10^{-5} $moldm^{-3}$)
= 1.79×10^{-10} $mol^2 dm^{-6}$ or 1.8×10^{-10} $mol^2 dm^{-6}$

(i) NaA is soluble in water and therefore it is completely ionized in the aqueous medium According to the following way.

$NaA \longrightarrow Na^+(aq) + A^-(aq)$

The essential condition for the precipitation of an electrolyte is that its ionic product Should exceed its solubility product.

Now for XA salt, $K_{sp} = [X^+(aq)][A^-(aq)]$

Then $[A^-(aq)] = K_{SP} / [X^+(aq)]$ [05]

K_{SP} value of the salt XA has already been determined and the concentration of X is given as 0.100 moldm^{-3}.

Therefore $[A^-(aq)] = 1.8 \times 10^{-10}$ mol^2 dm^{-6} / 0.100 moldm^{-3}

$[A^-(aq)] = 1.80 \times 10^{-9}$ moldm^{-3} [04 + 01]

Now you can see that the precipitation of XA will occur when the concentration of A^- (aq) is Just exceed the above value.

Now for YA salt, $K_{SP} = [Y^+(aq)][A^-(aq)]$

Then $[A^-(aq)] = K_{SP} / [X^+(aq)]$

$[A^-(aq)] = 1.8 \times 10^{-7}$ mol^{2}dm^{-6} / 0.100 moldm^{-3}

Therefore $[A^-(aq)] = 1.80 \times 10^{-6}$ moldm^{-3} [04 + 01]

The precipitation of YA will occur when the concentration of A^- (aq) is just exceed the above Value.
Now it is clear that the concentration of A^- ion need to precipitate XA salt is less than that of YA. As a result, when adding solid NaA slowly to the solution XA precipitates first. [05]

Alternative answer for (I)
XA an YA has same stoichiometry [05]
According to the given data $[X^+(aq)] = [Y^+(aq)]$ [05]
We found that K_{SP} of (XA) < K_{SP} of (YA)

Therefore, when adding solid NaA into the solution the K_SP value of XA will be satisfied First. As a result XA precipitates first. [05]

(II) The concentration of A^- ion, when the second salt (YA) begins to precipitate is 1.80 X 10^{-6} moldm^{-3}.At this moment XA has already been precipitated and therefore ionic product of XA in the solution is equal to its K_{SP} value.

Now K_{SP} (XA) $= [X^+(aq)][A^-(aq)]$
$[X^+(aq)]$ left in the solution $= 1.80 \times 10^{-10}$ mol^{2}dm^{-6} / 1.80×10^{-6} moldm^{-3} [05]

$= 1.0 \times 10^{-4}$ moldm^{-3} [04 + 01]
[6(a) : 50 marks]

(i) At the equivalent point

$HA(aq) + NaOH(aq) \longrightarrow NaA(aq) + H_2O(l)$ [04 + 01]

NaA ionized completely into Na^+ and A^- ions in the solution.
Now A^- ions undergo hydrolysis with water according to the following way.

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$ [04 + 01]

According to the above hydrolysis reaction it is clear that
$[HA(aq)] = [OH^-(aq)]$ [04 + 01]

It is given that $K_b = [HA(aq)][OH^-(aq)] / [A^-(aq)]$
Therefore $K_b = [OH^-(aq)]^2 / [A^-(aq)]$

Now $[OH^-(aq)] = [K_b [A^-(aq)]]^{1/2}$
Hence $\log [OH^-(aq)] = 1/2 \log K_b + 1/2 \log [A^-(aq)]$
When throughout the above equation multiplied by minus sign, we get

$-\log [OH^-(aq)] = -\frac{1}{2} \log K_b - \frac{1}{2} \log [A^-(aq)]$ [04 + 01]
Then $POH = 1/2\ pK_b - \frac{1}{2} \log [A^-(aq)]$

It is given that $PH + POH = pK_w$ and $pK_a + pK_b = pK_w$

Hence $POH = pK_w - PH$ and $pK_b = pK_w - pKa$

When above values are substitute into the equation $POH = 1/2pK_b - 1/2\log [A^-(aq)]$

We get $pK_w - PH = 1/2pK_w - 1/2pK_a - 1/2\log [A^-(aq)]$

Then $PH = 1/2\ pK_w + 1/2pK_a + 1/2\log [A^-(aq)]$

b (ii) $HA(aq) + NaOH(aq) \longrightarrow NaA(aq) + H_2O(l)$

The concentrations of both HA and NaOH are the same and therefore according to the Stoichiometric of the reaction the volume of HA solution used should be equal to that Of NaOH at the equivalence point. Now suppose the volume used at the equivalence Point is V cm^3 .

Now number of moles of HA used at the equivalence point $= \frac{1 \times 10^{-3}\ V\ cm^3}{10^3} = 10^{-6}V$ mol

number of moles of NaOH used at the equivalence point $= 10^{-6}$ V mol .

Therefore number of moles of NaA formed at the equivalence point $= 10^{-6}$ V mol

NaA is completely ionized in the solution according to the following way

$NaA(aq) \longrightarrow Na^+(aq) + A^-(aq)$

Therefore number of moles of A^- ions in the final solution is also 10^{-6}Vmol
Now you can see that the final volume of the solution is doubled (2V).

Hence the concentration of A^- ions in the solution $= \frac{10^{-6}\ V \times 1000}{2V} = 5 \times 10^{-4}$ moldm^{-3} .

Now by using the equation that has derived in b(i)

$PH = \frac{1}{2}\ pK_w + \frac{1}{2}\ pK_a + \frac{1}{2}\log [A^-(aq)]$
If the $Ka = 1.8 \times 10^{-5}$ moldm^{-3} , then $pKa = -\log 1.8 \times 10^{-5} = -\log 1.8 + -\log 10^{-5} = 4.74$.
Now $PH = \frac{1}{2} \times 14 + \frac{1}{2} \times 4.74 + \frac{1}{2}\log (5 \times 10^{-4})$

PH = 7.69 or any value in the range of 7.69 to 7.72

Alternative answer for b (ii)

We know $K_b \times K_a = K_w$, therefore $K_b = K_w / K_a$

But we know $K_b = [OH^-(aq)]^2 / [A^-(aq)]$

Therefore, $K_w / K_a = [OH^-(aq)]^2 / [A^-(aq)]$

Therefore, $\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[OH^-(aq)]^2}{[A^-(aq)]}$

Then $[OH^-(aq)] = 5.24 \times 10^{-7}$ moldm^{-3} .

Therefore, PH = 7.72 .

b (iii) When 500 cm^3 of 2×10^{-3} moldm^{-3} $Y^+(aq)$ solution is added to a 500 cm^3 of 2×10^{-3} moldm^{-3} solution of HA the both species are diluted each other.

Therefore, concentration of $Y^+(aq)$ in the mixed solution is
$2 \times 10^{-3} / 2 = 10^{-3}$ moldm^{-3}.

When YA (s) begins to precipitate, its K_{sp} value should be equal to its ionic products

Hence $K_{sp} = 1.8 \times 10^{-7}$ mol^2 dm^{-6} $= ([Y^+(aq)]\ [A^-(aq)])$

Now $[A^-(aq)]$ needed to precipitate YA $= 1.8 \times 10^{-7}$ mol^2 dm^{-6} / 10^{-3} moldm^{-3} .

$= 1.8 \times 10^{-4}$ moldm^{-3}

Now HA is partially ionized as follows
$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Then $K_a = [H^+(aq)]\ [A^-(aq)] / HA(aq)$

K_a value of HA acid is very small and therefore HA is very weak acid. As such concentration of HA assumed to be same as its initial concentration (10^{-3} moldm^{-3}).

therefore 1.8×10^{-5} moldm^{-3} = [H$^+$ (aq)] 1.8×10^{-4} moldm^{-3} / 10^{-1} moldm^{-3}

therefore, [H$^+$ (aq)] = 1.0×10^{-4} moldm^{-3}

then PH = 4 [04 + 01]

[05]

ternative answer for b (iii).

We know that K_a = [H$^+$ (aq)] [A$^-$ (aq)] / [HA (aq)]

Then [H+ (aq)] = K_a [HA(aq) / [A$^-$(aq)]

log [H$^+$(aq)] = log Ka + log [HA(aq)] – log[A$^-$(aq)]

Now throughout the equation multiplied by minus sign

We get - log [H$^+$(aq)] = - log K_a + log[A$^-$ (aq)] – log [HA(aq)]

Then PH = PK_a + log { [A$^-$ (aq)]/ [HA(aq)}

[04 + 01]

= 4.74 + log { 1.8×10^{-4}/ 10^{-1} }

[05]

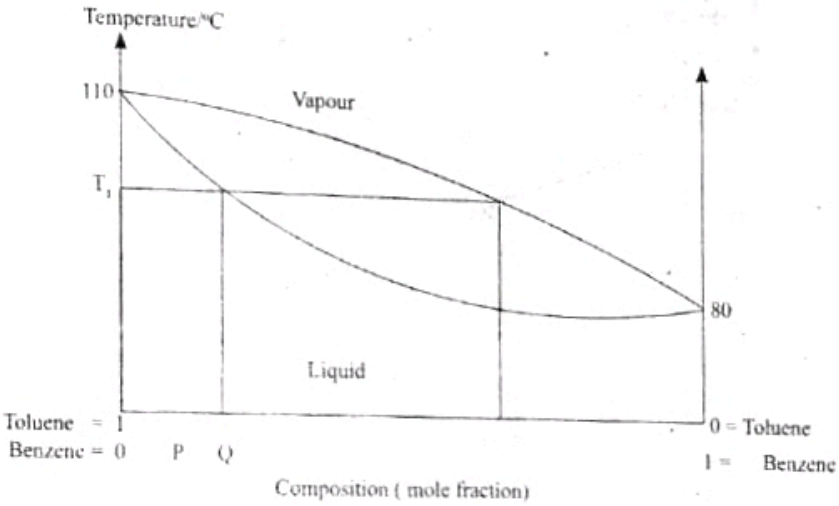
PH = 4.74 - 0.74 = 4

[05]

-: The (01) mark is allocated for the physical state.

[6(b): 70 marks]

(i) - (ii)



aking process -:

- Boiling point of pure benzene (mole fraction = 1.0) is 80°C while boiling point of Pure Toluene (mole fraction = 1) is 110°C.
- Vapour curve should be above the liquid curve.
- Whatever the composition, at the boiling point the temperature of the liquid Should be equal to the temperature of vapour phase.
- Consequently in order to obtain the composition of vapour at T_1 a line need to be drawn parallel to composition axis from T_1 until it meets the vapour curve.

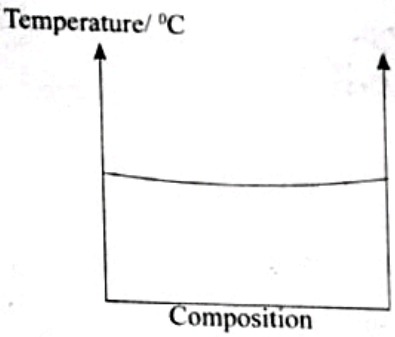
(III) Boiling point of benzene is less than that of Toluene and therefore benzene is more volatile than toluene. As a result, at T1 temperature, benzene contains more in the Vapour phase than that in liquid.

Composition :vapour> liquid for benzene. [05]

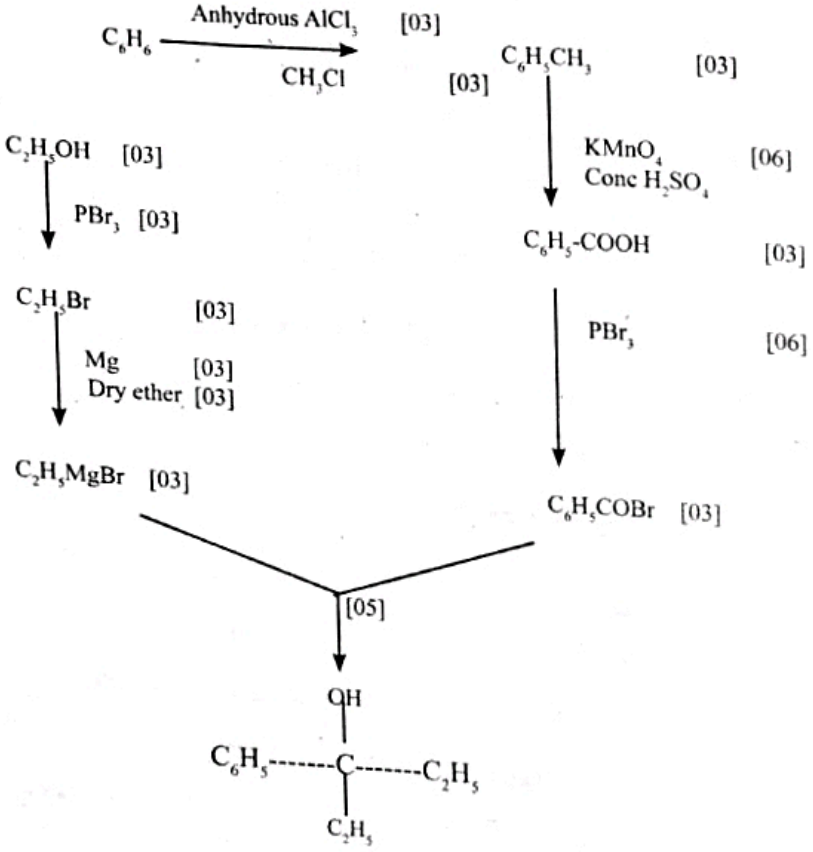
Fractional distillation [05]

(iv) If the boiling points of two fully miscible liquids in the binary mixture are the same,liquid curve should be coincided with its vapour curve at any composition. [05]

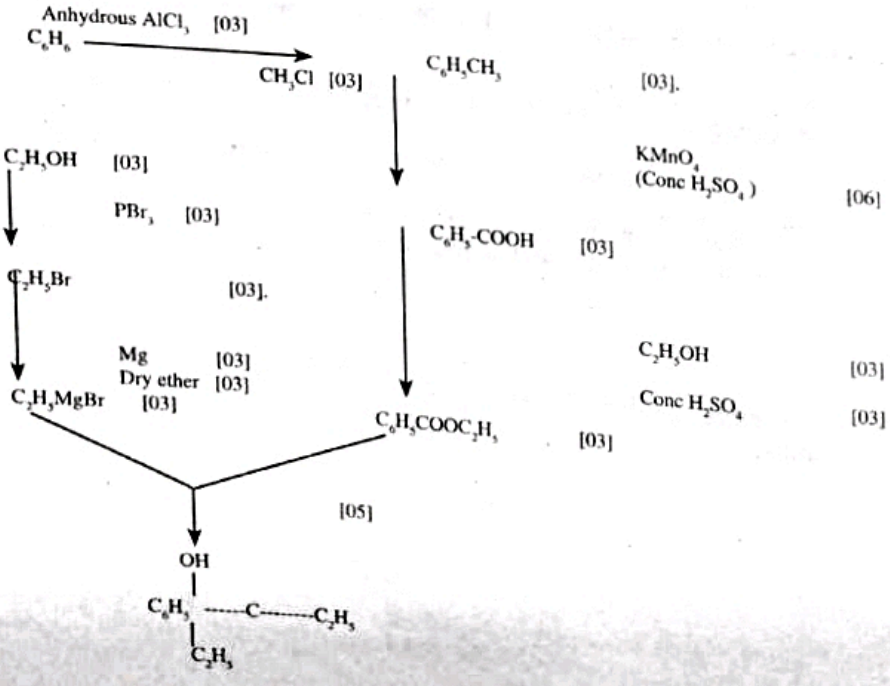
[6(b): 70 marks]



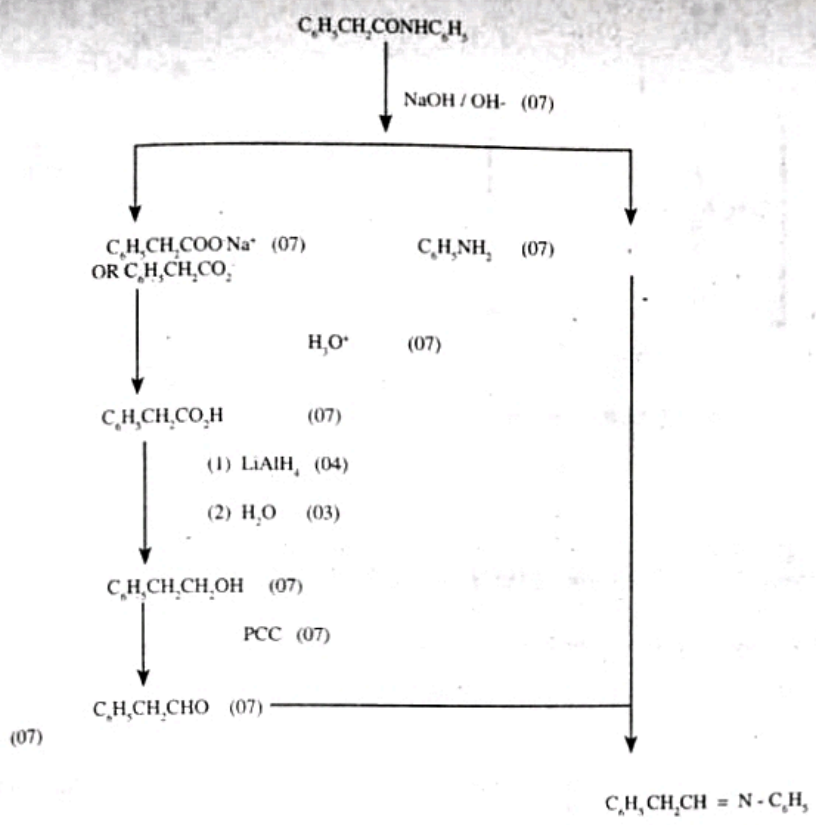
7 (a)



Alternative answer for 7(a)

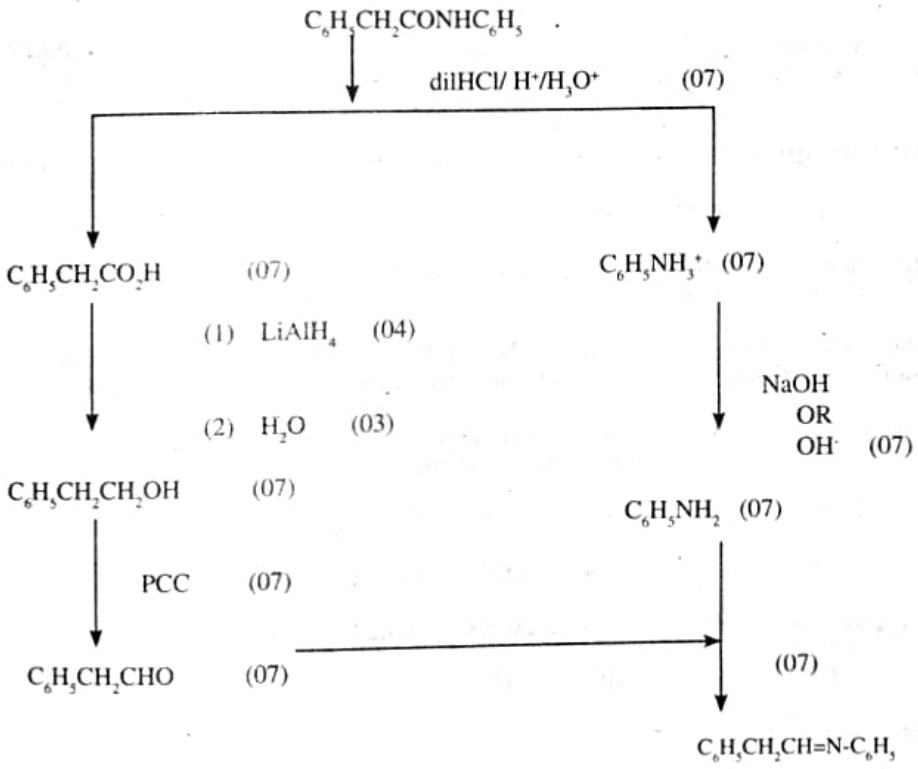


[03 X 15 + 05 =



[07 x 10 = 70 marks]

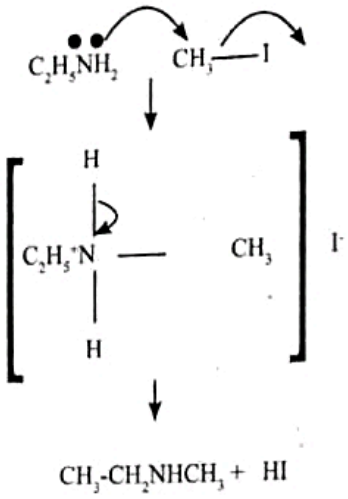
ive answer for 7(b)



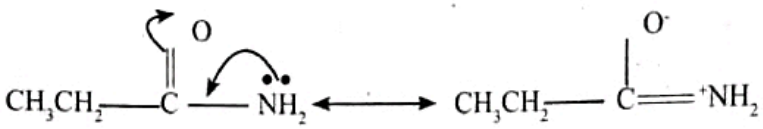
7(b): 70 marks

Nucleophile [ethylamine has lone pair,on the N atom, which can be donated In a reaction to positively charge or electron deficient specie] (05)

ii)



(20 marks)



(iii)

Due to above resonance the lone pair on N in propionamide is less available to take part in a nucleophilic reaction.

[7 (c): 30 ma

8 (a)

(i) Answer

$M = Na$, $M_1 = Na_2O_2$, $M_2 = NaOH$, $M_3 = H_2O_2$, $M_4 = O_2$
$M_5 = H_2$, $M_6 = NaAlO_2$, $M_7 = Al(OH)_2$, $T = Al$

[05 x

Thinking process-:

- It is given that metal M belongs to s- block and burns with a yellow flame. Therefore M should be Na.
- You know that Na burns in excess of oxygen to give Na_2O_2 and therefore M_1 should be Na_2O_2 .

$$2Na + O_2 \longrightarrow Na_2O_2$$

- Na_2O_2 reacts with cold water to give NaOH clear solution and H_2O_2 which is Covalent. Therefore M_2 is NaOH whilst M_3 is H_2

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

- H_2O_2 reduced Ag2O into Ag with evolution of diatomic gas O_2. Therefore M_4 should be O_2 .

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + O_2 + H_2O .$$

- Metals, except amphoteric metals, do not react with NaOH. But T reacts with excess of NaOH to give colourless gas and there T should be amphoteric metal such as Al,Zn, Sn, Pb, etc. Now colourless gas M_5 should be H_2
- If gelatinous precipitate is formed when HCl is added dropwise to the water Soluble compound the precipitate M_7 should be Al(O and therefore metal T Should be Al while water soluble compound M_6 is $NaAlO_2$.

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2 .$$

$$NaAlO_2 + HCl + H_2O \longrightarrow Al(OH)_3 \downarrow + NaCl$$

$Al(OH)_3$ gives water soluble $AlCl_3$ with excess of dilute HCl acid.

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

(ii) Answer -: NaOH (02) and O_2 (03)

Thinking process-:

- When Na_2O_2 (M_1) reacts with hot water instead of cold water, it gives O_2 gas due to dissociation of H_2O_2 .

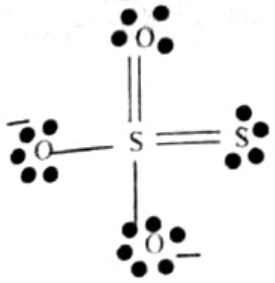
$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

[8 (a) : 50 marks]

[10]

[04]

Answer :- (i) Q = $Na_2S_2O_3 . 5H_2O$



ing process -:
The substance which turns anhydrous $CuSO_4$ blue should be water.

$CuSO_4 + 5H_2O \longrightarrow CuSO_4\ 5H_2O$

Blue

Mg when burning in SO_2 gas it gives white MgO and yellow S .

$2Mg + SO_2 \longrightarrow 2\ MgO + S\downarrow$

Therefore colourless gas evolved when Q is reacted with dilute HCl should be SO_2. Hence Q may be either sulphite or thaosulphate. But it says that the solution turns turbid when Q react with dilute HCl. Solution turned turbid due to formation of S and therefore Q should be thaosulphate.

Generally one mole of thaosulphate crystal has five moles of crystalline water. Therefore Q should be $M_xS_2O_3 . 5H_2O$ where M is cation of the compound.

Now suppose atomic mass of M is A ,then

Molecular mass of Q = XA + 2x 32 + 3 x 16 + 5 x 18 = 248

Therefore XA = 248 – 202 = 46

If X is 1 then, A = 46 [there is no such a cation which atomic mass is 46]
If X is 2 then, A = 23. Therefore A should be Na

Now it is clear that Q should be $Na_2S_2O_3 . 5H_2O$.

(1) $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + S\downarrow + SO_2 + H_2O$

OR

$S_2O_3^{2-} + 2H^+ \longrightarrow S\downarrow + SO_2 + H_2O$ [05]

$2Mg + SO_2 \longrightarrow 2MgO + S\downarrow$ [05]

(2) $Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$ [05]

OR

$S_2O_3^{2-} + 2AgNO_3 \longrightarrow Ag_2S_2O_3\downarrow + 2NO_3^-$

$Ag_2S_2O_3 + H_2O \xrightarrow{\Delta} Ag_2S\downarrow + H_2SO_4$ [05]

(3) $Pb(NO_3)_2 + Na_2S_2O_3 \longrightarrow PbS_2O_3\downarrow + 2NaNO_3$ [05]

OR

$Pb(NO_3)_2 + S_2O_3^{2-} \longrightarrow PbS_2O_3\downarrow + 2NO_3^-$

$PbS_2O_3 + H_2O \xrightarrow{\Delta} PbS\downarrow + H_2SO_4$ [05]

te : If the precipitate is not shown with an arrow in an equation, award only (04) marks For that question. For S, instead of the arrow, ding' can be accepted.]

(iii) You can give two of the following uses of Q

- Iodometry titrations
- photographic processing.
- Antidote for cyanide poisoning in medicine.
- preparation of colloidal sulphur.
- Gold extraction.
- neutralization of bleach, chlorinated water.

[03 + 03]

8 (c) Will start from the end of the question.
25 cm_3 of Y solution when heated with 30 cm^3 of 0.2 $moldm^{-3}$ Fe^{2+} solution, certain amount of Fe^{2+} ions oxidized to Fe^{3+} ions and remaining Fe^{2+} ions reacted with acidified $KMnO_4$ solution according to the following way.

$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ ——— (1)

Now, amount of $KMnO_4$ used $= 0.02 \times 20/10^3$mol
According to the above equation molar ratio of Fe^{2+} : MnO_4^- is 5:1
Therefore, amount of Fe^{2+}reacted $= 5 \times 0.02 \times 20 \times 10^{-3}$mol
Number of moles of Fe^{2+} ions in the initial 30 cm3 of the solution $= 0.2 \times 30 \times 10^{-3}$mol

Hence
amount of Fe^{2+} ions reacted with ClO_3^- ions
$= [0.2 \times 30 \times 10^{-3}] - [5 \times 0.02 \times 20 \times 10^{-3}]$ mol
$= 4 \times 10^{-4}$mol

Fe^{2+} ions reacted with ClO_3^- according to the following way.

$6Fe^{2+} + ClO_3^- + 6H^+ \longrightarrow 6Fe^{3+} + Cl^- + 3H_2O$ ——— (2)
You can see that molar ratio between Fe_3^+ and ClO_3^- is 6: 1.

Now, amount of ClO_3^- containing in 25 cm^3 of Y solution $= 4 \times 10^{-4}/6$ mol
According to the equation (2) one mole of ClO_3^- gives one mole of Cl^- ions.

Therefore amount of Cl^- ions formed by the reduction of ClO_3^- ions $= 4 \times 10^{-4}/6$ mol

When $AgNO_3$ solution is added to the above solution its reacted with Cl^- ions in the solution to form AgCl precipitate and the molar ratio of Cl- : AgCl is 1:1.

$Cl^- + AgNO_3 \longrightarrow AgCl\downarrow + NO_3^-$ ——— (3)

Therefore amount of AgCl precipitated is also $= 4 \times 10^{-4}/6$ mol
Therefore, mass of AgCl precipitated $= 4 \times 10^{-4} \times 143.5/6$ g =

ClO_3^- ions reduced to Cl^- ions by SO_2 and in addition to that certain amount of Cl^- ions are presented due to ionization KClin the solution. Therefore, when $AgNO_3$ is added its reacted with the both Cl^- ions to give AgCl precipitate. According the question total mass of AgCl precipitated was 0.135 g.

Therefore the mass of AgCl formed from the Cl^- ions due to ionization of KCl is

$[0.135 - 4 \times 10^{-4} \times 143.5/6]$ g $= 0.039$ g

$KCl + AgNO_3 \longrightarrow AgCl + KNO_3$ ——— (4)

Since molar ratio between KCl and AgCl is 1:1

Amount of KCl in the Y solution = amount of AgCl = 0.039g/ 143.5 $gmol^{-1}$.

Therefore mass of KCl in 25 cm^3 of Y solution
$= 0.039$ g x 74.5 $gmol^{-1}$ / 143.5 $gmol^{-1}$ = 0.020g
Hence mass of KCl in 250 cm3 of Y solution = 0.020 x 250/25 = 0.20 g

Therefore percentage of KCl in the mixture X = 0.2 X 100/ 1.1 = 18.2%

Now the mass of $KClO_3$ in 25 cm^3 of the solution Y = $4 \times 10^{-4} \times 122.5/6 = 0.082$ g
Hence the mass of $KClO_3$ in 250 cm^3 of Y solution = 0.082 g x 250/ 25 = 0.82 g

Therefore percentage of $KClO_3$ in the mixture X = 0.82 X 100/ 1.1 = 74.6%

[8c : 50 m
[03 + 03

9(a) (i) Answer = NH_3 , air and water

(ii) Answer:
$4NH_3(g) + 5O_2(g)$ (excess) $\xrightarrow[\text{Catalyst Pt containing 10\% Rh}]{\text{1 – 9 (atm)}}$ $4NO(g) + 6H_2O(g)$ ——(1)
850 – 1250 ^{0}C

Mixture cooled and maintain the temperature 150^{0}C or less than 150^{0}C

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

$4NO_2(g) + 2H_2O(l) + O_2(g) \xrightarrow[\text{(cold air)}]{\text{Extensive cooling}} 4HNO_3(l)$ (3)

OR

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

$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$

physical states are not required

(iii) First of all it is need to be obtained the relation between the initial reaction and final Product HNO_3. For that we will multiply the reaction (2) by 2 and add to the reaction (1).

Reaction(2) x 2 $\quad 4NO(g) + 2O_2(g) \longrightarrow 4NO_2(g)$

\+

Reaction (1) $\quad 4NH_3(g) + O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$

$4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + H_2O(g)$ ——— (4)

Now we will add the above reaction (4) to the reaction (3). Then you will get the following

$4NH_3(g) + 8O_2(g) \longrightarrow 4HNO_3(l) + 4H_2O(l)$ ——— (5)

Now according to the above reaction (5), 4 moles of HNO_3 acid can be obtained from 8 moles of O_2

therefore number of moles of HNO_3 can be obtained from one mole of O_2 = 4/8 = ½ mol.
Hence number of moles of HNO_3 can be obtained from 1000 mol of O_2 = 1000 x1/2 mol
= 500 mol [10]

(iv) You can mention any three of the following.

- Synthesis of fertilizers such as NH4NO_3 , KNO_3
- synthesis of food preservatives ($NaNO_2$, $NaNO_3$)
- To make aqua regia .
- Synthesis of explosive substances (TNT, TNG)
- $AgNO_3$ preparation for use in photographic films.
- To clean soldering surfaces
- To make gun powder (KNO_3)
- to make lacquers
- preparation of Drugs.
- Manufacturing of plastics

[03 x 3]

v) HNO_3 decomposes when exposed to light and gives a yellow colour due to the formation of NO_2 [04]

$4HNO_3(l) \longrightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$ [03]

vi) I) $S(g) + 6HNO_3 \xrightarrow{\Delta} H_2SO_4 + 6NO_2 + 2H_2O$

II) $Cu + 4HNO_3$ (conc) $\xrightarrow{\Delta} Cu(NO_3)_2 + 2NO_2 + 2H_2O$

III) $3Cu + 8HNO_3$ (dil) $\xrightarrow{\Delta} Cu(NO_3)_2 + 2NO + 4H_2O$ [05 X 3]

[9(a) = 75 marks]

9b)

(i) N_2 has a triple bond and therefore has a high bond dissociation energy. Consequently difficult to break this bond. [06]

(ii) (1) Lightening (atmospheric fixation) (2) Fixation of nitrogen in plants by bacteria (biological fixation) [04 + 04]

(iii) Haber process [04]

(iv) NO_2 , NO [04 + 04]

(v) The combustion of petroleum in automobile engines produces hydrocarbons as well as oxides of nitrogen. NO_2 is an effective absorber of ultraviolet rays present in sun light. Thus when exposed to sun light, NO_2 undergoes photolysis giving NO and O (atomic oxygen).

$NO_2 \xrightarrow{h\nu} NO + O$ [03]

The oxygen atom formed reacts with O_2 to form ozone.

$O + O_2 + M \longrightarrow O_3 + M^*$ [04]

[M is a external body such as N_2, airborne particles which removes some of the excess Energy of the reaction as M*]

Similarly the following reaction is also taking place

$O + H_2O \longrightarrow 2OH^*$

NO_2, NO, O_3,O and OH^* convert airborne chemicals to produced various organic compounds. [04]

(vi) Any two of the following.
1) PAN (peroxyacetyl nitrate)
2) CH_3ONO_2 (methyl nitrate) (3) PBN (peroxybenzoyl nitrate)

(vii) (1) It is toxic to plants (2) reduces visibility (3) effect on fabric, rubber [04 + 0

(viii) The main nitrogen compound that contributes to the greenhouse effect is N_2O

(ix) NO and NO_2 [02 + 0

(x) $NH_4NO_2(s) \xrightarrow{\Delta} N_2(g) + 2H_2O$ [04 +

$(NH_4)_2Cr_2O_7(s) \xrightarrow{\Delta} N_2(g) + Cr_2O_3(s) + 4H_2O$

Note: physical states are not required.

10(a) [9 (b)= 75ma

(i) Answer -: +3 or +III

Thinking process -:

- These complex compounds consist of one chromium ion, three chlorine atoms and variable number of water molecu
- Oxidation number of the chlorine atoms which combined to chromium ion either with ionic or covalently should -1.
- Since there are three Cl atoms the algebraic sum of the oxidation numbers of these Cl atoms should be -3 (-1 x 3)
- Water molecules are neutral.
- Since complex compound is neutral, in order to balance the -3 charge, the charge On the chromium ion should +3 .

(ii) Answer -: $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6 3d^3$

(iii) Answer -:

A : $[Cr(H_2O)_6]Cl_3$ OR $[Cr(H_2O)_6]_3 + 3Cl^-$

B: $[CrCl(H_2O)_5]Cl_2$ OR $[CrCl(H_2O)_5]_2 + 2Cl^-$

C: $[CrCl_2(H_2O)_4]\ Cl_2$ OR $[\ CrCl_2(H_2O)_4] + Cl^-$

D: $[\ CrCl_3\ (H_2O)_3\ ]$ OR $[\ Cr(H_2O)_3Cl_3]$

Thinking process -:

- Since the complex part has octahedral geometry the number of ligands combined to Cr ion should be six.
- The oxidation number of both Cr ion and the complex part in A is +3 and therefore all ligands which combined to Cr in the complex part should be neutral. Hence complex part should be $[Cr(H_2O)_6]^{3+}$. Therefore A should be $[Cr(H_2O)_6]Cl_3$.
- The charge of the complex part of B is +2 and therefore only one chlorine atom should be combined to Cr ion. remaining five ligands in the complex part should be neutral water molecules. Hence the complex part should $[CrCl(H_2O)_5]^{2+}$. Now we can identify the structure of B as $[CrCl(H_2O)_5]Cl_2$.
- Similarly you can determine the structures of C and D

(iv) Answer -: hexaaquachromium(III) chloride

(v) Answer -: Add $AgNO_3$ or $Pb(NO_3)_2$ solution into each solution A and D. A gives white precipitate (AgCl /$PbCl_2$) but D d not.

OR [10]

Heat with conc H_2SO_4 and $K_2Cr_2O_7$(Chromyl chloride test). A gives deep red Vapour but D does not.

Thinking process-:

- The structure of A is $[Cr(H_2O)_6]^{3+}\ 3Cl^-$. Therefore it gives Cl^- ions in the aqueous medium
- But the structure of D is $[CrCl_3\ (H_2O)_3]$ and therefore Cl atoms in this compound
- Attached to Cr ion with dative bonds. As such it does not give Cl^- ions in the aqueous Solution.

(vi) Answer -: $[Cr(OX)_3]^{3-}$ [10] wit

Thinking process-:

- Since the complex part has octahedral geometry there should be six bonds around Cr Ion.
- Each C_2O_4 ion can be formed two dative bonds and therefore three $C_2O_4^{2-}$ ions bondedthre to Cr^{3+} ion with six dative bonds.
- The charge of three $C_2O_4^{2-}$ ions is -6 (3 x -2) and therefore net charge of the complex part which consist of Cr ion and three oxalate ions should be -3.
- Now it is crystal clear that the structure of ion is $[Cr(C_2O_4)_3]^{3-}$. But you are asked to us Abbreviation " OX" to denote the oxalate ion. Therefore answer should be $[Cr(OX)_3]^{3-}$. [10(a) : 75 marks]

10(b) (i) Answer -:
Now it has shown that the electrode $E^0 M_1^{2+}(aq)/ M_1(s)$ is more negative than $E^0 M_3^{2+}(aq) / M_3(s)$ [08]

Therefore oxidation reaction takes place at M_1 and reduction reaction takes place at electrode M_3. Hence M_1 acts as a anode while M_3 acts as a cathode.

Now Cell-1 , Anode is M_1 andcathodeis M_2
Cell - 2, Anode is M_2 and cathode is M_3 [04]

Alternative answer-: According to the given diagram electrons are given out from M_1 (oxidation) and therefore, M_1 is the anode. Electrons are taken up by M_3 (reduction) and therefore, M_3 is the cathode.
Now you must be able to identify anode and cathode in each Cell.

(ii) Answer-:

Cell-1 -: At the anode $M_1(s) \longrightarrow M_1^{2+}(aq) + 2e$ [04]

At the cathode $M_2^{2+}(aq) + 2e \quad M_2(s)$ [04]

Cell-2 -: At the anode $M_2(s) \longrightarrow M_2^{2+}(aq) + 2e$ [04]

At the cathode $M_3^{2+}(aq) + 2e \longrightarrow M_3(s)$ [04]

(iii) Answer -:

Reading P = $E^0 M_3^{2+}(aq) / M_3(s) - E^0 M_1^{2+}(aq) / M_1(s)$

OR

Reading P = $E^0_{cathode} - E^0_{anode}$ [04]

= 0.34 – (-2.36) V [04]

= 2.7 V [01 + 01]

Alternative answer -:

Reading P = $E_{cell-1} + E_{cell-2}$

P = $E^0 M_2^{2+}(aq)/ M_2(s) - E^0 M_1^{2+}(aq)/M_1(s) + E^0 M_3^{2+}(aq)/M_3(s) - E^0 M_2^{2+}(aq)/M_2(s)$

= $E^0 M_2^{2+}(aq)/M_2(s) -- (--2.36) + (+ 0.34) -- E^0 M_2^{2+}(aq)/M_2(s) = 2.7$ V

(iv) $E^0_{cell-1} = E^0 M_2^{2+}(aq) / M_2(s) -- E^0 M_1^{2+}(aq) / M_1(s)$ [04]

1.6 = $E^0 M_2^{2+}(aq) / M_2(s) -- (-- 2.36)$ [04]

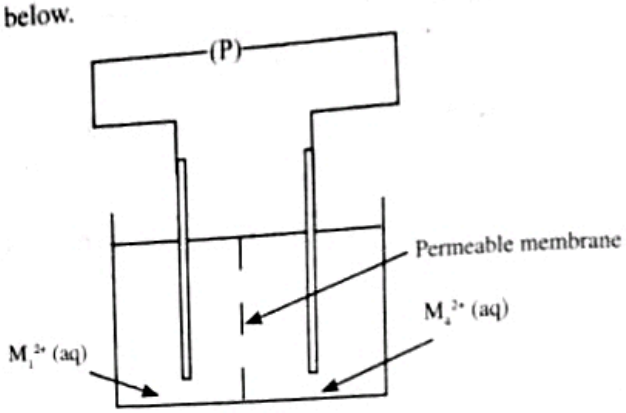
Therefore $E^0 M_2^{2+}(aq) / M_2(s)$ = 1.6 – 2.36 = -- 0.76 V [03 + 01]

(v) $E0_{cell-2} = E^0_{cathode} - E^0_{anode}$ [04]

= 0.34 -- (--0.76) V [04]

= 1.1 V [01 + 01]

(vi) First of all construct a cell given below.



[cell can be drawn with salt bridge instead of permeable membrane]

Either diagram or cell notation in either direction and measure P.
If P = Digital voltmeter reading (assuming a positive reading)

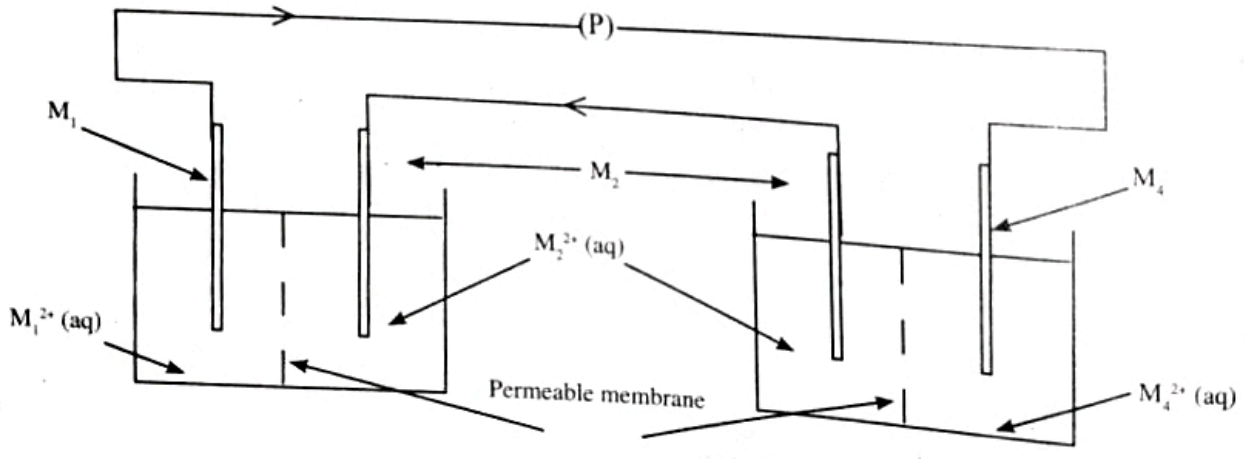
$P = E^0M_4^{2+}(aq)/ M4(s) -- E^0M_1^{2+}(aq)/ M_1(s)$

Since $E^0M_1^{2+}(aq)/M_1(s)$ is known

$E^0 M_4^{2+}(aq) / M_4(s)$ can be obtained.

Note : instead of M_1, M_2 or M_3 can be used.

Instead of the above cell it is possible to use the cell given in the question with necessary changes to determine the value of $E^0M_4^{2+}(aq)/M_4(s)$.



[10(b) : 75 marks]