

CHEMISTRY

CLASS : XI

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SHEET SOLUTION

PERIODIC TABLE & PERIODICITY

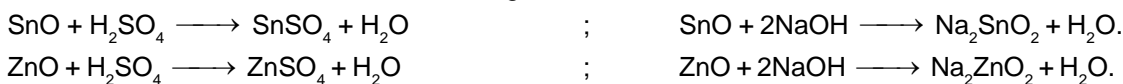
EXERCISE # 1

PART - I

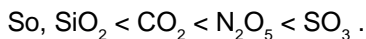
- A-8.** (i) Alkali metal, potassium forms K^+ (number of electrons = 18) which is isoelectronic with P^{3-} (number of electrons = 18) \rightarrow Q.
(ii) Transition element, chromium show maximum oxidation state of +6 in $Cr_2O_7^{2-}$ and CrO_4^{2-} and they are coloured \rightarrow S.
(iii) Noble gas, Kr has largest atomic radius because radius is expressed as vander Waal's radius and there is interelectronic repulsions due to completely filled outer most shell. Inert gas has highest first ionisation energy in the respective period because of stable valence shell electron configuration \rightarrow T.
(iv) Element ($Z = 13$), aluminium has intermediate value of electronegativity and therefore its oxide is amphoteric in nature \rightarrow R.
- A-10.** d-block has 10 columns.
- A-12.** Electron configuration is $[Ar]^{18} 3d^{10} 4s^2 4p^3$. As last electron enters in p-subshell it is p-block element and thus its group number is equal to $10 + 5 = 15$. As principal quantum number of valence shell is 4, so it is 4th period element.
- B-3.** ${}_{30}Zn - 1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^2$
 $\sigma = 0.35 \times 1 + 18 \times 0.85 + 10 \times 1 = 25.65$
 $\Rightarrow Z_{\text{eff}} = 30 - 25.65 = 4.35$
- B-8.** Due to 4f-orbital electrons (poor shielding effect) there is increase in effective nuclear charge which leads to the contraction of the size of atoms. This is called lanthanide contraction.
- C-2.** (A) Al^{3+}, Mg^{2+}, Na^+ and F^- are isoelectronic and thus follows the order ${}_{13}Al^{3+} < {}_{12}Mg^{2+} < {}_{11}Na^+ < {}_9F^-$. Al belongs to third period and has no charge so it is largest. $Na^+ = 102 \text{ pm}; Mg^{2+} = 72 \text{ pm}; Al = 143 \text{ pm}, F^- = 133 \text{ pm}$.
(B) Isoelectronic series of ions; all have the xenon electron configuration.
- Ionic radius $\propto \frac{1}{\text{nuclear charge}}$
- Atomic number : Te = 52; I = 53; Cs = 55; Ba = 56.
(D) Across the period the nuclear charge increases and thus the size of atoms decreases. $Mg = 160 \text{ pm}; Al = 143 \text{ pm}; Si = 118; P = 110 \text{ pm}$.
- C-8.** $D_2 = T_2 = P_2$
(The ionisation potential of isotopes of an elements will be same)
- D-1.** Be and N has $1s^2 2s^2$ and $1s^2 2s^2 2p^3$ stable configurations respectively. So addition of extra electron is difficult in their valence shell. The atomic size of C is smaller than B and also C has higher nuclear charge; so addition of electron will be easier in C than B.
- D-7.** (A) IE (I) of N is more than O due to stable half filled electronic configuration of valence shell.
(B) is true as electron affinity of O (-141 kJ mol^{-1}) is less than sulphur and selenium due to its exceptionally small to atomic size.
(C) Electronegativity on Mulliken's scale is 2.8 larger than electronegativity on Pauling scale.
(D) The ionic radius decreases as more electrons are ionized off. $Cr^{6+} = 44 \text{ pm}, Cr^{3+} = 61.5 \text{ pm}$.
- D-8.** All are isoelectronic species so with increasing effective nuclear charge.
(i) size decreases (as $r = 1/\text{nuclear charge}$).
(ii) Ionisation energy increases (as it depends on the magnitude of nuclear charge).
(iii) electron affinity increases (as it depends on the magnitude of nuclear charge).
- E-1.** X, Y and Z are phosphorus, aluminium and sodium respectively because of the following reasons.
(A) the P_4O_{10} when dissolve in water forms acid H_3PO_4 which turns blue litmus red.
(B) the Al_2O_3 is amphoteric in the nature so reacts with both strong acids as well as with strong alkalis forming salts.

(C) the Na_2O when dissolves in water forms an aqueous solution which is strongly alkaline in nature. All these elements belong to third period. So across the period the size decreases and electronegativity increases.

E-4. Both react with acid as well as base forming salts.



E-6. As ΔE_n (difference in electronegativities between element and oxygen) decreases, the acidic character increases.



PART - II

- (A) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 σ for 3d electron = $0.35 \times 5 + 1.0 \times 18 = 19.75$
 so $Z_{\text{eff}} = 26 - 19.75 = 6.25$

(B) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 σ for 4s electron = $0.35 \times 1 + 0.85 \times 14 + 1.0 \times 10 = 22.25$
 so $Z_{\text{eff}} = 26 - 22.25 = 3.75$

(C) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 σ for 2s electron = $0.35 \times 1 + 0.85 \times 2 = 2.05$
 so $Z_{\text{eff}} = 26 - 2.05 = 23.95$

(D) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 σ for 2p electron = $0.35 \times 7 + 0.85 \times 2 = 4.15$
 so $Z_{\text{eff}} = 26 - 4.15 = 21.85$
 So outer most shell 4s electrons experience maximum shielding effect. Therefore 4s electron feels minimum attraction force from nucleus.
- $\text{Fe} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 $S = 0.3$
 $Z^* = 26 - 0.3 = 25.7$
- $\text{Na} = 1s^2 2s^2 2p^6 3s^1$
- Orbitals bearing lower value of n will be more closer to the nucleus and thus electrons will experience greater attraction from nucleus and so its removal will be difficult not easier.
- $Z = 19 = \text{K}$; $Z = 17 = \text{Cl}$; $Z = 30 = \text{Zn}$; $Z = 20 = \text{Ca}$; $Z = 51 = \text{Sb}$
 (A) K has larger atomic volume. It has lower density than the Na and Rb.
 (B) Cl ($Z = 17$) has less inter electronic repulsions than F ($Z = 9$) due to bigger size of 3p-subshell.
 (C) ${}_{30}\text{Zn} = [\text{Ar}]^{18} 3d^{10} 4s^2$; so no unpaired electron and because of completely filled configuration there is inter electronic repulsion. So electron cloud expands and so, Zn($Z = 30$) has higher atomic radius than Cu($Z = 29$). ZnO is amphoteric in nature.
 (D) ${}_{20}\text{Ca} = [\text{Ar}]^{18} 4s^2$; so no unpaired electron and across the period size decreases, so Ca is bigger than Cu.
 (E) $Z = 51$ which is Sb. The Sb is metalloid because it is able to form Sb^{3+} (as metals form) and Sb^{3-} (as nonmetals form).

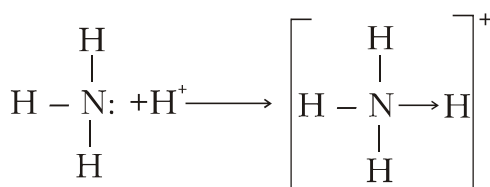
EXERCISE # 2

- 13.** IP is always endothermic , First EA is normally exothermic and Second EA is always endothermic

EXERCISE # 3

- Co is neutral towards litmus. SnO_2 and ZnO are amphoteric as they form salts and water with acids and bases. SiO_2 is acidic as it forms salts with bases. $\text{SiO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$.
- IE_2 of Na > Mg as in Na second electron is to be removed from stable inert gas configuration i.e., $1s^2 2s^2 2p^6$.
- For alkaline earth metal hydroxides down the group the change in lattice energy is more as compared to change in hydration energy with increasing atomic radii. So down the group with increasing atomic number, the solubility of their hydroxides increase.

4. Negative electron gain enthalpy of F is less than Cl. This is due to the fact that when an electron is added to F, the added electron goes to the smaller $n = 2$ energy level and experiences significant repulsion from the other electrons present in this level. In Cl, the electron goes to the larger $n = 3$ energy level and consequently occupies a larger region of space leading to much less electron-electron repulsion.
5. Larger the charge on the ion smaller will be the size of ion for the same element. For P^{3+} , there are 15 protons for 12 electrons while for P^{5+} , there are 15 protons for 10 electrons. Thus in P^{5+} the valence electrons are more strongly attracted by the nucleus than those of P^{3+} . As a result, there is a larger contraction in the size of P^{5+} than that of P^{3+} . Hence P^{3+} is bigger than P^{5+} .
6. All are isoelectronic species having 10 electrons in each species but different nuclear charge and thus ionic radius $\propto \frac{1}{\text{Nuclear charge}}$.
So correct order is ${}_{9}\text{F}^{-} < {}_{8}\text{O}^{2-} < {}_{7}\text{N}^{3-}$.
7. As non-metallic character of element attached to oxygen atom increases, the difference between the electronegativity values of element and oxygen decreases and the acid character of oxides increases and vice-versa.
8. Be has completely filled stable $2s^2$ orbital and thus Be has higher ionisation energy than B. $2s$ orbital has less energy than $2p$ orbital.
9. Down the group the effective nuclear charge remains almost constant. But down the group with increasing atomic number the number of atomic orbits increases and there by atomic size increases. As a result, the distance of valence shell electron from nucleus increases and attraction between them decreases and therefore ionization energy decreases.
10. As the metallic character decreases, the basic character decreases and acidic character increases. In other words if electronegativities difference between elements and oxygen decreases the acidic character increases. CaO is most basic, CuO is weakly basic, H_2O is neutral and CO_2 is acidic.
11. ${}_{3}\text{Li}^{-}$ - $1s^2 2s^2$ completely filled stable configuration, so more stable.
 ${}_{4}\text{Be}^{-}$ - $1s^2 2s^2 2p^1$
 ${}_{5}\text{B}^{-}$ - $1s^2 2s^2 2p^2$
 ${}_{6}\text{C}^{-}$ - $1s^2 2s^2 2p^3$ half filled stable configuration, so more stable.
As Be^{-} has less nuclear charge than B^{-} , so it will have lower ionisation energy than B^{-} .
12. According to their positions in the periods, these values are in the order.
- | | | | | | | | |
|------------------|------------------|---|------------------|---|------------------|---|------------------|
| | Yb^{+3} | < | Pm^{+3} | < | Ce^{+3} | < | La^{+3} |
| At. Nos. | 70 | | 61 | | 58 | | 57 |
| Ionic radii (pm) | 86 | | 98 | | 103 | | 106 |
- This is due to lanthanide contraction.
13. According to modified modern periodic law, the properties of elements are periodic functions of their atomic numbers.
14. ZnO is an amphoteric oxide and dissolves readily in acids forming corresponding zinc salts and alkalies forming zincates.
- $$\begin{array}{l} \text{ZnO} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O} \quad \text{zinc sulphate} \\ \text{ZnO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} \quad \text{sodium zincate} \end{array}$$
15. Number of electrons in $\text{N}^{3-} = 7 + 3 = 10$.
Number of electrons in $\text{F}^{-} = 9 + 1 = 10$
Number of electrons in $\text{Na}^{+} = 11 - 1 = 10$.
16. Ammonia is a Lewis base, accepting proton to form ammonium ion as it has tendency to donate an electron pair.



17. The basic nature of oxides can be predicted on the basis of the factors given below.
- If electronegativity difference between element and oxygen is less than 1.4, the oxide is generally acidic and if this difference is more than 1.4, the oxide is generally basic.
 - The basic character increases with increasing metallic character down the groups and decreases across the period.
 - For the same element the basic character of their oxides increases with decreasing oxidation state.

Hence the correct of increasing Bronsted basicity order is $\overset{+7}{\text{Cl}_2\text{O}_7} < \overset{+6}{\text{SO}_3} < \overset{+4}{\text{CO}_2} < \overset{+3}{\text{B}_2\text{O}_3} < \overset{+2}{\text{BaO}}$

18. Isoelectronic species are those which have same number of electrons but different number of protons (i.e. nuclear charge).

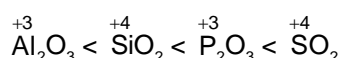
$$\begin{aligned} {}_{19}\text{K}^+ &= 19 - 1 = 18; {}_{20}\text{Ca}^{2+} = 20 - 2 = 18 \\ {}_{21}\text{Sc}^{3+} &= 21 - 3 = 18; {}_{17}\text{Cl}^- = 17 + 1 = 18 \end{aligned}$$

Thus all these ions have 18 electrons in them.

19. O_2^- has the highest value of ionic radii as this can be explained on the basis of $z/e \left\{ \frac{\text{nucleus charge}}{\text{no. of electrons}} \right\}$.

When z/e ratio increases, the size decreases and when z/e ratio decreases the size increases.

20. With decrease in size from Al to S the basic nature of oxides decreases and acidic nature increases.



Al_2O_3 is amphoteric. SiO_2 is slightly acidic whereas P_2O_3 and SO_2 are the anhydrides of the acids H_3PO_3 and H_2SO_3 .

21. CaO - basic, CO_2 and SiO_2 - acidic, SnO_2 - amphoteric, as it reacts with both acids and bases.



22. Nitrogen has half filled stable configuration, ns^2np^3 . So, ionization enthalpy of nitrogen is greater than oxygen. Across the period with increasing effective nuclear charge and decreasing atomic size the ionization energies increases but down the group decreases due to increasing atomic radii. So, the correct of increasing the first ionization enthalpy is $\text{B} < \text{P} < \text{C} < \text{O} < \text{N}$. (Ionisation energy in kJ mol^{-1} $\text{B} = 801$; $\text{P} = 1011$; $\text{C} = 1086$; $\text{O} = 1314$; $\text{N} = 1402$).

23. Number of electrons in $\text{SO}_3^{2-} = 16 + 8 \times 3 + 2 = 42$

$$\text{Number of electrons in } \text{CO}_3^{2-} = 6 + 8 \times 3 + 1 = 32$$

$$\text{Number of electrons in } \text{NO}_3^- = 7 + 8 \times 3 + 1 = 32$$

These are not isoelectronic species as number of electrons are not same.

24. Element : B S P F
I.E. (kJ mol^{-1}) : 801 1000 1011 1681

In general as we move from left to right in a period, the ionization enthalpy increases with increasing atomic number. The ionization enthalpy decreases as we move down a group. P ($1s^2, 2s^2, 3s^2, 3p^3$) has a stable half filled electronic configuration than S ($1s^2, 2s^2, 2p^6, 3s^2, 3p^4$). For this reason, ionization enthalpy of P is higher than S.

25. $\text{K}^+ = 19 - 1 = 18 e^-$ $\text{Cl}^- = 17 + 1 = 18 e^-$
 $\text{Ca}^{2+} = 20 - 2 = 18 e^-$ $\text{Sc}^{3+} = 21 - 3 = 18 e^-$

Thus all the species are isoelectronic.

26. All have same number of electron i.e. 14.

$$\text{NO}^+ = 7 + 8 - 1 = 14 ; \text{C}_2^{2-} = 2 \times 6 + 2 = 14$$

$$\text{CN}^- = 6 + 7 + 1 = 14 ; \text{N}_2 = 7 + 7 = 14.$$

27. Down the group ionic radii increases with increasing atomic number because of the increase in the number of atomic shells but across the period the ionic radii decreases due to increase in effective nuclear charge as electrons are added in the same shell. Li^+ and Mg^{2+} are diagonally related but Mg^{2+} having higher charge is smaller than Li^+ , so correct order is $\text{Na}^+ > \text{Li}^+ > \text{Mg}^{2+} > \text{Be}^{2+}$.

$$\text{Be}^{2+} = 0.31 \text{ \AA}$$

$$\text{Mg}^{2+} = 0.72 \text{ \AA}$$

$$\text{Li}^+ = 0.76 \text{ \AA}$$

$$\text{Na}^+ = 1.02 \text{ \AA}$$

28. In hydrides of 15th group elements the basic strength decreases down the group and the correct order is,
 $\text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$
29. O^{2-} , F^- , Na^+ , Mg and Al^{3+} have same number of electrons (i.e. 10 electrons) but different nuclear charges and, therefore, they are isoelectronic species.
 For isoelectronic species ionic radii $\propto \frac{1}{\text{nuclear charge}}$.
 So, correct order of ionic radii is ${}_8\text{O}^{2-} > {}_9\text{F}^- > {}_{11}\text{Na}^+ > {}_{12}\text{Mg}^{2+} > {}_{13}\text{Al}^{3+}$.
30. Order of ionic radii $\text{Ca}^{2+} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}$
 in isoelectronic species as Z/e increases size decreases.

SOLUTION OF ADVANCED LEVEL PROBLEM

1. As magnetic moment = $\sqrt{n(n+2)} = 1.73$; So, $n = 1$
 Since atom has only one unpaired electron hence it must be ${}_{29}\text{Cu}$ [${}_{29}\text{Cu} = [\text{Ar}]^{18} 3d^{10} 4s^1$].
 Hence element below it in periodic table has atomic number $29 + 18 = 47$.
17. (i) N has half filled stable electronic configuration which is reluctant to accept an additional electron. Therefore, nitrogen has less negative value of electron gain enthalpy than oxygen.
 (ii) Because of interelectronic repulsion in compact small fluorine atom (2p-subshell), the addition of extra electron is difficult as compared to chlorine (3p-subshell). So fluorine has less negative electron gain enthalpy than chlorine.
18. $M = 2.1$ $F = 4$
 $x_A - x_B = (4 - 2.1) = 1.9$
 $\% \text{ ionic character} = 16(1.9) + 3.5(1.9)^2 = 43.03\%$
 So, $\% \text{ covalent character} = 100 - 43.03 \cong 57\%$.

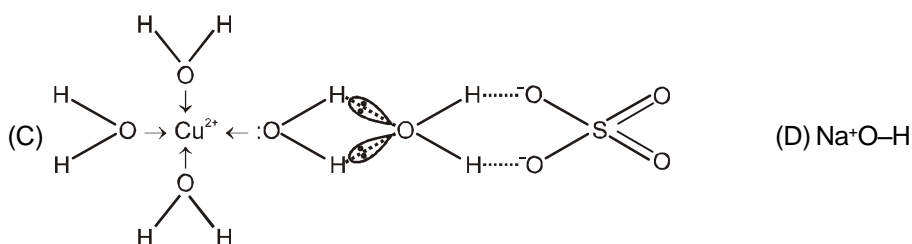
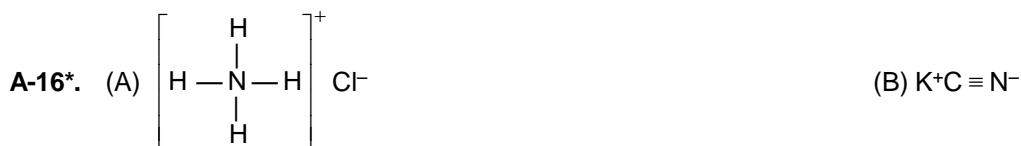
CHEMICAL BONDING

Chemical Bonding Part-1

EXERCISE # 1

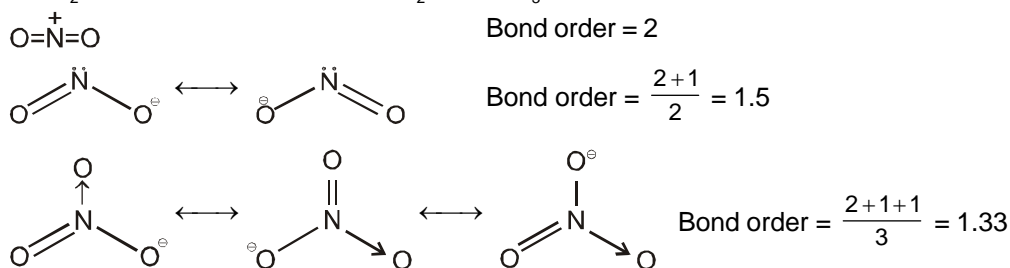
PART - I

- A-9.** Here $\Delta_{xz} = 3 - 1 = 2 > 1.7$ \therefore XZ is ionic
 $\Delta_{yz} = 2 - 1 = 1 < 1.7$ \therefore YZ is covalent.



- B-3.** Fluorine has no vacant d-orbital in its valence shell.

- B-12.** N atom in NO_2^+ is sp hybridised while in NO_2^- and NO_3^- , it is sp^2 hybridised.



$$\text{Bond order} \propto \frac{1}{\text{Bond length}}$$

So, bond length order is $\text{NO}_3^- > \text{NO}_2^- > \text{NO}_2^+$.

- B-13.** Bond length $\propto \frac{1}{\text{Bond order}}$

Bond order of CO = 3 (as isoelectronic with N_2)

$$\text{Bond order} = \frac{\text{No. of bonds in all possible sides}}{\text{No. of resonating structures}}$$

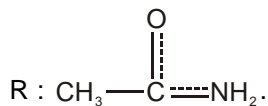
$$\text{Bond order of } \text{CO}_2 = \frac{4}{2} = 2$$

$$\text{Bond order of } \text{CO}_3^{2-} = \frac{4}{3} = 1.33$$

So, order of bond length of C - O is $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$

- B-14.** (i) Negative charge should be at more electronegative atom.
 (ii) Less formal charge provides more stability.

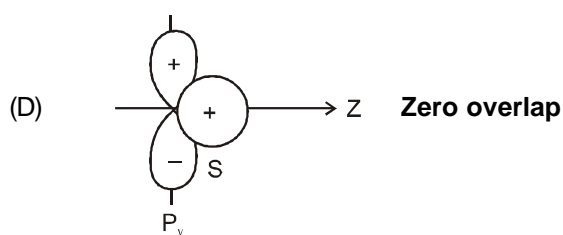
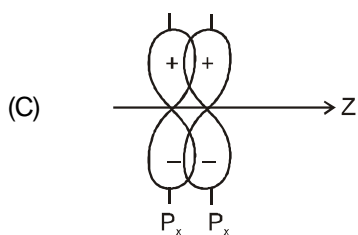
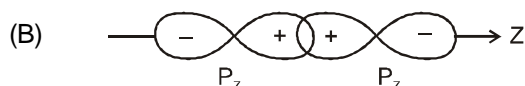
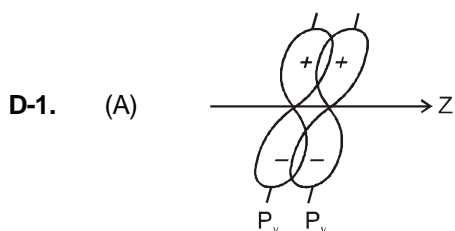
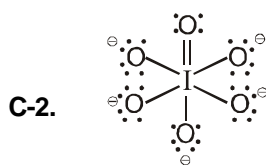
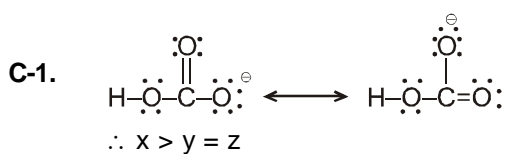
- B-15.** P : $\text{CH}_3 - \text{C} \equiv \text{N}$
 Q : $\text{H} - \text{N} = \text{C} = \text{O}$



- B-16.** Bond energy \propto Bond order
- | Species | Bond order |
|-------------------------------|------------|
| CO | 3 |
| CO ₂ | 2 |
| CO ₃ ²⁻ | 1.33 |

- B-17.** (D) Position of atoms are different.
 (E) Has unpaired electrons and this is not possible since the molecule is diamagnetic.

- B-18.** $\text{H} - \text{N}^+ - \text{N}^+ = \text{N}^{2-}$; there is positive charge on two adjacent nitrogen atoms. This leads to repulsion and thus (II) increases the energy of the molecule.

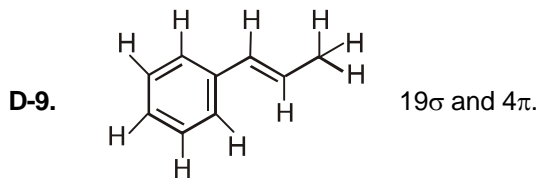


- D-3*.** (b) If X-axis is internuclear axis, then it will result in π bond.
 (c) It will result in σ bond.
 (d) It shows zero overlap with no bond formation.

- D-6.** Since π bond is weaker than σ bond the stated value of bond energies are wrong.

- D-7.** Structure of C_3^{4-} is $(\overset{2-}{\text{C}} = \text{C} = \overset{2-}{\text{C}})$

- D-8.** CaC_2 exists as Ca^{2+} and C_2^{2-} $[\overset{\ominus}{\text{C}} \equiv \overset{\ominus}{\text{C}}]$.



- D-13*. $C^* \rightarrow 1s^2 2s^1 2p^3$ 4 unpaired electron \therefore 4 bonds
 $B^* \rightarrow 1s^2 2s^1 2p^2$ 3 unpaired electron \therefore 3 bonds
 $I^* \rightarrow 5s^2 5p^4 5d^1$ 3 unpaired electron \therefore 3 bonds
 $P^* \rightarrow 3s^2 3p^3$ 3 unpaired electron \therefore 3 bonds
 * represent excited state

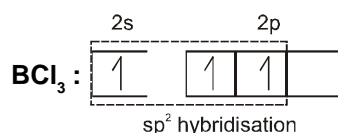
E-3. Hybridization does not take place without s-orbital

E-7.

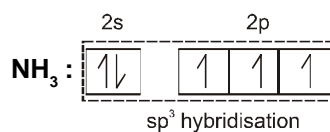
Species	Hybridisation
$CO_3^{2\ominus}$	sp^2
XeF_4	sp^3d^2
I_3^\ominus	sp^3d
NCl_3	sp^3
$BeCl_2$	sp

- E-9. $SnCl_2 - sp^2$
 $XeF_4 - sp^3d^2$
 $I_3^- - sp^3d$
 $NCl_3 - sp^3$
 $HgCl_2 - sp$

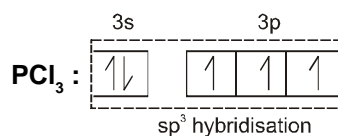
E-11. (a) Electronic configuration of boron in ground state is $1s^2 2s^2 2p^1$.



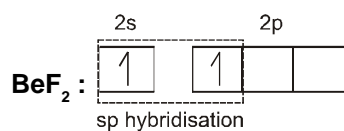
(b) Electronic configuration of nitrogen in ground state is $1s^2 2s^2 2p^3$.



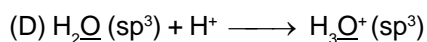
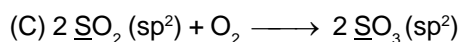
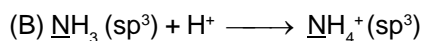
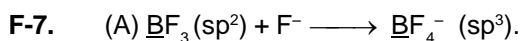
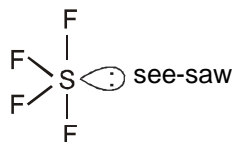
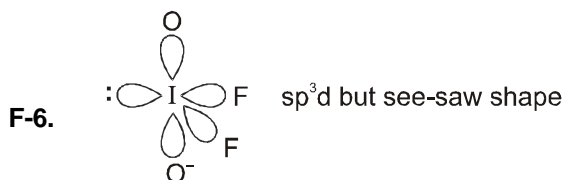
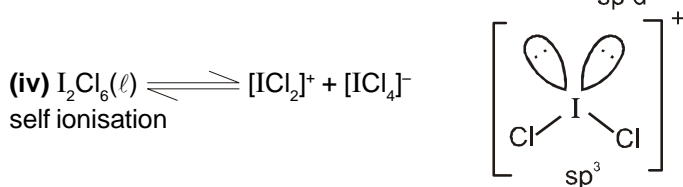
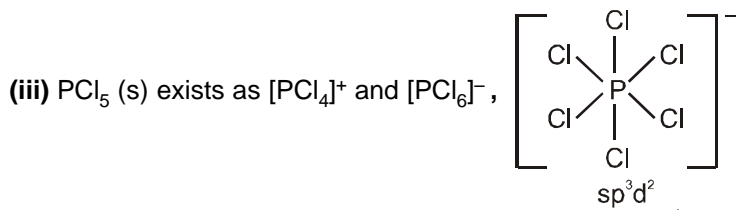
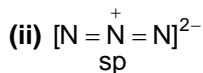
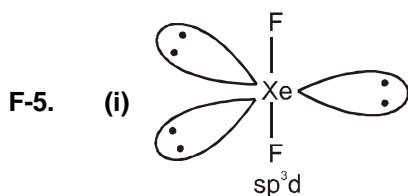
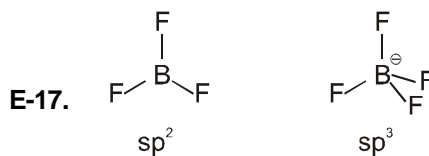
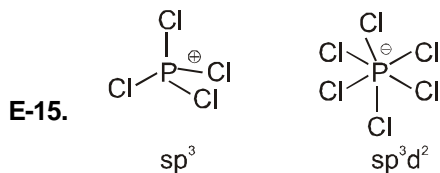
(c) Electronic configuration of phosphorus in ground state is $1s^2 2s^2 2p^6 3s^2 3p^3$.



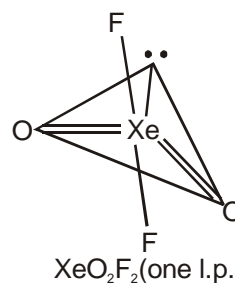
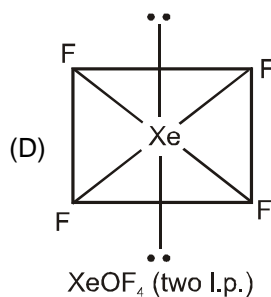
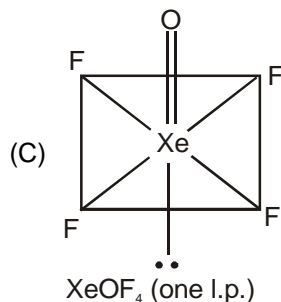
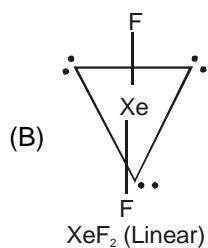
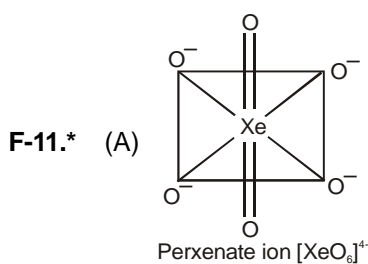
(d) Electronic configuration of boron in ground state is $1s^2 2s^2$.



- E-12. $CH_2 = CH^\oplus$
 steric No. = 2
 \therefore Hybridisation sp .

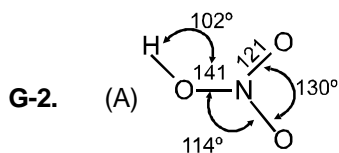
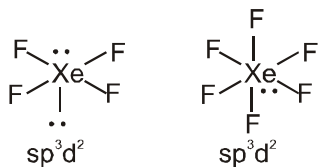


F-9. The hybridization & shape of ClO_3^- is sp^3 & pyramidal but hybridization & shape of NO_3^- is sp^2 & trigonal planar.

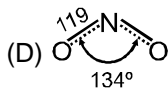
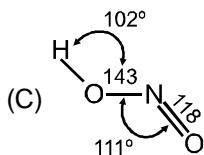


F-14. The cation should be
 $[H-C \equiv N - Xe - F]^+$
 Hybridisations sp sp sp^3d

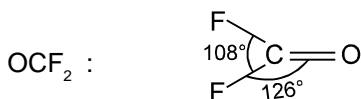
F-19. $:N \equiv C - C \equiv N:$ $[F - \overset{\cdot\cdot}{Xe} - F]^{4+}$ sp but bent structure due to LP-BP repulsion.
 sp sp



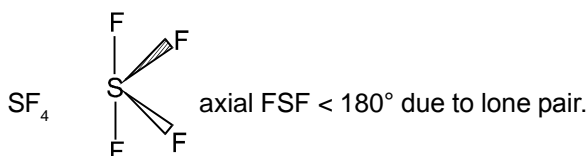
(B) $O = \overset{+}{N} = O$ Bond angle is 180° because of sp hybridisation of nitrogen.
 115 pm



G-4. Generally lone pair causes more distortion than a double bond so
 equatorial $\angle FSE$ in SOF_4 $>$ equatorial $\angle FSE$ in SF_4

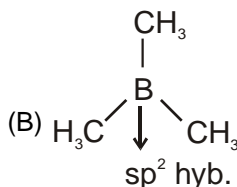


due to low bond pair bond pair repulsion because of fluorine & large repulsion due to double bond.



Similar orbitals on hybridisation can not decrease their energy due to energy conservation law

G-6*. (A) Due to the presence of lone pair bond angle decreases.



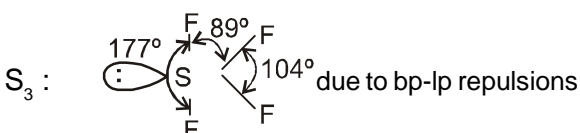
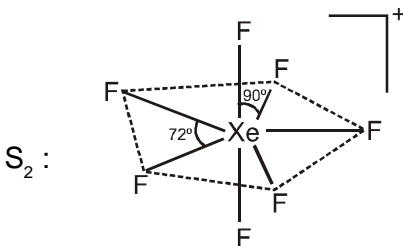
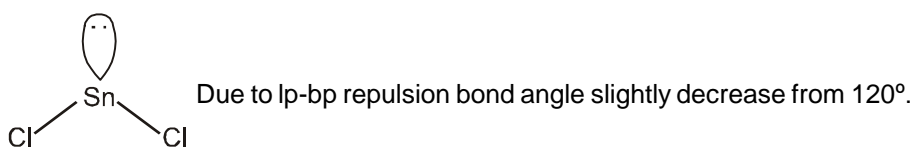
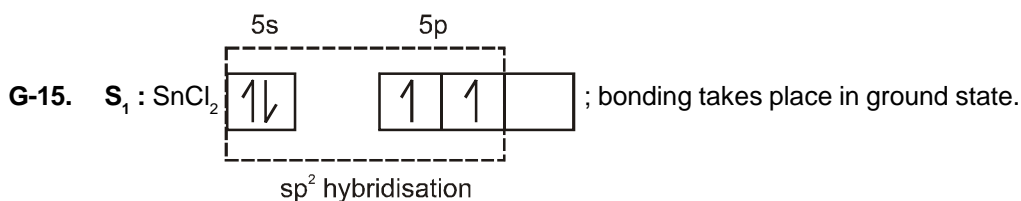
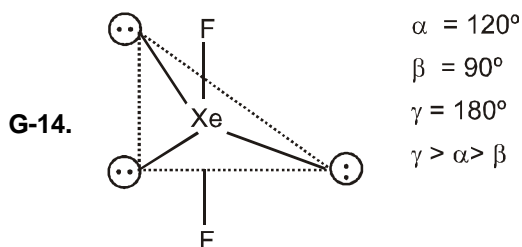
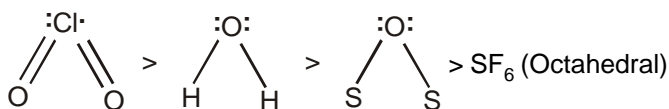
(C) NH_4Cl is an ionic compound and 'N' is in sp^3 hybridisation.
 (D) S_8 molecule has 16 electron pairs left behind after the bonding.

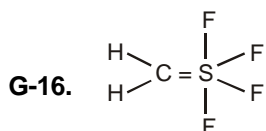
G-7. As the electronegativity of central atom increases the bond angle increases due to repulsion between bond pair and bond pair as bond pairs are more close to the central atom.

G-9. H_2S – No hybridisation bond angle $\approx 93^\circ$
 NH_3 – Pyramidal 104.5°
 CH_4 – Tetrahedral $109^\circ 28'$
 BF_3 – Triagonal planar 120°

G-11. P_4 bond angle = 60°
 PH_3 bond angle $\approx 90^\circ$ (Drago's rule)
 H_2O bond angle = 104.5°

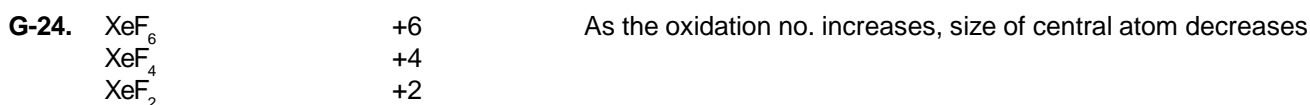
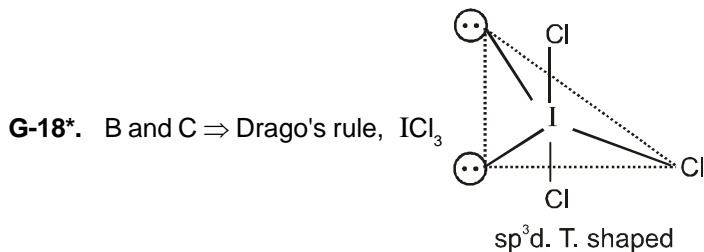
G-13. (a) According to VSEPR as electronegativity of central atom decreases, bond angle decreases. So bond angle of $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$
 (b) $\text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{CH}_4 > \text{NH}_3$ with bond pair- lone pair repulsion
 $\text{sp} \quad \text{sp}^2 \quad \text{sp}^3 \quad \text{sp}^3$
 (c) $\text{SF}_6 < \text{NH}_3 < \text{H}_2\text{O} < \text{OF}_2$ in this case bond angle of NH_3 is highest because lp - lp repulsion is absent in it.
 (d) $\text{ClO}_2 > \text{H}_2\text{O} > \text{H}_2\text{S} > \text{SF}_6$
 ClO_2 bond angle is highest due to its sp^2 hybridisation, rest all are sp^3 or sp^3d^2 hybridised more repulsion in double bond electrons.





Hydrogen atoms are in a vertical plane with axial fluorine atoms, π -bond involving a p-orbital of carbon atom must lie in equatorial plane of the molecule.

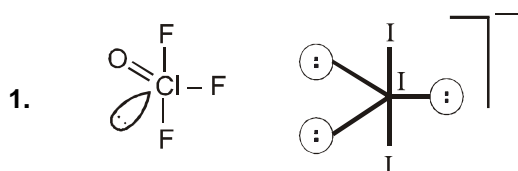
Six atoms, i.e. 2 H-atoms, C, S. and both axial F-atoms lie in one plane.



G-28. Due to small size of nitrogen, the lp-lp repulsion is more than that in P. Hence statement B is correct

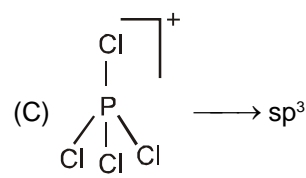
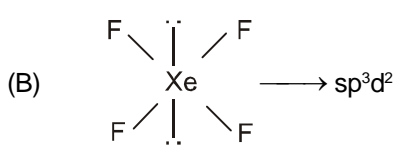
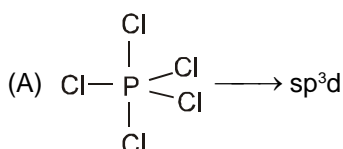
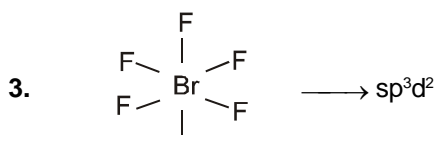
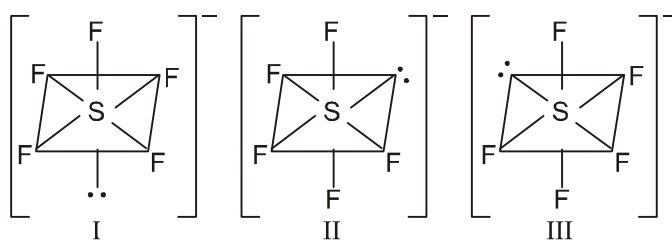
G-29. Oxidation no. of N in N_2O_5 is +5
 Anhydride of HOCl is Cl_2O .
 The bond length decreases with increase in difference of electronegativity.

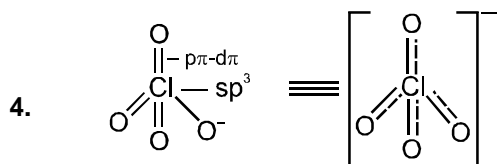
PART - II



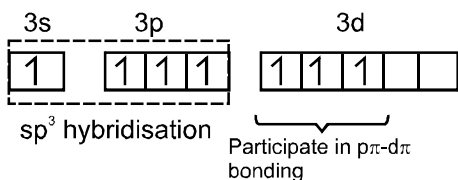
Cl-atom is in sp^3d hybridisation state. Hence geometry is trigonal bi-pyramidal which is similar to I_3^-

2. Number of electrons pairs = 6 ; number of bond pairs = 5 ; number of lone pairs = 1. According to VSEPR theory geometry of the molecule is square bipyramidal. As all positions are equivalent the lone pair of electrons can occupy any position in octahedral geometry as given below.



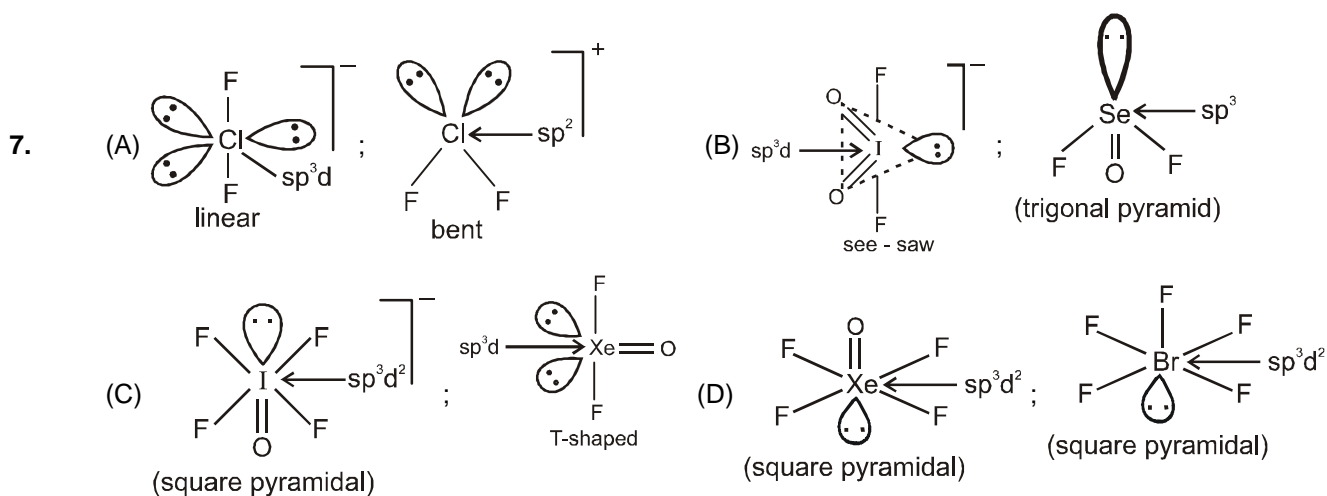


Valence shell electron configuration of Cl, $3s^2 3p^5$

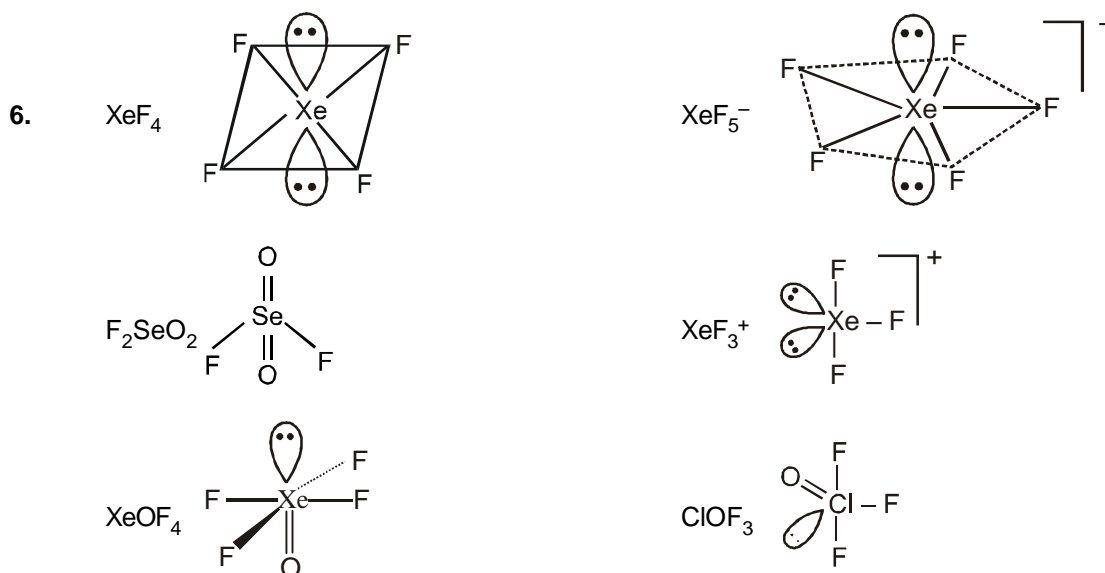


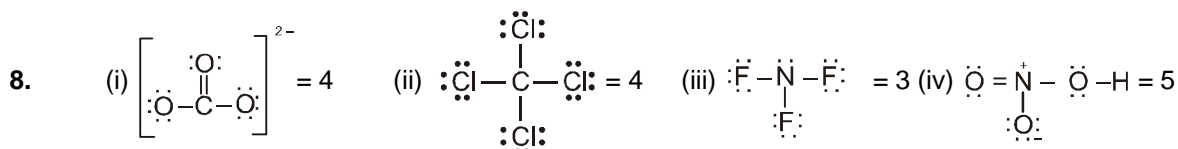
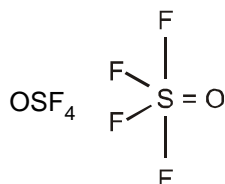
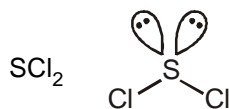
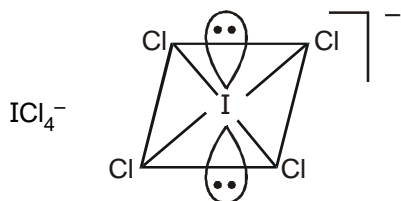
To obtain effective $p\pi - d\pi$ overlap the size of the d orbital must be similar to size of the p orbital. Hence in chlorine, $p\pi - d\pi$ bonding is so strong that no polymerization of oxoanions occurs.

5. (A) With hydrogen sulphur does not undergo sp^3d^2 hybridisation because of larger difference in energies between s, p and d-orbitals. Sulphur show +6 oxidation state with highly electronegative elements like O and F.
 (B) As fluorine is smaller and more electronegative than oxygen.
 (C) I⁻ being stronger reducing agent reduces Fe^{3+} to Fe^{2+} .



EXERCISE # 2

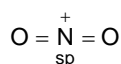




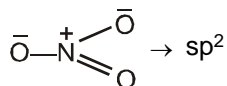
20. As the s character in hybrid orbital decrease, size of hybrid orbital increases.

EXERCISE # 3

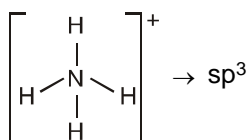
1. NO_2^+ Number of electron pairs = 2
 Number of bond pairs = 2
 Number of lone pair = 0
 So, the species is linear with sp hybridisation.



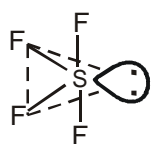
- NO_3^- Number of electron pairs = 3
 Number of bond pairs = 3
 Number of lone pair = 0
 So, the species is trigonal planar with sp^2 hybridisation.



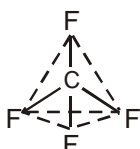
- NH_4^+ Number of electron pairs = 4
 Number of bond pairs = 4
 Number of lone pair = 0
 So, the species is tetrahedral with sp^3 hybridisation.



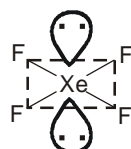
2. According to VSEPR theory



$lp = 1$
 $sp^3 d$ -hybridisation
 see-saw shape



$lp = 0$
 sp^3 -hybridisation
 tetrahedral shape

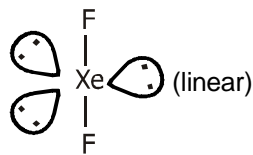


$lp = 2$
 $sp^3 d^2$ -hybridisation
 square planar shape

3. According to VSEPR theory

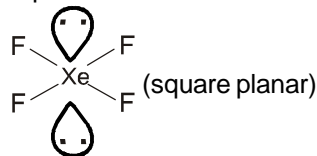
XeF_2
 Number of electron pairs = 5,
 Number of bond pairs = 2,
 So, Number of lone pairs = 3

Thus XeF_2 is linear with 3 lone pairs occupying
 3 equatorial positions of trigonal bipyramidal so as to minimize the repulsions.



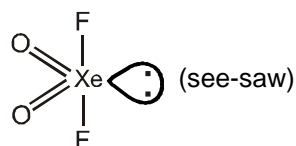
XeF_4
 Number of electron pairs = 6,
 Number of bond pairs = 4,
 So, Number of lone pairs = 2

Thus XeF_4 is square planar with 2 lone pairs occupying
 2 axial positions of octahedral pyramidal so as to minimize the repulsions.



XeO_2F_2
 Number of electron pairs (including super electron pairs) = 5,
 Number of bond pairs = 4,
 So, Number of lone pairs = 1

Thus XeO_2F_2 is see-saw with 1 lone pair occupying
 one equatorial position and two double bonds occupying other
 two equatorial positions of trigonal bipyramidal so as to minimize the repulsions.



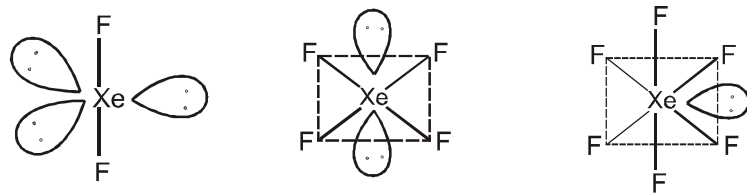
4. steric number = 5, so sp^3d hybridisation;

steric number = 3, so sp^2 hybridisation;

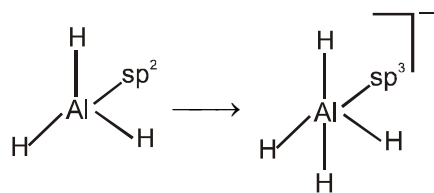
steric number = 4, so sp^3 hybridisation;

$[\text{PtCl}_4]^{2-}$ is $5d^8$ configuration so square planar i.e. dsp^2 .

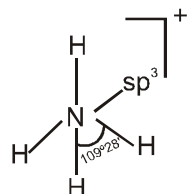
5.



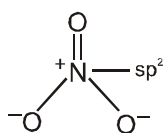
6.



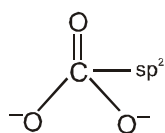
7.



8. Number of electrons in $\text{NO}_3^- = 7 + 3 \times 8 + 1 = 32$.
 Number of electrons in $\text{CO}_3^{2-} = 6 + 3 \times 8 + 2 = 32$.
 So both are isoelectronic.
 NO_3^- steric number = 3 ; CO_3^{2-} steric number = 3.

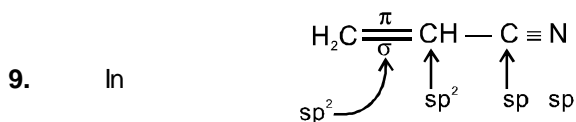


trigonal planar



trigonal planar

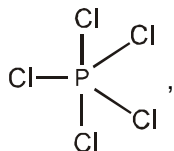
As both have same shapes they are also isostructural (same hybridisation and no lone pair of electrons).



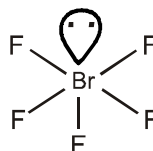
From left to right.

Note : Hybrid orbitals always form σ -bonds due to overlapping on their axis.

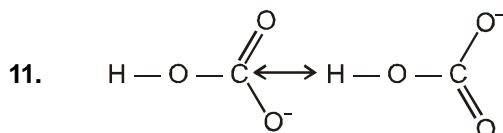
10. There are 5 electron pairs and all are bonds pairs in PCl_5 . So to have the minimum repulsions between bond pairs it acquires trigonal bipyramidal shape. In BrF_5 , there are 6 electrons pairs out of which one lone pair and rest all are bond pairs. So to have the minimum repulsions between bond pairs and lone pairs it acquires square pyramidal shape.



PCl_5 (trigonal bipyramidal),



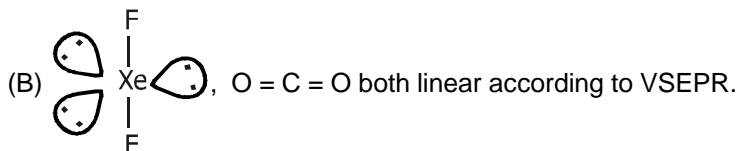
BrF_5 (square pyramidal)



12. (A) The sulphur is in sp^2 hybridisation but due to lp-bp repulsion the bond angle decreases to 119.5° .
 (B) The oxygen is in sp^3 hybridisation but due to lp-lp repulsion the bond angle decreases to 104.5° .
 (C) It is believed that pure p atomic orbitals participate in bonding and due to lp-lp repulsion the bond angle decreases to 92.5° .
 (D) The nitrogen is in sp^3 hybridisation but due to lp-bp repulsion the bond angle decreases to 107° .

	SO_2	OH_2	SH_2	NH_3
Bond angle :	119.5°	104.5°	92.5°	107°

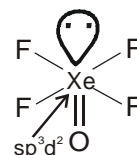
13. (A) CF_4 is tetrahedral where as SF_4 is see-saw shaped.



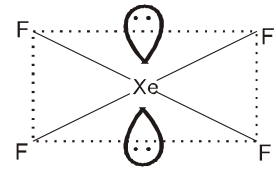
- (C) BF_3 is trigonal planar and PCl_3 is pyramidal.
 (D) PF_5 is trigonal bipyramidal and IF_5 is square pyramidal.

14. According to VSEPR theory,
 total number of electron pairs = 6.
 total number of bond pairs = 5.
 so total number of lone pair = 1.

There is one Xe—O double bond. The π -electrons of double bond create more repulsion than single covalent bond. To minimize the repulsions the lone pair and Xe—O double bond are trans to each other in octahedral geometry.

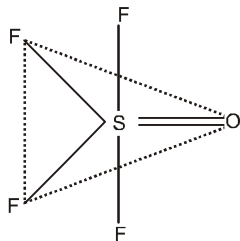


15. According to VSEPR theory two lone pairs out of six electron pairs are trans to each other to have minimum repulsion. The shape of XeF_4 is square planar and geometry is octahedral with sp^3d^2 hybridisation. The molecule looks like :

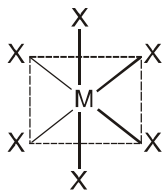


In OSF_4 , there are five electron pairs and all are bond pairs. So geometry is trigonal bipyramidal. As double bond creates more repulsion than single bond, the double bond acquires one of equatorial position of trigonal bipyramidal to have minimum repulsions.

The structure looks like:

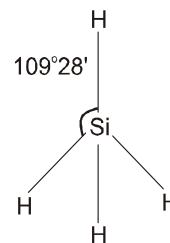
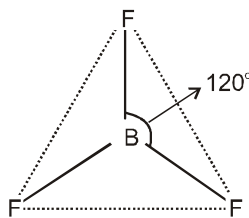
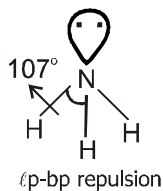
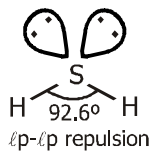
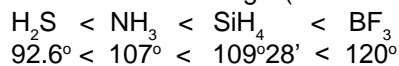


16.

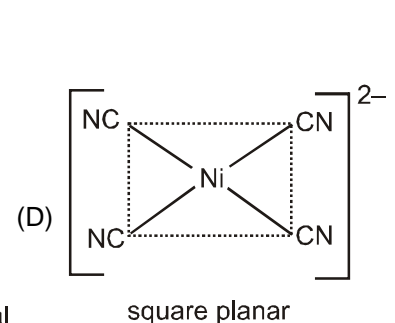
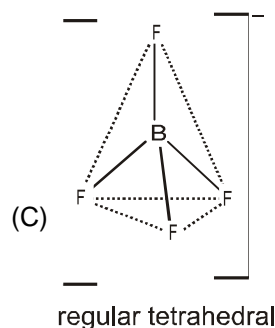
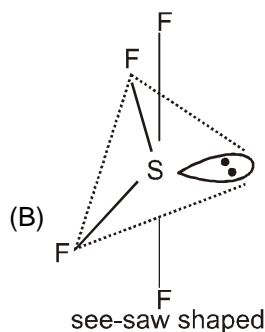
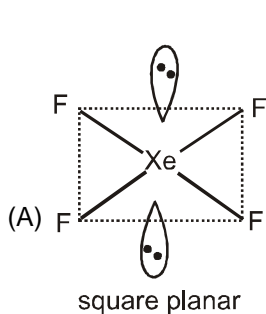


Maximum 12 bond angles are of 90° .

17. The correct order of bond angle (smallest first) is

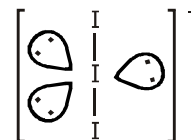


18.

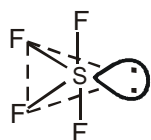


19. (A) $\text{CH}_3-\overset{sp^3}{\text{C}}-\overset{sp^2}{\text{C}}-\text{CH}_3$ Acetone
 (B) $\text{CH}_3-\overset{sp^3}{\text{C}}-\overset{sp^2}{\text{C}}-\text{OOH}$ Acetic acid
 (C) $\text{CH}_3-\overset{sp^3}{\text{C}}-\overset{sp}{\text{C}}\equiv\text{N}$; Acetonitrile
 (D) $\text{CH}_3-\overset{sp^3}{\text{C}}-\overset{sp^2}{\text{C}}-\text{NH}_2$ Acetamide

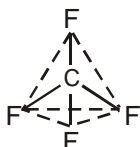
20. According to VSEPR theory
 The number of electron pairs around I = 5
 The number of bond pairs around I = 2
 The number of lone pairs around I = 3
 To have minimum repulsions among lone pair and bond pairs, the lone pairs acquire the three equatorial positions of trigonal bipyramidal as given in the structure, ClO_3^- , XeF_4 and SF_4 have 1, 2 and 1 lone pair of electrons respectively.



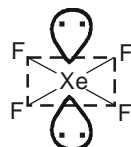
21. According to VSEPR theory



$\ell p = 1$
 $sp^3 d$ -hybridisation
 see-saw shape

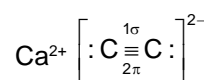


$\ell p = 0$
 sp^3 -hybridisation
 tetrahedral shape



$\ell p = 2$
 $sp^3 d^2$ -hybridisation
 square planar shape

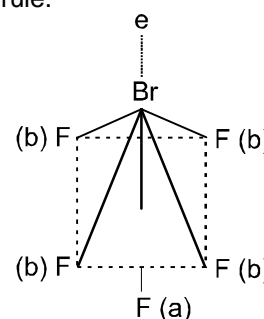
22. Calcium carbide is ionic carbide having $[\text{C} \equiv \text{C}]^{2-}$



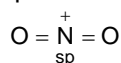
23. Due to small size of B, it is very difficult to remove the electrons from boron to form ionic bond as it will require very high energy. On the other hand, due to its very small size having high polarising power causes greater polarisation and eventually significant covalent character according to Fajan's rule.

24. The spatial arrangement of six electron clouds (five bond pairs and one lone pair) round the central Br-atom is octahedral. Due to the presence of one lone pair of electrons in the axial hybrid orbital, the shape of BrF_5 gets distorted and becomes square pyramidal. Basal F-atoms are slightly displaced upwards from the base of the square pyramid.

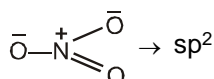
Br – F(b) distance = 1.79 Å
 Br – F(a) distance = 1.68 Å
 F(b) – Br – F(b) angle = $89^\circ 48'$
 F(b) – Br – F(a) angle = $86^\circ 30'$
 F(b) – Br – e angle = $93^\circ 30'$



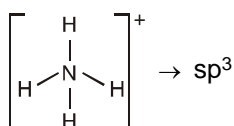
25. NO_2^+ Number of electron pairs = 2
 Number of bond pairs = 2
 Number of lone pair = 0
 So, the species is linear with sp hybridisation.



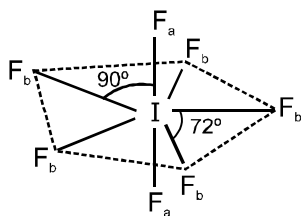
- NO_3^- Number of electron pairs = 3
 Number of bond pairs = 3
 Number of lone pair = 0
 So, the species is trigonal planar with sp^2 hybridisation.



- NH_4^+ Number of electron pairs = 4
 Number of bond pairs = 4
 Number of lone pair = 0
 So, the species is tetrahedral with sp^3 hybridisation.



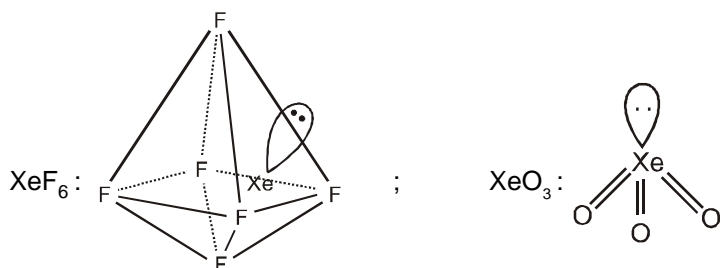
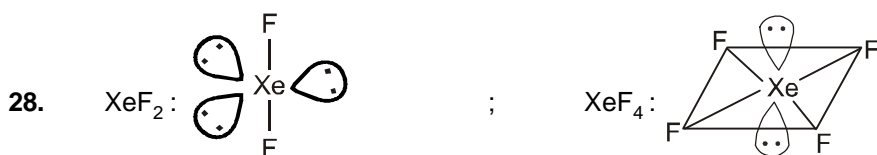
26. The structure is pentagonal bipyramid having sp^3d^3 hybridisation as given below :



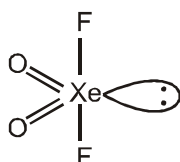
$$F_b - I - F_b = 72^\circ \text{ (5 number)} \quad ; \quad F_b - I - F_a = 90^\circ \text{ (10 number)}$$

$$F_b - I \text{ bond length} = 1.858 \pm 0.004 \text{ \AA} \quad ; \quad F_a - I \text{ bond length} = 1.786 \pm 0.007 \text{ \AA}$$

27. Calcium carbide exists as Ca^{2+} and C_2^{2-} . According to the molecular orbital model, C_2^{2-} should have a bond order of 3 (configuration $\pi_u^2 \pi_u^2 \sigma_g^2$). MOT configuration suggests that it contains one σ and two π -bonds $[:C \equiv C:]^{2-}$.



29. XeO_2F_2 has trigonal bipyramidal geometry. Due to presence of lone pair on equatorial position, the shape is see-saw.



30. As electronegativity of central atom decreases, bond angle decreases.
(Hybridisation and number of lone pair on central atom are same in all options)
31. PF_5 trigonal bipyramidal
 BrF_5 square pyramidal (distorted)

SOLUTION OF ADVANCED LEVEL PROBLEM

7. Two terminal carbons can be assumed to be at A and B, while the central carbon at O. Then, $AB = 2AP$

$$\text{But } \frac{AP}{AO} = \sin \left(\frac{\theta}{2} \right)$$

$$= \sin \left(\frac{109^\circ 28'}{2} \right)$$

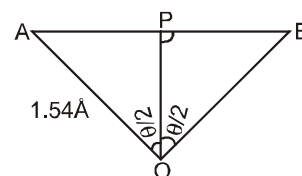
\therefore (in tetrahedral structure $\theta = 109^\circ 28'$)

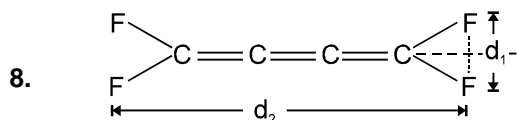
$$= \sin (54^\circ 44')$$

$$\therefore AP = AO \sin (54^\circ 44') = 1.54 \times 0.82 = 1.26 \text{ \AA}$$

$$\therefore AB = 2AP = 2.52 \text{ \AA}$$

Ans. 2.52 \AA





$$d_1 = 2 \times 134 \times \sin 60^\circ \text{ pm} = 227.8 \text{ pm} = 228 \text{ pm}$$

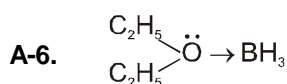
$$d_2 = 134 \times 3 + 2 \times 134 \cos 60^\circ \text{ pm} = 536 \text{ pm}$$

Chemical Bonding Part-2

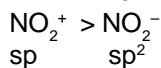
EXERCISE # 1

PART - I

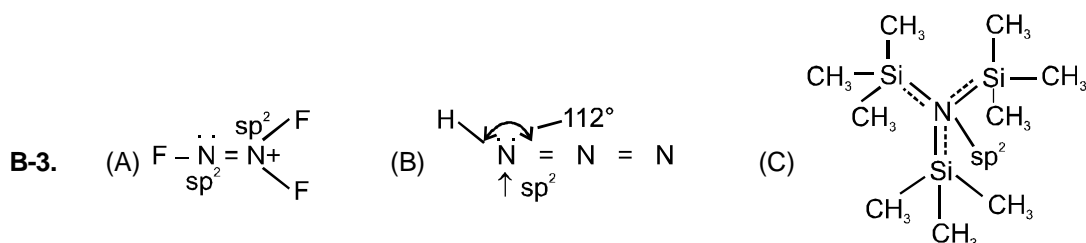
A-4. Boron trimethyl is a weaker Lewis acid than the boron trihalides or monoborane. The electron donating effect of the methyl groups hinders the complex formation with trimethyl amine. Hence the bond $N \rightarrow B$ is weakest in $[(CH_3)_3 N \rightarrow B(CH_3)_3]$. Me_3N as donor (capacity). $BBr_3 > BCl_3 > BF_3 \sim BH_3 > BMe_3$.



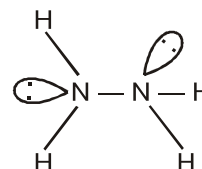
A-12*. $Cl_2O > F_2O$ and $F_2O < H_2O$
 $111^\circ \quad 102^\circ \quad 102^\circ \quad 104^\circ$



$AsI_3 > AsBr_3 > AsCl_3$ (due to size of halogen)



B-5*. (A) Structure is similar to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecules are rotated 95° about N – N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å.

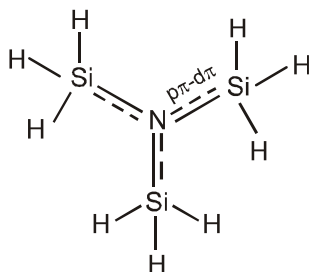


(B) Has partial double bond character due to $p\pi-d\pi$ delocalisation.

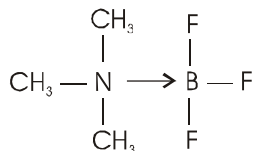
(C) $OF_2 = 103^\circ$ (approximate) and $OCl_2 = 112^\circ$ (approximate).

(D) Exist in polymeric structure as in solid state.

B-7. There is $p\pi-d\pi$ delocalization of lone pair of electron on nitrogen atom and empty d-orbital of silicon but not $p\pi-p\pi$, one of the 2s-orbital electrons jumps to the last P_z orbital and does not participate in sp^2 hybridisation.



- B-9.** In BF_3 the B - F bond length is shorter than normal bond character on account of $p\pi - p\pi$ back bonding (1.30 Å). In 1 : 1 complex there is no $p\pi - p\pi$ back bonding and hence the B - F bond length is longer, (1.35 Å).

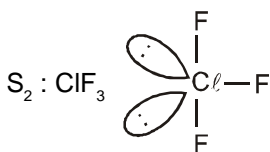


Steric number 4 4

Hence both N and B have tetrahedral geometry with sp^3 hybridisation.

- B-12*.** (A) Steric repulsions of bulkier groups and $p\pi - d\pi$ dative bonding favour for a linear Si-O-Si group.
 (B) Due to stabilization of the conjugate base anion by $O(p\pi) \rightarrow Si(d\pi)$ bonding motion.
 (C) It is pyramidal because $p\pi - d\pi$ bonding is not effective on account of bigger phosphorus atom.
 (D) It has most effective $p\pi - d\pi$ overlapping due to small size of Cl and O.

- C-7.** S_1 : as it does not have d-orbitals.



S_3 : In B_2 mixing of the $\sigma_g(2s)$ orbital with the $\sigma_g(2p)$ orbital lowers the energy of the $\sigma_g(2s)$ orbital and increases the energy of the $\sigma_g(2p)$ orbital to a higher level than the π orbitals. As a result, the last two electrons are unpaired in the degenerate (having the same energy) π orbitals, and the molecule is paramagnetic. In N_2 the $\sigma_g(2s)$ and $\sigma_g(2p)$ levels of N_2 interact (mix) less than the B_2 and C_2 levels, and the $\sigma_g(2p)$ and $\pi_u(2p)$ are very close in energy.

- C-9.** N_2^{2-} : $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2 \pi 2p_x^1 \pi^* 2p_y^1$.

$$\text{B.O. } N_2^{2-} = \frac{10-6}{2} = 2. ; \quad \text{B.O. } O_2 = \frac{10-6}{2} = 2.$$

NO^- isoelectronic with O_2 so $\text{B.O.} = \frac{10-6}{2} = 2$.

All have same number of electrons (i.e. 16) so isoelectronic.

- D-1.** M.O for $C_2 = \sigma_1 s^2 < \sigma_1^* s^2 < \sigma_2 s^2 < \sigma_2^* s^2 < \underbrace{\pi_2 p_y^2 = \pi_2 p_z^2}_{\text{HOMO}} < \underbrace{\sigma_2 p_x}_{\text{LUMO}}$

It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals $C_2^{2-} \left[C \equiv C \right]^{2-}$.

- D-3.** $N_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$

The bond order of N_2 is $1/2(10 - 4) = 3$.

$N_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$

The bond order of N_2^+ is $1/2(9 - 4) = 2.5$.

$O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

The bond order of O_2 $1/2(10 - 6) = 2$.

$O_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$

The bond order of O_2^- $1/2(10 - 7) = 1.5$.

NO^+ derivative of O_2 and isoelectronic with O_2^{2+} ; so $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

The bond order of NO^+ $1/2(10 - 4) = 3$.

NO derivative of O_2 and isoelectronic with O_2^+ ; $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x)^1$

The bond order of NO is $1/2(10 - 5) = 2.5$.

bond order \propto 1/bond length \propto bond dissociation energy.

- D-8.** (A) O_2^- B.O = $1 \frac{1}{2}$ (B) O_2 B.O = 2 (C) O_2^+ = $2 \frac{1}{2}$ (D) O_2^{2-} = 1

Bond order $\propto \frac{1}{\text{bond length}}$.

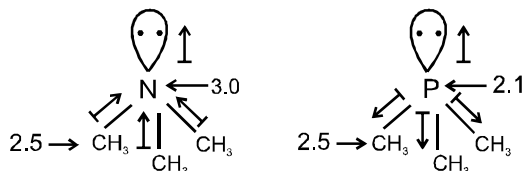
- D-11.** (A) $H_2O_2 = 1.48 \text{ \AA}$ due to repulsions between non-bonded pairs of electron on O-atoms and $O_2F_2 = 1.217 \text{ \AA}$.
 (B) In O_2^{2-} very slightly increases due to charge ($-ve$) on two O atoms.

(C)	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
O_2^+ (dioxygenyl)	2.5	112.3	1
O_2 (dioxygen)	2.0	120.07	2
O_2^- (superoxide)	1.5	128	1
O_2^{2-} (peroxide)	1.0	149	0

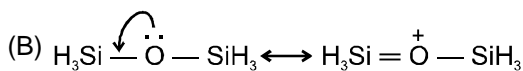
- D-15.**
- | | | |
|---|-------------------------------------|-----------------------|
| | $NO^- > NO > NO^+$ | (bond length) |
| Bond order | 2.0 2.5 3 | |
| | $H_2 > H_2^+ > He_2^+$ | (bond energy) |
| Bond order | 1 0.5 0.5 | |
| (In He_2^+ more electron in antibonding MO's) | | |
| | $NO_2^+ > NO_2 > NO_2^-$ | (bond angle) |
| Bond angle | 180° 133° 115° | |
| | $O_2^{2-} < O_2^+ < O_2$ | (paramagnetic moment) |
| No. of unpaired e^- | 0 1 2 | |

D-19.* O_2^{2+} bond order = 3, NO^+ bond order = 3, CN^- bond order = 3, CN^+ bond order = 2

D-20.* (A) Nitrogen is more electronegative than phosphorus.



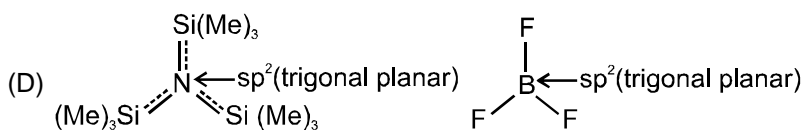
So, dipole moment of trimethylamine is greater than trimethyl phosphine.



In trisilyl ether the lone pair of electron on oxygen atom is less easily available for donation because of $p\pi-d\pi$ delocalisation due to presence of the vacant d-orbital with Si. This however is not possible with carbon in CH_3-O-CH_3 due to the absence of d-orbital making it more basic.

(C) Bond order of C_2 and O_2 are same i.e., 2. In C_2 molecules both bonds are π -bonds whereas, there is one σ and one π -bond in O_2 molecule

$C_2 = 131 \text{ pm}$; $O_2 = 121 \text{ pm}$.



- D-22*.** In FO^+ total no. of electrons = 16, so bond order will be 2.
 In FO^- total number of electrons = 18, so bond order will be 1.

D-25. He_2^+ bond order = $\frac{2-1}{2} = \frac{1}{2}$; O_2^- bond order = $\frac{10-7}{2} = 1.5$

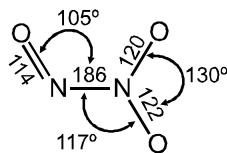
C_2 bond order = $\frac{8-4}{2} = 2$; NO bond order = $\frac{10-5}{2} = 2.5$

Bond order \propto bond dissociation energy.

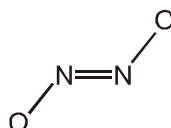
- D-27*.** (A) $O_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$
 (B) NO is derivative of O_2 : $NO(O_2^+) (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$
 (C) $O_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$
 (D) $B_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^1 = \pi 2p_y^1) (\sigma 2p_z)^0$

D-28*.		$\text{NO}^- > \text{NO} > \text{NO}^+$	(bond length)
Bond order	2.0	2.5	3
		$\text{H}_2 > \text{H}_2^+ > \text{He}_2^+$	(bond energy)
Bond order	1	0.5	0.5
		$\text{NO}_2^+ > \text{NO}_2 > \text{NO}_2^-$	
Bond angle	180°	133°	115°
		$\text{O}_2^{2-} = \text{O}_2^{2+} > \text{O}_2$	(paramagnetic moment)
No. of unpaired e^-	0	0	2

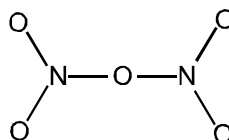
E-3. (A) N_2O_3 Dinitrogen trioxide



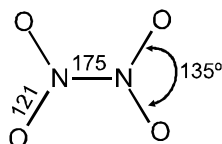
(B) $\text{N}_2\text{O}_2^{2-}$ Hyponitrite ion



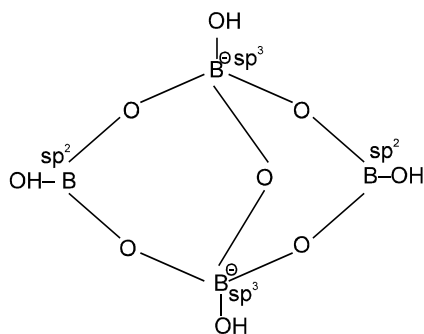
(C) N_2O_5 Dinitrogen pentoxide



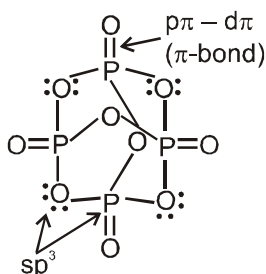
(D) N_2O_4 Dinitrogen tetroxide



E-4. The correct formula of borax is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$. The structure of anion is :

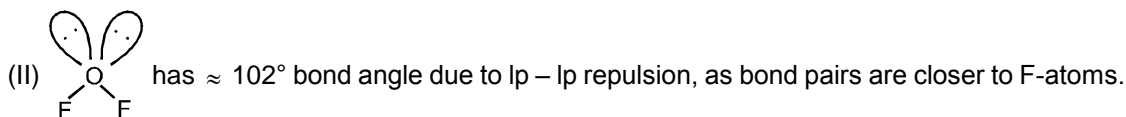


E-8.* P_4O_{10}

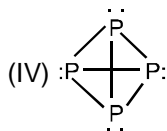


The P – O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P = O bonds on the corners are 1.43 Å and this P = O is formed by $p\pi - d\pi$ back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P – P bonds.

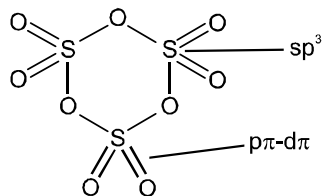
E-11. (I) $[\text{PCl}_4]^+ \rightarrow sp^3$



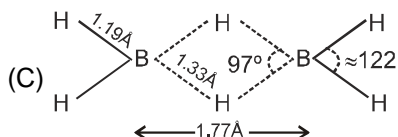
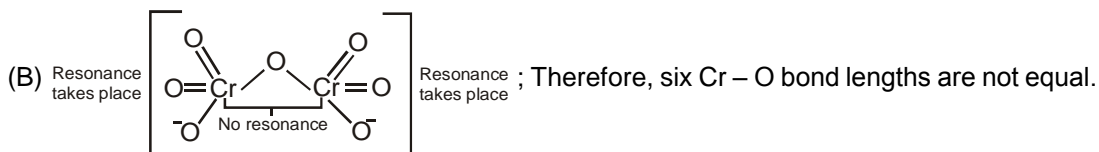
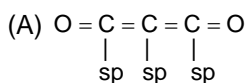
(III) All have sp^3 hybridisation and one lone pair.



E-12.

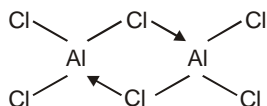


E-13.

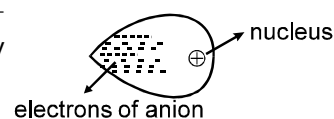


This is an example of 3-centre $2-e^-$ bond which is also known as Banana bond.

But Al_2Cl_6 have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



(D) AgI is bright yellow coloured compound due to the polarisation of anion, I^- . The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

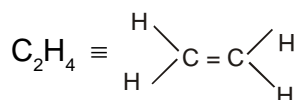


E-17.

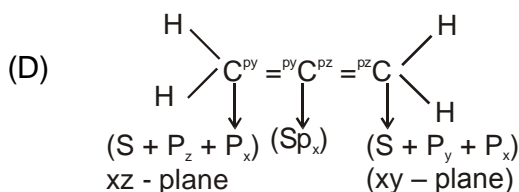
(A) NO B.O = 3 triple bond.

$\text{O}=\text{N}-\text{Cl}$ there is a double bond between N and 'O' atom

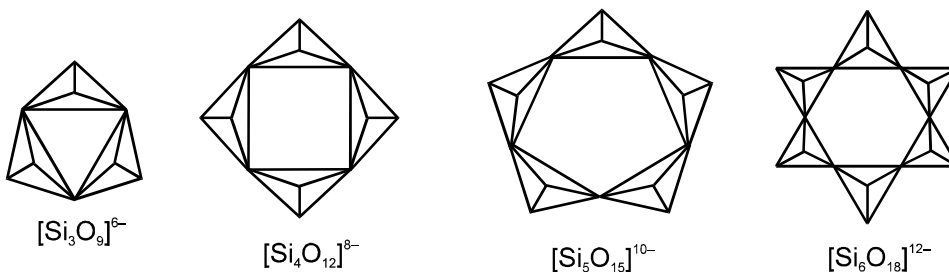
(B) $\text{CaC}_2 \equiv \text{Ca}^{2+} + \text{C}_2^{2-}$ ($-\text{C} \equiv \text{C}-$)



(C) $\text{KO}_2 \equiv \text{O}_2^-$ B.O = 1.5
 $\text{Na}_2\text{O}_2 \equiv \text{O}_2^{2-}$ B.O = 1



E-18.



general formula of cyclic silicates is $[\text{Si}_n\text{O}_{3n}]^{2n-}$

PART - II

1.	(A)	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons /Magnetic property
	O_2^+ (dioxygenyl)	2.5	112.3	1 (paramagnetic)
	O_2 (dioxygen)	2.0	120.07	2 (paramagnetic)
	O_2^- (superoxide)	1.5	128	1 (paramagnetic)
	O_2^{2-} (peroxide)	1.0	149	0 (diamagnetic)

Bond order \propto stability (i.e., bond strength)

(B) **Helium molecule (He_2)**: $\text{He}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$

Bond order of He_2 is $\frac{1}{2}(2 - 2) = 0$

The molecular orbital description of He_2 predicts two electrons in a bonding orbital and two electrons in an antibonding orbital, with a bond order of zero - in other words, no bond. The noble gas He has not significant tendency to form diatomic molecules and, like the other noble gases, exists in the form of free atoms.

(C) **Carbon molecule (C_2)**: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ or KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

Lithium molecule (Li_2): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

Peroxide (O_2^{2-}): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$

As all electrons are paired so C_2 , Li_2 and O_2^{2-} are diamagnetic.

(D) **Fluorine molecule (F_2)**: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$

2. (D) It is correct statement.

3.		Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons /Magnetic property
	O_2^+ (dioxygenyl)	2.5	112.3	1 (paramagnetic)
	O_2 (dioxygen)	2.0	120.07	2 (paramagnetic)
	O_2^- (superoxide)	1.5	128	1 (paramagnetic)
	O_2^{2-} (peroxide)	1.0	149	0 (diamagnetic)

4. **Oxygen molecule (O_2)**: $\text{O}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

Bond order = $\frac{1}{2}(10 - 6) = 2.0$,

$\text{O}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$

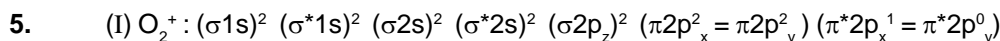
Bond order = $\frac{1}{2}(10 - 5) = 2.5$.

Nitrogen molecule (N_2): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$

The bond order of N_2 is $\frac{1}{2}(10 - 4) = 3$.

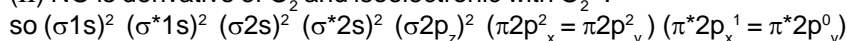
$\text{N}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$

Bond order = $\frac{1}{2}(9 - 4) = 2.5$.

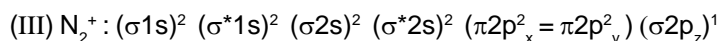


Bond order = $1/2(10 - 5) = 2.5$.

(II) NO is derivative of O_2 and isoelectronic with O_2^+ :



Bond order = $1/2(10 - 5) = 2.5$.



Bond order = $1/2(9 - 4) = 2.5$.

O_2^+ , NO and N_2^+ have same bond order i.e. 2.5 and have same magnetic property having one unpaired electron.

10. (A) $N_2^+ : BO=2.5$ (4 electron in antibonding MO) 1 unpaired electron (Paramagnetic)
 $N_2^- : BO=2.5$ (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic)
 (B) NO : $BO=2.5$ (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic). Last electron in antibonding MO. So, easily removed.
 $N_2 : BO = 3$ (4 electron in antibonding MO) 0 unpaired electron (diamagnetic). Last electron in bonding MO. So, not easily removed.
 (C) $NO^+ : BO = 3$ (0 unpaired electron) diamagnetic [$BO \uparrow \Rightarrow BL \downarrow$].
 (D) $He_2^+ : BO = 0.5$ (1 unpaired electron) paramagnetic [1 electron in antibonding MO].
 $H_2^+ : BO = 0.5$ (1 unpaired electron) paramagnetic [0 electron in antibonding MO].

EXERCISE # 2

11. (a) **Hydrogen molecule (H_2)** : $H_2 : (\sigma 1s)^2$
 Its bond order, therefore, is $= \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$
 (b) **Cation of hydrogen molecule (H_2^+)** : $H_2^+ : (\sigma 1s)^1$
 Its bond order, therefore, is $= 1/2 (1 - 0) = 1/2$
 (c) **Helium molecule (He_2)** : $He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$
 Its bond order, therefore, is $1/2(2 - 2) = 0$
 (d) **Lithium molecule (Li_2)** : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$
 Its bond order, therefore, is $1/2(4 - 2) = 1$.
 (e) **Beryllium (Be_2)** : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$
 Its bond order, therefore, is $1/2(4 - 4) = 0$.
 (f) **Boron (B_2)** : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^1 = \pi 2p_y^1) (\sigma p_z)^0$
 Its bond order, therefore, is $1/2(6 - 4) = 1$.

13. $\begin{array}{cccc} * \sigma 3p & - & - & - \\ * \pi 3p & \downarrow & \downarrow & \downarrow \uparrow \\ \pi 3p & \downarrow \uparrow & \downarrow \uparrow & \downarrow \uparrow \\ \sigma 3p & \downarrow \uparrow & & \downarrow \uparrow \\ * \sigma 3s & \downarrow \uparrow & & \downarrow \uparrow \\ \sigma 3s & \downarrow \uparrow & & \downarrow \uparrow \\ & S_2 & & S_2^{2-} \end{array}$
 Bond order $S_2 = \frac{8 - 4}{2} = 2$ (paramagnetic with two unpaired electrons)

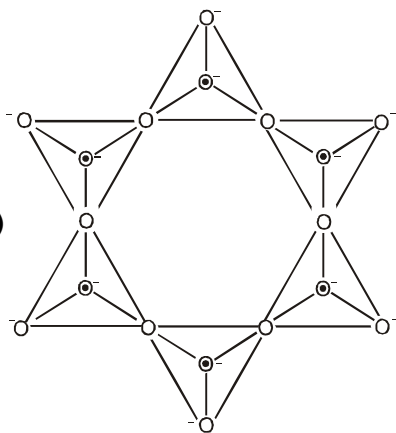


Bond order $S_2^{2-} = \frac{8 - 6}{2} = 1$ (diamagnetic, as all electrons are paired).

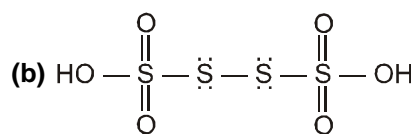
16. Complex exists as NO^+ and $[BF_4]^-$. NO^+ is isoelectronic with N_2 ; so $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$, then its bond order is $\frac{10 - 4}{2} = 3$

20.

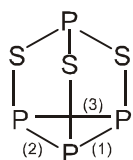
(a)



6 shared 'O' atoms.

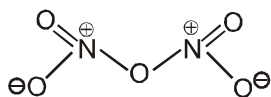


(c)



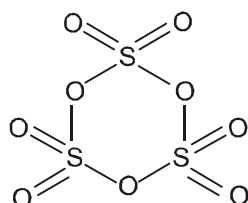
3 P-P bond

(d)



4 equivalent N-O bonds due to resonance.

(e)

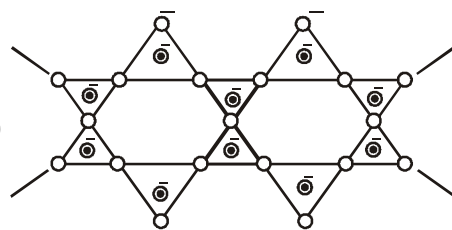


3 S-O-S bond

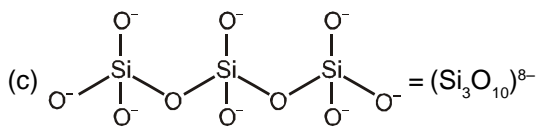
22.

(a) $(\text{SiO}_3^{2-})_n$

(b)



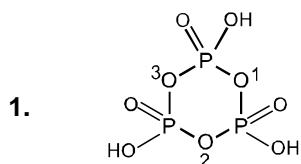
$((\text{Si}_4\text{O}_{11})^{6-})_n$



(d) $(\text{SiO}_3^{2-})_3$

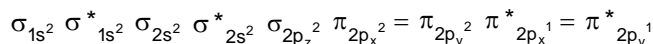
(e) $(\text{Na}^+(\text{PO}_3^-))_6 = \text{Na}_6(\text{PO}_3)_6$

EXERCISE # 3



According to the structure of cyclic metaphosphoric acid, $(\text{HPO}_3)_3$, there are three P – O – P bonds.

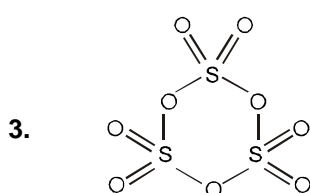
2. Molecular orbital electronic configuration of O_2 is as follows (Z is taken as molecular axis).



$$\text{Bond order} = \frac{10 - 6}{2} = 2.$$

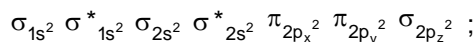
As it contains two unpaired electrons in bonding π molecular orbitals O_2 is paramagnetic.

So, Magnetic moment = $\sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.83 \text{ B.M.}$



There is no S-S bond in S_3O_9 .

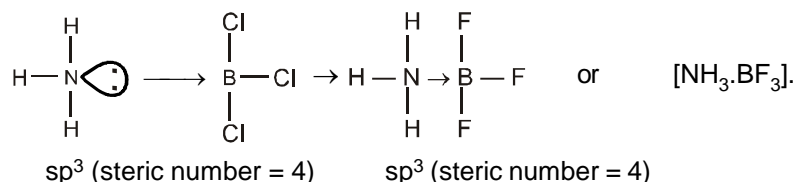
4. CN^- , CO and NO^+ all have same number of electrons i.e. 14. So all are isoelectronic species. Further all the species are isoelectronic with N_2 which have molecular orbital electronic configuration as follows



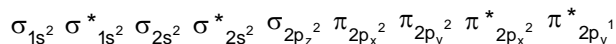
$$\text{So, Bond order} = \frac{10 - 4}{2} = 3.$$

Hence all will have same bond order and that is three.

5. Here ammonia acts as a Lewis base and boron trifluoride as Lewis acid as represented below. Hence in this complex both N and B acquire tetrahedral geometry and sp^3 hybridisation.



6. O_2^- is derivative of O_2 and has 17 electrons. So its molecular orbital electronic configuration is



As it contains one unpaired electron in $\pi_{2p_y^1}^*$ molecular orbital so it is paramagnetic. Rest all species have paired electrons so diamagnetic.

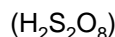
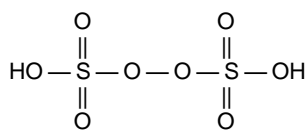
7. O_2 bond order = 2 ; O_2^- bond order = 1.5 ; O_2^{2-} bond order = 1.0 ; O_2^+ bond order = 2.5.

8. In diethyl ether ($\text{C}_2\text{H}_5-\ddot{\text{O}}-\text{C}_2\text{H}_5$) oxygen atom has two lone pairs of electrons, thus acts as Lewis base while in anhydrous AlCl_3 aluminium has vacant $3p$ -orbital of valence shell and thus acts as Lewis acid. AlCl_3

accepts a lone pair of electrons from diethyl ether to complete its octet forming a complex

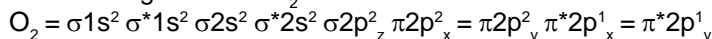
Hence, anhydrous AlCl_3 is more soluble in diethyl ether by means of solvolysis in comparison to hydrous AlCl_3 (i.e., $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$). Hydrous AlCl_3 is a polar compound, while ether is non-polar, so on basis of Thumb's rule, like dissolve in like solvents. Hence hydrous AlCl_3 is least soluble in ether.

9. It is peroxodisulphuric acid, the Marshall's acid and contains one – O – O – linkage as given in structure



10. Molecular orbital electronic configuration is $\sigma_{1s^2} \sigma^*_{1s^2} \sigma_{2s^2} \sigma^*_{2s^2} \sigma_{2p_z^2} \pi_{2p_x^2} \pi_{2p_y^2} \pi^*_{2p_x^1} \pi^*_{2p_y^0}$
As it contains one unpaired electron it is paramagnetic and bond order = $(10 - 5) / 2 = 2.5$ ($\text{O}_2 = 2.0$).

11. The electronic configuration of O_2 will be:

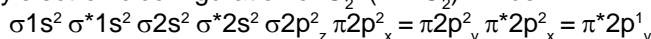


$$\text{Now bond order} = \frac{N_b - N_a}{2}$$

Where, N_b = Number of electrons in bonding orbitals N_a = Number of electrons in antibonding orbitals

$$\text{bond order} = \frac{10 - 6}{2} = 2$$

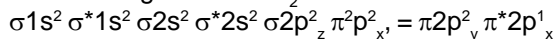
Similarly electronic configuration of O_2^- (in KO_2) will be



$$\text{Bond order} = \frac{10 - 7}{2} = \frac{3}{2} = 1.5$$

In $\text{O}_2 [\text{AsF}_4]^-$, O_2 is O_2^- .

The electronic configuration of O_2^+ will be

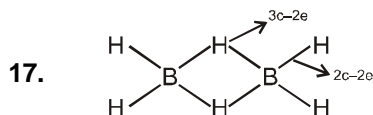


$$\text{bond order} = \frac{10 - 5}{2} = 2.5$$

Hence bond length order will be $\text{O}_2^+ < \text{O}_2 < \text{O}_2^-$ because Bond order $\propto \frac{1}{\text{Bond length}}$.

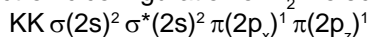
13. NO and NO^+ are derivative of O_2 .
NO (isoelectronic with O_2^+): $(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 = \pi_{2p_y^2} (\pi^*_{2p_x})^1 = \pi^*_{2p_y}$
Bond order = $1/2(10 - 5) = 2.5$.
 NO^+ (isoelectronic with O_2^{2+}): $(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 = \pi_{2p_y^2} (\pi^*_{2p_x})^0 = \pi^*_{2p_y}$
Bond order = $1/2(10 - 4) = 3$.
Bond order $\propto 1/\text{bond length}$.
So NO^+ has shorter bond length.

14. (A) In two dimensional sheet silicates, three oxygen atoms of $[\text{SiO}_4]^{4-}$ are shared with adjacent tetrahedral $[\text{SiO}_4]^{4-}$ units,
(B) One oxygen atom is shared between two adjacent tetrahedra, $[\text{SiO}_4]^{4-}$.
(C) All four oxygen atoms are shared between adjacent tetrahedra, $[\text{SiO}_4]^{4-}$.
(D) Two oxygen atoms are shared between adjacent tetrahedra, $[\text{SiO}_4]^{4-}$ forming a linear chain.

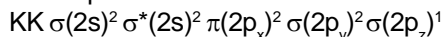


18. $\text{He}_2^+ \rightarrow \sigma (1s)^2 \sigma^* (1s)^1$, one unpaired electron.
 $\text{H}_2 \rightarrow (1s)^2, \sigma^* (1s)^0$, no unpaired electron.
 $\text{H}_2^+ \rightarrow \sigma (1s)^1, \sigma^* (1s)^0$, one unpaired electron.
 $\text{H}_2^- \rightarrow \sigma (1s)^2, \sigma^* (1s)^1$, one unpaired electron.
19. The electronic configuration of oxygen atom is $1s^2, 2s^2, 2p^4$. Each oxygen atom has 8 electrons. Hence in each O_2^{2-} ion there are $16 + 2 = 18$ electrons. The electronic configuration of O_2^{2-} ion is
 $\text{KK} \sigma (2s)^2 \sigma^* (2s)^2 \pi (2p_z)^2 \pi (2p_x)^2 \pi (2p_y)^2 \pi^* (2p_x)^2 \pi^* (2p_y)^2$
Here KK represents non-bonding molecular orbital of 1s orbital. O_2^{2-} contains no unpaired electrons.

The electronic configuration of B₂ molecule is

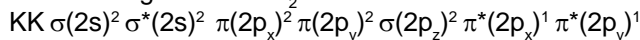


it contains 2 unpaired electrons. The electronic configuration of N₂⁺ ion is



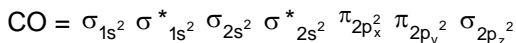
it contains one unpaired electron.

The electronic configuration of O₂ molecule is

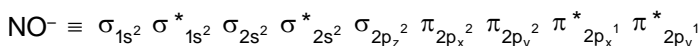


It contains 2 unpaired electron.

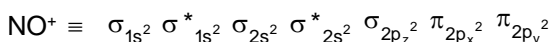
20. Bond order = $\frac{N_b - N_a}{2}$



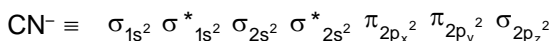
$$\text{Bond order of CO} = 10 - 4 / 2 = 3$$



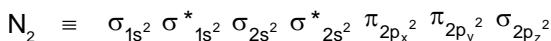
$$\text{Bond order of NO}^- = 10 - 6 / 2 = 2$$



$$\text{Bond order of NO}^+ = 10 - 4 / 2 = 3$$



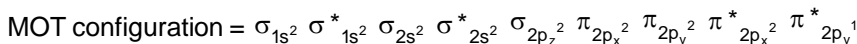
$$\text{Bond order of CN}^- = 10 - 4 / 2 = 3$$



$$\text{Bond order of N}_2 = 10 - 4 / 2 = 3.$$

21. KO₂ exists as K⁺ & O₂⁻.

In O₂⁻, superoxide ion there are total number of electrons = 16 + 1 = 17.



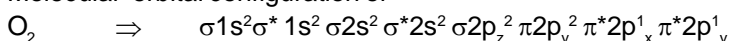
O₂⁻ has one unpaired electron in antibonding π*2p_y¹. So it is paramagnetic.

22. Steric number = 4 ; thus sp³ hybridisation in P₄. As each phosphorus is sp³, so

$$\% \text{ p character will be} = \frac{3}{4} \times 100 = 75.$$

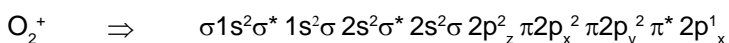
23. O₂²⁻ (8 + 8 + 2 = 18) : $\sigma_{1s^2} \sigma_{1s^2}^* \sigma_{2s^2} \sigma_{2s^2}^* \sigma_{2p_z^2} \pi_{2p_x^2} \pi_{2p_y^2} \pi_{2p_x^2}^* \pi_{2p_y^2}^*$; all electrons are paired. So diamagnetic.

24. Molecular orbital configuration of



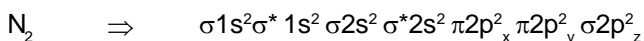
⇒ Paramagnetic

$$\text{Bond order} = \frac{10 - 6}{2} = 2$$



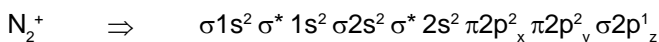
⇒ Paramagnetic

$$\text{Bond order} = \frac{10 - 5}{2} = 2.5$$



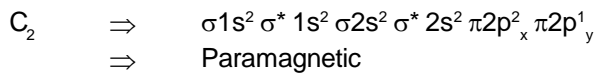
⇒ paramagnetic

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

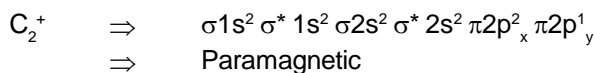


⇒ Paramagnetic

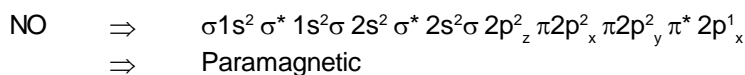
$$\text{Bond order} = \frac{9 - 4}{2} = 2.5$$



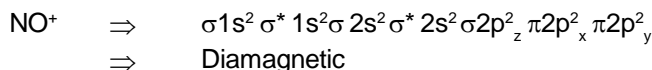
$$\text{Bond order} = \frac{8-4}{2} = 2$$



$$\text{Bond order} = \frac{7-4}{2} = 1.5$$



$$\text{Bond order} = \frac{10-5}{2} = 2.5$$



$$\text{Bond order} = \frac{10-4}{2} = 3.$$

25. NO^+ is derivative of O_2 ; NO^+ (isoelectronic with O_2^{2+}) $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$

$$\text{Bond order} = \frac{10-4}{2} = 3.$$

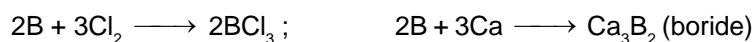
CN^- is derivative of N_2 ; CN^- (isoelectronic with N_2) $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$

$$\text{Bond order} = \frac{10-4}{2} = 3.$$

26. (A) $\text{B}_2 \quad \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 = \pi 2p_y^1$

$$\text{Bond order} = \frac{6-4}{2} = 1 \quad \text{Paramagnetic with two unpaired electrons.}$$

It undergoes oxidation as well as reduction which can be explained by taking the following reactions.



Mixing of 's' and 'p' orbitals takes place.

(B) $\text{N}_2 \quad \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$

$$\text{Bond order} = \frac{10-4}{2} = 3 \quad \text{Diamagnetic}$$

It undergoes oxidation as well as reduction which can be explained by taking the following reactions.



Mixing of 's' and 'p' orbitals takes place.

(C) $\text{O}_2^- \quad \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_x^2 \pi^* 2p_x^2 = \pi^* 2p_y^1$

$$\text{Bond order} = \frac{10-7}{2} = 1.5 \quad \text{Paramagnetic with one unpaired electron.}$$

It undergoes oxidation as well as reduction which can be explained by taking the following reactions.



Mixing of 's' and 'p' orbitals does not take place.

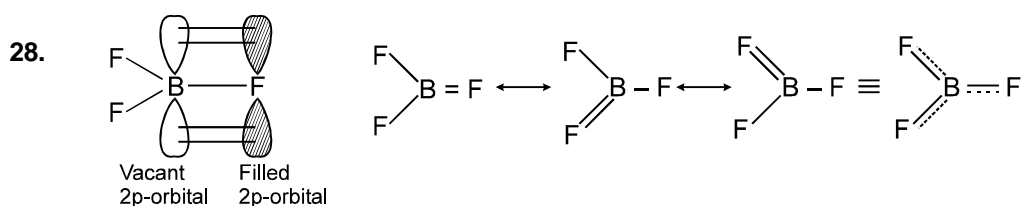
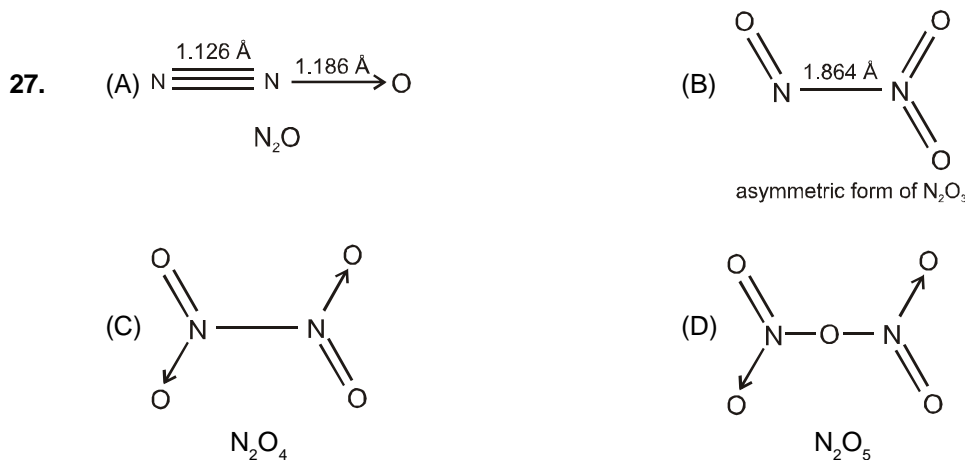
(D) $\text{O}_2 \quad \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_x^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$

$$\text{Bond order} = \frac{10-6}{2} = 2 \quad \text{Paramagnetic with two unpaired electrons.}$$

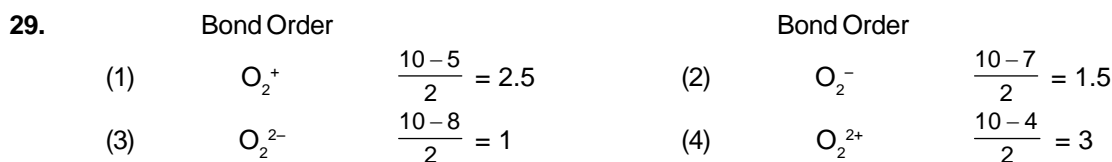
It undergoes oxidation as well as reduction which can be explained by taking the following reactions.



Mixing of 's' and 'p' orbitals does not take place.



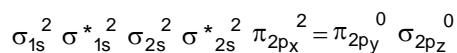
Decrease in B – F bond length which results in the higher bond dissociation energy of B – F in BF_3 is due to delocalised $\text{p}\pi-\text{p}\pi$ bonding between filled p-orbital of F atom and vacant p-orbital of B atom.



$$\text{Bond order} \propto \frac{1}{\text{bond length}}$$

So, O_2^{2+} has the shortest bond length.

30. B_2 ; total number of electrons = 10. The MOT electron configuration violating the Hund's rule will be thus :



$$\text{So, bond order} = \frac{6-4}{2} = 1$$

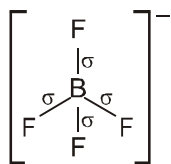
As all electrons are paired, the molecule is diamagnetic.

SOLUTION OF ADVANCED LEVEL PROBLEM

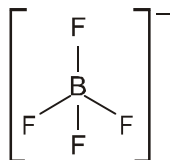
3. Phosphorous acid (H_3PO_3) Dibasic $\therefore x = 2$
 Di meta phosphoric acid ($\text{H}_2\text{P}_2\text{O}_6$) Dibasic $\therefore y = 2$
 Pyro phosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) tetrabasic $\therefore y = 4$
Ans. 224

13. (P) Molecular orbital electronic configuration ;
 NO^+ is derivative of O_2 , so MOT configuration is :
 $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_x}^2 \pi_{2p_y}^2 = \pi_{2p_z}^2$ (x is taken as molecular axis)
- $$\text{Bond order} = \frac{10-4}{2} = 3$$
- One σ bond and two π bonds.

(Q) Number of σ bonds in NO^+ is one and in BF_4^- are four. So total number of σ bonds are five.



(R) Number of π bonds in NO^+ are two.

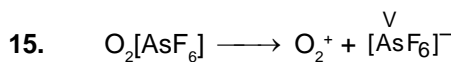


(S)

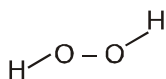
Steric number of central atom boron is $4 + 0 = 4$; so its hybridisation is sp^3 and thus the number of hybrid orbitals involved in sp^3 hybridisation is four.

Ans.

3	5	2	4
P	Q	R	S

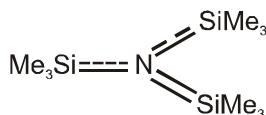


O_2^{2-} peroxide ion B.O = $\frac{1}{2}(10 - 8) = 1$.



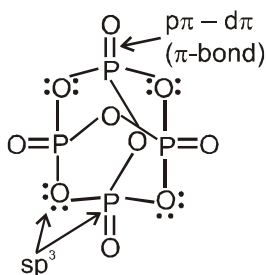
O – O bond is non polar so 2 polar bond.

carbon suboxide is C_3O_2



Number of l.p is present in $\text{N}(\text{SiMe}_3)_3$ is zero.

16.



The P – O bond lengths shows that the bridging bonds on the edges are 1.60 \AA but the P = O bonds on the corners are 1.43 \AA and this P = O is formed by $p\pi - d\pi$ back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P – P bonds.

(i) P = O have bond length of 1.43 \AA (8 covalent bonds)

(ii) P – O have bond length of 1.60 \AA (12 covalent bonds)

(iii) Number of P – O – P linkage = 6.

(iv) Number of lone pair on each phosphorus atom is zero.

Ans.

4	12	6	0
(i)	(ii)	(iii)	(iv)

Chemical Bonding Part-3

EXERCISE # 1

PART - I

- A-2.** As Pb^{2+} has low polarising power. So PbCl_2 is ionic.
- A-3.** As charge on cations increases, their polarising power increases and thus covalent character increases.
$$\overset{+}{\text{LiCl}} < \overset{2+}{\text{BeCl}_2} < \overset{3+}{\text{BCl}_3} < \overset{4+}{\text{CCl}_4}$$
- A-5.** As the size of anions decrease the distance of valence shell electrons from nucleus decreases and so polarizability decreases.
- A-6.** Sn^{4+} has highest polarising power amongst Na^+ , Pb^{2+} , Sn^{4+} and Al^{3+} because of smaller size and higher charge. So SnCl_4 is most covalent and thus has least melting point.
- A-7.** Because of high charge density on Sn^{4+} it has high polarising power and thus leads to greater polarisation of anion i.e., greater distortion of electron clouds of the Cl^- ions. So SnCl_4 is most covalent.
- A-9.** Solubility BaCO_3 and MgCO_3 can be explained on the basis of their hydration and lattice energies.
- A-10.** AgI is less soluble than AgF due to covalent nature. LiI is more soluble than LiF due to high size difference of ions more ionic nature, more melting point. Higher the charge density, larger will be the hydrated radii.
- A-12.** Polarisation of the I^- by the Cu^{2+} results in the transference of an electron towards Cu^{2+} makes it as oxidising agent and I^- as a reducing agent, reduces Cu^{2+} to Cu^+ and itself oxidised to I_2 .
- B-2.** Metallic bond results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.
- B-4.** (A) N_2 contains one σ and two π bonds but C_2 contains only two π bonds as four electrons are present in bonding π molecular orbitals.
(B) Cu^{2+} has higher hydration energy than Cu^+ so Cu^{2+} is more stable than Cu^+ . Moreover, Cu^+ undergoes disproportionation. $2\text{Cu}^+ \rightarrow 2\text{Cu}^{2+} + \text{Cu}$. (a fact)
(C) Can be explained by electron sea model as it is due to the presence of mobile electrons.
- B-6*.** (A) It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.
(B) In general, greater the number of $(n-1)d$ and ns electrons, stronger is the resultant bonding.
(C) Strength of metallic bond depend on the type of hybrid orbitals participating in metallic bonding.
(D) As the size of atom increases the attraction between the positive part of the atom and delocalised electrons decreases and thus the strength of the metallic bond decreases.

PART - II

- For more covalent character, small cation and large anion are favourable factors. In MgS , Mg^{2+} will have higher polarising power and S^{2-} will have higher polarisability. Hence there will be higher polarisation of anion resulting in higher covalent character.
- Due to smaller size of Be^{2+} and largest size of I^- amongst all anions i.e. F^- , Cl^- , Br^- and I^- , there will be greater polarisation of anion. Thus BeI_2 will be most covalent i.e. least ionic.
- As the size of the cations increases in the order
$$\text{Si}^{4+} < \text{Sn}^{4+} < \text{Sn}^{2+}$$
and for size of anions
$$\text{F}^- < \text{Cl}^-$$
so the order of increasing ionic character is
$$\text{SiCl}_4 < \text{SnCl}_4 < \text{SnF}_4 < \text{SnCl}_2 < \text{SnF}_2$$
- As polarizability of anion increases covalent character increases.
- Larger anion has higher polarisability.

EXERCISE # 3

- Statement-1** : Germanium is a semiconductor, where the energy gap between adjacent bands is sufficiently small for thermal energy to be able to promote a small number of electrons from the full valence band to the empty conduction band. This leaves both bands partially filled, so the material can conduct electricity.

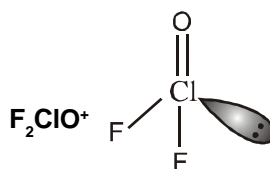
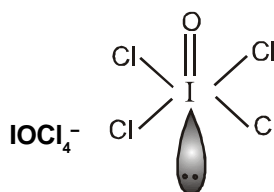
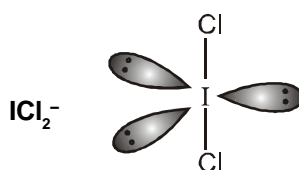
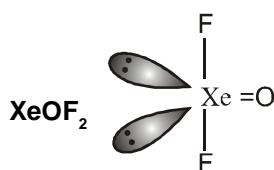
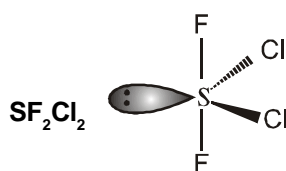
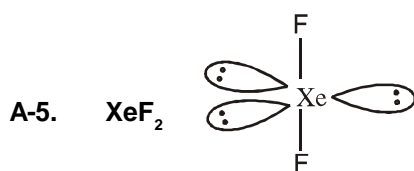
Statement-2 : Incorrect statement.
- The elements of group 14 show an oxidation state of +4 and +2. The compounds showing an oxidation state of +4 forms covalent compound and have tetrahedral structures. e.g. SnCl_4 , PbCl_4 , SiCl_4 , etc. whereas those which show +2 oxidation state are ionic in nature and behave as reducing agent. e.g. SnCl_2 , PbCl_2 etc. Further as we move down the group the tendency of the element to form covalent compound decreases but the tendency to form ionic compound increases.
- High charge and small size of the cations increases polarisation.
As the size of the given cations decreases as
 $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Be}^{2+}$
Hence, polarising power increases as
 $\text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$
- Covalent character in ionic compounds is governed by Fajan's Rule. AlCl_3 will show Maximum covalent character on account of higher polarising power of Al^{3+} because of its having higher positive charge and smaller size.

Solution of advanced level problem already given in sheet booklet

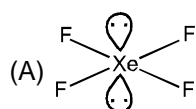
Chemical Bonding Part-4

EXERCISE # 1

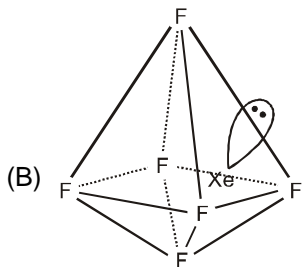
PART - I



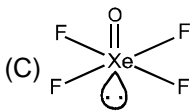
- A-9*. Polarity depend on net dipole moment. If dipole moment $\mu = 0$ it is nonpolar.



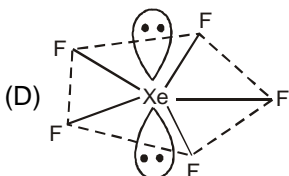
XeF_4 $\mu = 0$ non polar



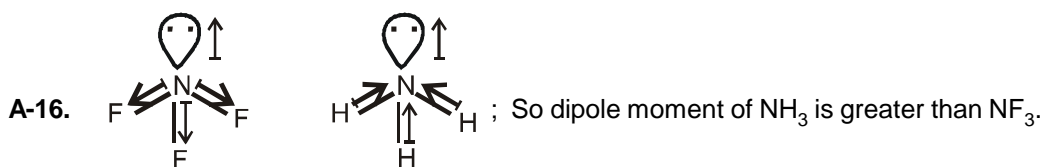
XeF_6 $\mu \neq 0$ polar



XeOF_4 $\mu \neq 0$ polar



XeF_5^- $\mu = 0$ non polar



A-19. Dipole moment of compound if it would have been completely ionic
 $= (4.8 \times 10^{-10} \text{ esu}) (2.67 \times 10^{-8} \text{ cm}) = 12.8 \text{ D}$

$$\text{so \% ionic character} = \frac{4.0}{12.8} \times 100\% = 31.25\%$$

A-22. This is based on the decreasing electronegativity difference between H (2.1) and Sb (1.9), As (2.0), P (2.1) and N (3.0).

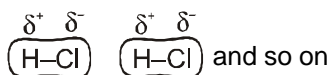
B-1. S_1 :

S_2 : Hydration of ions due to force of attraction between ion and water molecule. Which is a dipole.

S_3 : Due to intermolecular H-bonding, boiling point increases.

S_4 : A symmetrical molecule with identical bonds have zero dipole moment.

B-2. All molecules have London dispersion force because of number of polarizable electrons.
 Non polar molecules have only London dispersion force because of polarisable electron. Benzene is non polar molecule.
 Polar molecules have dipole-dipole attraction in addition to London dispersion force.



Molecules with, O-H, N-H, or F-H bond have hydrogen bonding in addition to London dispersion force.
 Molecule ICl is polar, so in addition to London dispersion force it has dipole-dipole attraction also.

B-3. Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C-C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and make three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet.

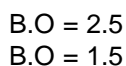
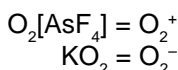
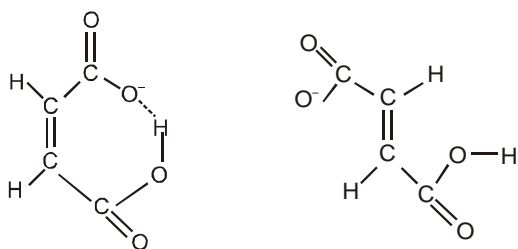
- B-9.** (A) As δ^+ charge on central atom increases, the attraction between δ^+ and δ^- increases and thus Xe–F bond length decreases. The correct order is $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$
 (B) PH_5 can not undergo sp^3d hybridisation as there is much large difference in size of s, p and d orbitals. PH_5 does not exist as no partial positive charge develops on P atom.
 (C) Dipole moment of CH_3Cl is greater than CH_3F due to greater charge separation on carbon and chlorine atoms in CH_3Cl .
 (D) it is a correct order.

The strength of hydrogen bond depends upon :

(i) size (ii) electronegativity and (iii) ease of donation of electron pair by electronegative element.

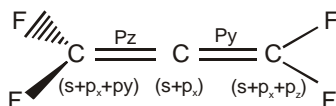
Higher the value of electronegativity and smaller the size of the covalently bonded atom to H atom stronger is the hydrogen bonding.

- B-13*.** maleic acid fumaric acid



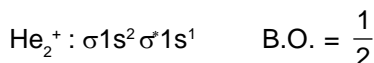
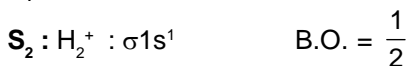
so O_2^+ has smaller bond length than O_2^-

Greater the size of the halogen atom greater will be bond angle.



- C-1** S_1 : Due to intermolecular H-bonding in HF it boils at higher temperature than HCl
 S_2 : Mol. wt. of HBr < Mol. wt. of HI
 S_3 : Bond order of N_2 is more than N_2^+ .
 S_4 : Molecular mass of F_2 is less than that of Cl_2

- C-3.** S_1 : Polarising power of a cation is inversely proportional to its size.



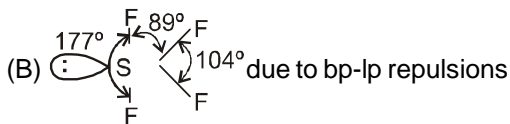
But He_2^+ has electron in antibonding molecular orbital so its is unstable.

S_3 : H-bond formation requires the availability of lone pair of electron.

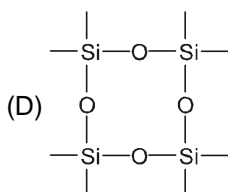
S_4 : In Cl_2O , the bond angle is more than $109^\circ 28'$ due to steric repulsion.

- C-4.** As molecular weight increases, magnitude of Van der Waal's force of attraction increases. Therefore, boiling point increases. Though NH_3 has strong H-bonding but boiling point of SbH_3 is highest due to highest molecular weight. Boiling point $\text{NH}_3 = 238.5 \text{ K}$ and $\text{SbH}_3 = 254.6 \text{ K}$.

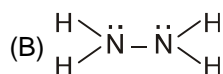
- C-6.** (A) in S_8 hybridisation of each S-atom is sp^3 , in P_4 hybridisation of each P-atom is sp^3

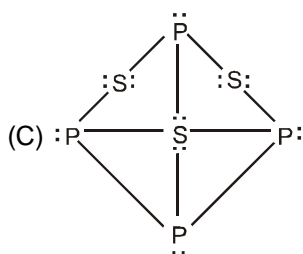


(C) Inter molecular H-bonding (PO_4^{3-} groups are bonded by many H-bonds)



C-7*. (A) Boiling point of $\text{ICl} > \text{Br}_2$ as ICl is polar and Br_2 is non-polar in nature.

(B)  pyramidal about each N-atom.



C-8*. (A) $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$ (order of B.Pt)

(B) As D_2O has higher molecular mass than H_2O so its density is more.

(C) $\text{Mn} \rightarrow 4s^2 3d^5$

$\text{Ca} \rightarrow [\text{Ar}] 4s^2$

$\text{Sr} \rightarrow [\text{Kr}] 5s^2$

$\text{Rb} \rightarrow [\text{Kr}] 5s^1$

Refer notes

(D) $\text{H}_2 \rightarrow$ weak VDW forces

$\text{CO}_2 \rightarrow$ weak VDW force but stronger than H_2 .

$\text{H}_2\text{O} \rightarrow$ H-bonding.

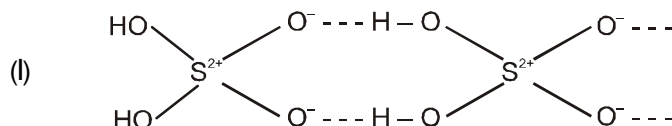
C-9*. (A) Ethyne being non-polar is more soluble in acetone.

(B) CD_3F is more polar than CH_3F . In CD_3F , C–D bond is more polar as deuterium is more electropositive than hydrogen.

(C) Silyl isocyanate (SiH_3NCO) is linear in shape because of $p\pi-d\pi$ delocalisation of lone pair of electrons on nitrogen. While in methyl isocyanate (CH_3NCO) there is no $p\pi-d\pi$ delocalisation of electron as carbon does not have empty d-orbital and thus is bent in shape.

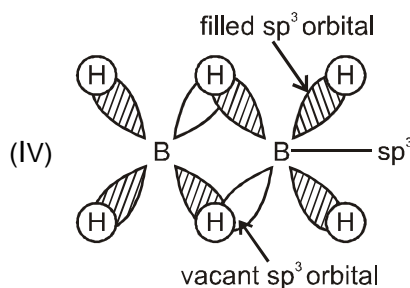
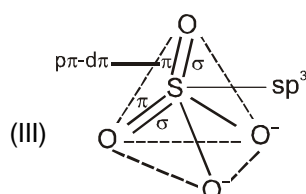
In $\text{CH}_2=\text{C}=\text{C}=\text{CH}_2$, the 2H-atoms on one C-atom lie in a plane perpendicular to the plane in which 2H-atoms on other C-atom lie.

C-12.

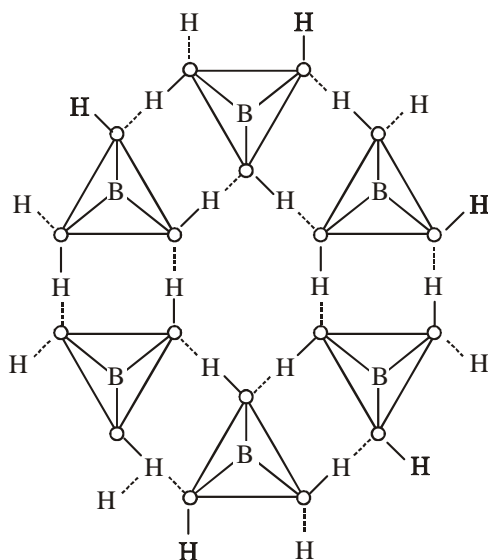


As a result of H-bonding, number of sulphuric acid molecules are associated to form cluster. Hence it has high boiling point and viscosity.

(II) All S — O bond lengths are equal due to resonance.

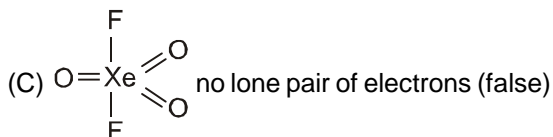
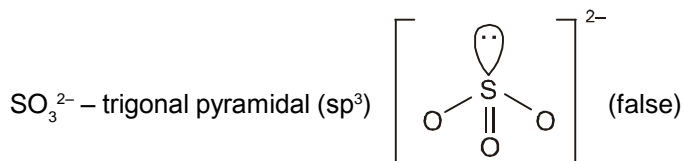
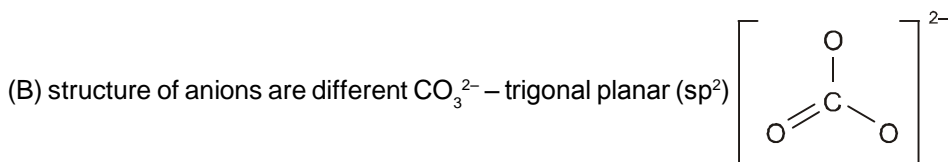


- C-13.** (A) A fact
 (B) In the solid state and in liquid HF, the HF_2^- ion is held together by hydrogen bonding. In aqueous solutions there is hydrogen bonding but each HF molecule forms hydrogen bonds with the much more prevalent H_2O present, instead of with other HF molecules and H_3O^+ and F^- are much more likely to be formed.
 (C) H_3BO_3 (solid) has inter molecular hydrogen bonding.



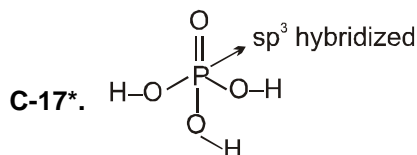
- C-14.** (A) Like hydrated copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in which one water molecule is hydrogen bonded to coordinated water molecule, one water molecule is coordinated to lone pair of electrons on SnCl_2 and the other is hydrogen bonded to coordinated water molecule.

- C-15** (A) intermolecular hydrogen bonded. (true)



- (D) True. $\text{D}_2\text{O} = 374.4 \text{ K}$; $\text{H}_2\text{O} = 373.0 \text{ K}$

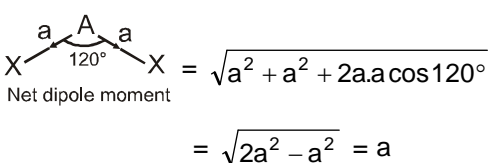
- C-16.** $\text{S}_2\text{O}_3^{2-}$ ion :
 Individual O.N. of S atoms = +6 and -2. Average O.N. = +2
 SbH_3 has higher bp than NH_3 , due to vander waal forces.
 In hydricids, the acidity increases down the group while for oxyacids, the acidity decreases down the group.



The P = O contain one $p\pi-d\pi$ bond. The PO_4^{3-} ion show resonance. Due to the presence of H-bonded to O, it show intermolecular H-bonding due to which it is syrupy.

- C-24. (i) H_2O has highest boiling point because of H-bonding.
 (ii) Boiling point also depends on the magnitude of van der Waal's force of attraction, which in turns depends on molecular weight of the compounds. Thus the correct order is $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$.
- C-28 D is less electronegative than H-atom so the results

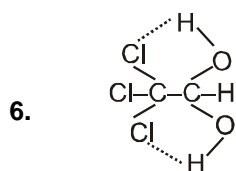
PART - II

4. 
 Net dipole moment

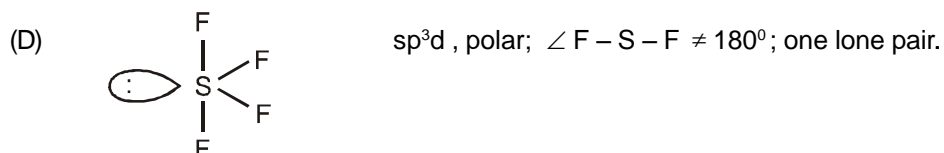
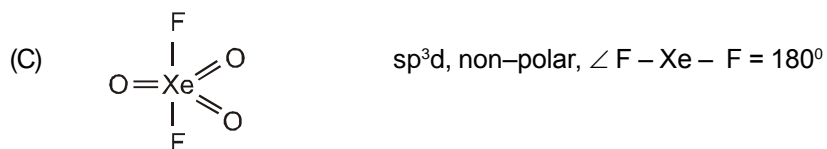
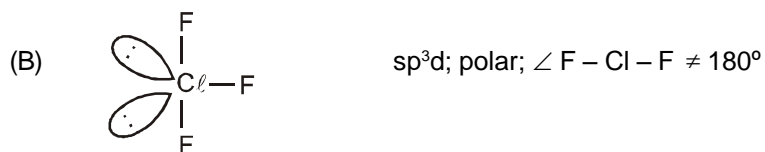
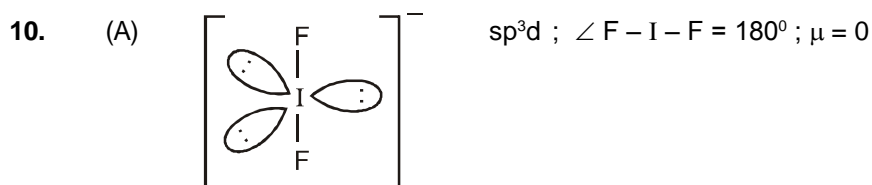
$$= \sqrt{a^2 + a^2 + 2a \cdot a \cos 120^\circ}$$

$$= \sqrt{2a^2 - a^2} = a$$

5. IF_7 has symmetrical Pentagonal bipyramidal shape.

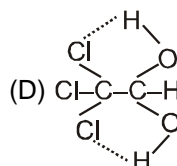
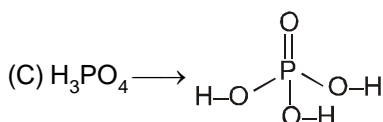
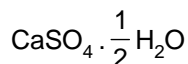


7. o-nitrophenol has intramolecular H-bonding so it will be vaporised first.
 8. D_2O has different physical properties than H_2O max. density of D_2O is at approximately 10°C



11. HF shows stronger H-bond than H-Cl.
Dipole moment of HF is more than of HCl. (fact) Due to H-bond, boiling point of H-F is more than that of HCl. Due to differences in electro negativity, the H-F bond is stronger than H-Cl bond.
(B) N is more electronegative than P. So the strength of H-bond is more in NH_3 . Due to this boiling point of NH_3 is more. For the same reason, boiling point and bond energy are also more for NH_3 than PH_3 .

12. (A) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ SO_4^{2-} is resonance stabilized
(B) $\text{Ca}^{2+} / \text{SO}_4^{2-}$ are held together by electrostatic force of attraction i.e., ionic bond but alternate layers by H-bonds with water molecules

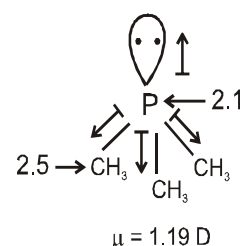
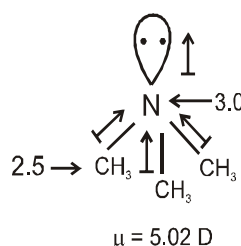
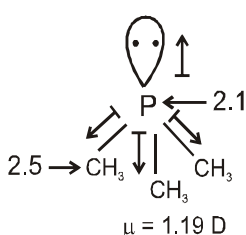
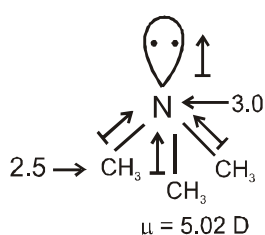


13. (A) Br_2 is non-polar in nature. All molecules experience London dispersion forces which results from the motion of electrons.
(B) HF has hydrogen bonding in liquid as well as in solid state. HF molecules also experience dispersion forces.
(C) Ion-dipole forces are found in the solutions of ionic compounds in polar solvent where solvated species such as $\text{Na}(\text{OH}_2)_x^+$ and $\text{F}(\text{H}_2\text{O})_y^-$ exist. Hydrogen bond exist between water molecules. In addition they also experience dispersion London forces.
(D) CH_3NH_2 is a polar molecule that can form hydrogen bonds. In addition, it has dispersion forces.
(E) Induced dipole-dipole interaction exists between non-polar molecules and polar molecules such as clathrate compound of Xe gas with water, when water is frozen under a high pressure of the gas. They have formulae approximating to $6\text{H}_2\text{O} : 1$ gas atom (i.e. $\text{Xe} \cdot 6\text{H}_2\text{O}$).
In addition, $\text{Xe} \cdot 6\text{H}_2\text{O}$ has H-bonding and dispersion forces.

EXERCISE # 2

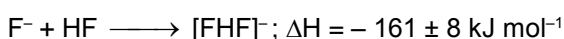
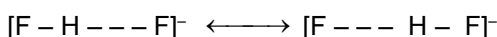
6. % ionic character = $\frac{6.32 \times 10^{-18}}{4.8 \times 10^{-10} \times 156 \times 10^{-10}} \times 100 = 84.5 \%$

7. Nitrogen is more electronegative than phosphorus.



So, dipole moment of trimethylamine is greater than trimethyl phosphine.

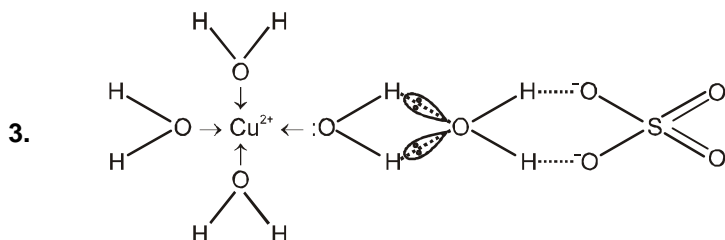
12. Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $\text{M}[\text{HF}_2]$; there is a linear symmetrical anion having an over all, F-H-F distance of 2.26 Å.



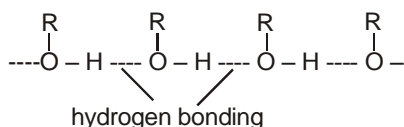
EXERCISE # 3

1. Intermolecular forces between H_2S , H_2Se and H_2Te molecules are purely Van der Waal's force of attraction while in water there is stronger H-bonding between the water molecules. H-bond is stronger than Van der Waal's force of attraction and thus more energy is required for converting $\text{H}_2\text{O}(\ell)$ to $(\text{H}_2\text{O})(\text{g})$.

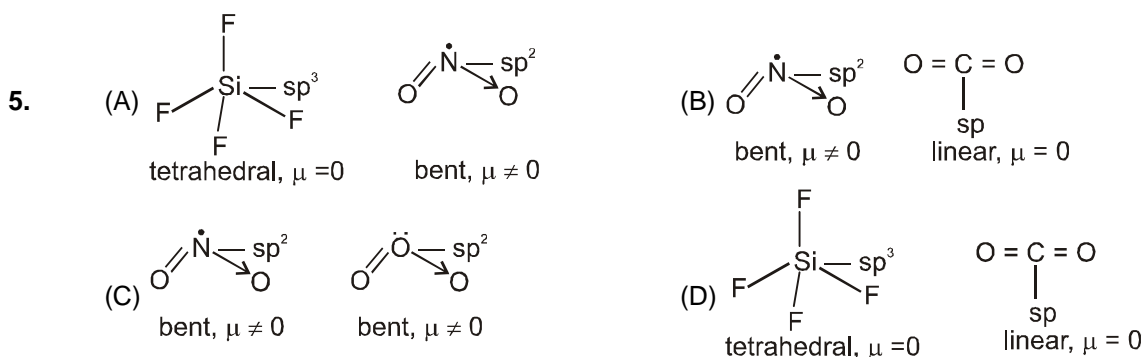
2. (i) In carboxylic acid H-bonding is stronger than that in alcohol.
(ii) In aldehyde there is dipole-dipole attraction.
(iii) H-bonding is stronger than dipole-dipole attraction.
(iv) Boiling point \propto strength of intermolecular force of attraction.



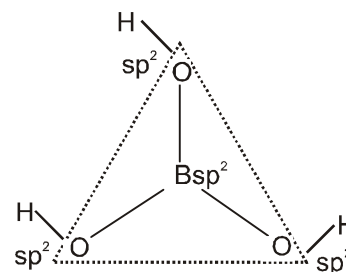
4. The reason for the lesser volatility of alcohol than ethers is the intermolecular association of a large number of molecules due to hydrogen bonding as $-OH$ group is highly polarised.



No such hydrogen bonding is present in ethers.



6. For planar BO_3 groups, the B–O bond length is usually close to 1.36 Å but for tetrahedral BO_4 groups the length increases to about 1.48 Å. This suggests that in the planar grouping π -bonding involving lone pairs of electrons from the oxygen atoms occurs; this π -bonding is necessarily lost in the tetrahedral group, in which a lone pair from the extra oxygen atom occupies the previously empty orbital on the boron atom.



7. Because of highest electronegativity of F, hydrogen bonding in $F-H \cdots F$ is strongest.

SOLUTION OF ADVANCED LEVEL PROBLEM

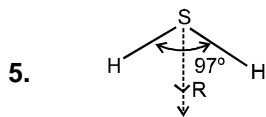
1. % Ionic character = $\frac{\mu_{\text{obs}}}{\mu_{\text{Th}}} \times 100$

$$= \frac{1.44 \times 10^{-18} \text{ esu cm}}{4.8 \times 10^{-10} \times 1.2 \times 10^{-8} \text{ esu cm}} \times 100 = 20\%$$

 \therefore % covalent character = $100 - 20 = 80\%$
3. Percentage of IC = $\frac{6 \times 10^{-18}}{4.8 \times 10^{-10} \times 2.5 \times 10^{-8}} \times 100 = 50\%$

4. Dipole moment of compound would have been completely ionic
 $= (4.8 \times 10^{-10} \text{ esu}) (2.25 \times 10^{-8} \text{ cm}) = 4.8 \times 2.25 \text{ D}$

$$\text{so \% ionic character} = \frac{9}{4.8 \times 2.25} \times 100\% = 83.33\%$$



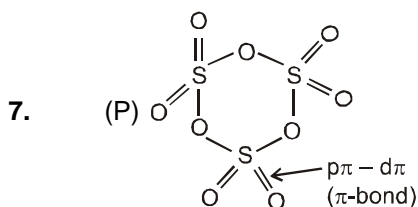
$$\mu_R = \sqrt{2\mu_{\text{S-H}}^2 + 2\mu_{\text{S-H}}^2 \times \cos 97^\circ} \quad ; \quad \mu_R = \sqrt{2} \times \mu_{\text{S-H}} \times \sqrt{1-0.12}$$

$$\mu_R = \sqrt{2} \times \mu_{\text{S-H}} \times \sqrt{0.88} \quad ; \quad \mu_{\text{S-H}} = \frac{1.5}{\sqrt{2} \times 0.94} \text{ D}$$

$$(\mu_{\text{S-H}})_{\text{Cal}} = \frac{0.15 \times 10^{-9} \times 1.6 \times 10^{-19}}{\frac{10}{3} \times 10^{-30}}$$

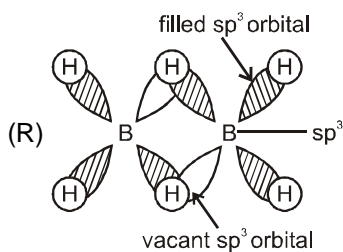
$$(\mu_{\text{S-H}})_{\text{Cal}} = 3 \times 0.15 \times 1.6 \times 10 \text{ D}$$

$$\text{So \% ionic character} = \frac{1.5}{\sqrt{2} \times 0.94} \times \left[\frac{1}{0.15 \times 16 \times 3} \right] \times 100 = 16\%$$

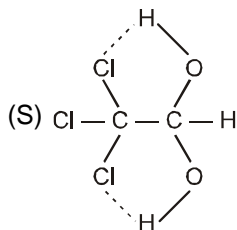


No of $p\pi-d\pi$ bonds = 6.

(Q) NOHSO_4 exists as NO^+ and HSO_4^- ; NO^+ is derivative of oxygen and isoelectronic with O_2^{2+} . Bond order is $1/2 (10 - 4) = 3$.



No of vacant sp^3 hybrid orbitals participating in the formation of banana bonds are 2.



6	3	2	2
(P)	(Q)	(R)	(S)

9. Theoretical value of dipole moment of a 100% ionic character = $e \times d$
 $= (1.60 \times 10^{-19} \text{ C}) (1.41 \times 10^{-10} \text{ m})$
 $= 2.26 \times 10^{-29} \text{ Cm}$

Observed value of dipole moment = 2.60×10^{-30} Cm

$$\text{Percent ionic character} = \frac{\text{observed value}}{\text{theoretical value}} \times 100 = \frac{2.60 \times 10^{-30}}{2.26 \times 10^{-29}} \times 100 = 11.5\% \text{ Ans.}$$

10. For a diatomic molecule dipole moment $\mu = e \times d$

$$\therefore \text{Electronic charge} = \frac{\mu}{d} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}}$$

$$\text{Actual value of electronic charge} = 4.8 \times 10^{-10} \text{ esu}$$

$$\therefore \text{Fraction of the electronic charge} = \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25$$

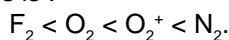
11. (i) Bond order of $N_2 = 1/2 (10 - 4) = 3$

$$\text{Bond order of } O_2 = 1/2 (10 - 6) = 2$$

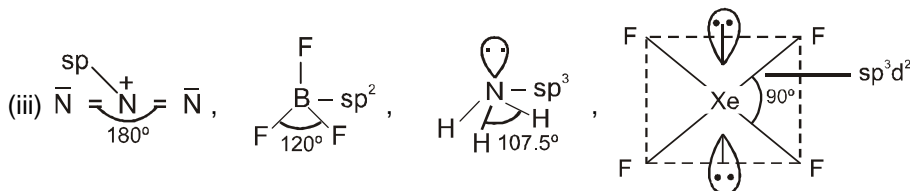
$$\text{Bond order of } F_2 = 1/2 (10 - 8) = 1$$

$$\text{Bond order of } O_2^+ = 1/2 (10 - 5) = 2.5$$

Bond order is directly proportional to the bond strength and so, the increasing order of their bond dissociation energies is :

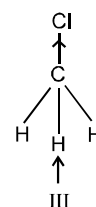
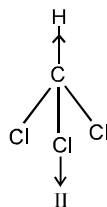
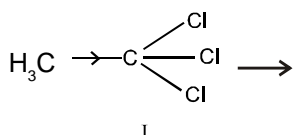


(ii) The strength of H – bond mainly depends on the electronegativity of the atom attached to the H atom and it increases with increasing electronegativity of the atom attached to polar H atom. So the increasing order of strength of hydrogen bonding (X – H – – – X) is : S < Cl < N < O < F



So, the increasing order of bond angles is $XeF_4 < NH_3 < BF_3 > N_3^-$

13. (i)

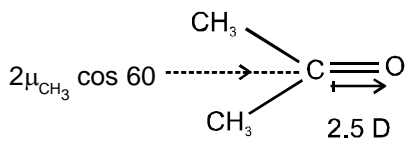


$$\mu_I = 3 \mu_{C-Cl} \times \cos 70.5 + \mu_{CH_3} = 1.5 + 0.4 = 1.9 \text{ D}$$

$$\mu_{II} = 3 \mu_{C-Cl} \times \cos 70.5 - \mu_{C-H} = 1.5 - 0.4 = 1.1 \text{ D}$$

$$\mu_{III} = 3 \mu_{C-H} \times \cos 70.5 + \mu_{C-Cl} = 1.9 \text{ D}$$

(ii)



$$\mu_{\text{net}} = 2.5 + \mu_{CH_3} = 2.5 + 0.4 = 2.9 \text{ D.}$$

LIQUID & GASEOUS STATE

EXERCISE # 1

PART - I

- A-2.** The pressure on the bubble = 1 atm (when it is at the surface)
 The volume of the bubble = $\frac{1}{6} \pi (0.4)^3$ ml.
 The pressure on the bubble = P atm (say) (when it is at the bottom)
 The volume of the bubble = $\frac{1}{6} \pi (0.1)^3$

$$P \times \frac{1}{6} \pi \times (0.1)^3 = 1 \times \frac{1}{6} \pi (0.4)^3$$

or P = 64 atm. Thus the pressure due to water is 63 atm (\because atmospheric pressure = 1 atm)

Now, consider the depth of pond is h cm

$$\therefore 63 \times 76 \times 13.6 \times g = h \times 1 \times g$$

$$\therefore \text{or } h = 63 \times 76 \times 13.6 \text{ cm} = 65116.8 \text{ cm} = 0.65116 \text{ km.}$$

$$\therefore \text{The depth of the lake is } 0.65116 \text{ km.}$$

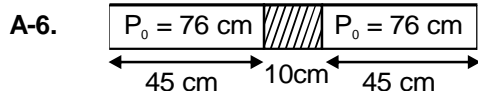
- A-3.** Since the vessel is open, the gas can escape out on heating. In this case we can imagine a imaginary boundary to trace the final volume of the gas.

(a) Now in the given situation, 3/5th of the gas (by amount) has escaped which means only 2/5th of the amount is occupying the complete volume of the open container.

And the Pressure is constant, $\frac{n_2}{n_1} = \frac{T_1}{T_2} \Rightarrow \frac{2n/5}{n} = \frac{300}{T_2} \Rightarrow T_2 = 750 \text{ K.}$

(b) Similarly, $\frac{n_2}{n_1} = \frac{300}{900} \Rightarrow$ 1/3rd of the gas remained in the container. Hence, 2/3rd of the gas escaped.

(c) Half of the gas will escape out by doubling the temperature. Hence, the final temperature = 600 K.



Initially : (A) $76 \times 45 \times A = 76 \times 45 \times A$ (B)

A = Area of cross section.

When tube is made vertical, let Hg column gets displaced by x cm towards A.

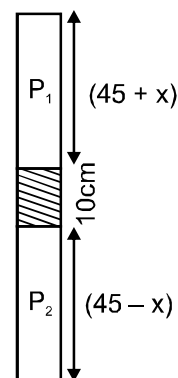
For A side : $P_1 \times (45 - x) \times A = 76 \times 45 \times A$

For B side : $P_2 \times (45 + x) \times A = 76 \times 45 \times A$

also $P_1 = P_2 + 10$

$$\frac{76 \times 45}{(45 - x)} = \frac{76 \times 45}{(45 + x)} + 10 \quad \Rightarrow \quad 76 \times 45 \left[\frac{1}{(45 - x)} - \frac{1}{(45 + x)} \right] = 10$$

$$76 \times 45 \left[\frac{45 + x - 45 + x}{(45 - x)(45 + x)} \right] = 10$$



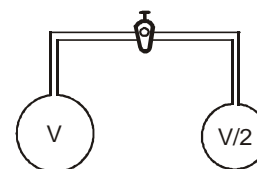
- A-9.**

Let the total number of molecules of the gas be n, of which n_1 are in the larger sphere and n_2 in the smaller sphere after the stopcock is opened

$$n = n_1 + n_2 \text{ and } pV = nRT$$

$$\frac{pV}{RT_1} = \frac{p'V}{RT_1} + \frac{p'V}{2T_2R}$$

$$p' = \frac{2pT_2}{2T_2 + T_1}$$

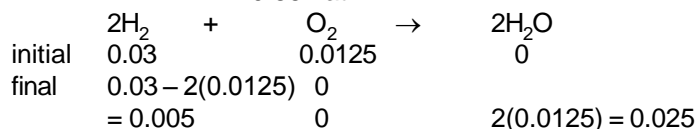


A-11. $\frac{n_1 T_1}{P_1} = \frac{n_2 T_2}{P_2} \quad \therefore \frac{10 \times 300}{24.6} = \frac{n_2 \times 400}{1}$
 $\therefore n_2 = 0.3$
 \therefore Mass of oxygen left = $0.3 \times 32 = 9.6$ g
 \therefore Mass of oxygen escaped = $320 - 9.6 = 310.4$ g.

B-2. $PV = nRT$

$$P \times 1.5 = \left(\frac{400 \times 10^{-3}}{32} + \frac{60 \times 10^{-3}}{2} \right) \times 0.082 \times 373$$

$$\therefore P = 0.867 \text{ atm}$$



$$\therefore m_{\text{H}_2} \text{ left} = 0.005 \times 2 = 0.01 \text{ g}$$

$$\& m_{\text{H}_2\text{O}} \text{ produced} = 0.025 \times 18 = 0.45 \text{ g}$$

$$P_{\text{H}_2} = \frac{n_{\text{H}_2} \times R \times T}{V} = \frac{0.005 \times 0.0821 \times 373}{1.5} = 1.102 \text{ atm.}$$

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}} \times R \times T}{V} = \frac{0.025 \times 0.0821 \times 373}{1.5} = 0.509 \text{ atm.}$$

C-1. At constant volume and temperature $P \propto W$ (here, volume of balloon is assumed to be constant)

Thus, for N_2 : $P_1 = 2 \text{ atm}$ $P_2 = 1/2 \text{ atm}$ at $t = 1 \text{ hr}$

$$\frac{P_1}{P_2} = \frac{w_1}{w_2} \quad \text{or} \quad w_2 = \frac{P_2}{P_1} \times w_1 \quad \text{or} \quad w_2 = \frac{1}{2} \times 14 = \frac{14}{4}$$

$$\therefore \text{wt of } \text{N}_2 \text{ diffused} = 14 - \frac{14}{4} = \frac{21}{4} \text{ kg}$$

For H_2 : $P_1 = 2 \text{ atm}$ $P_2 = 1/2 \text{ atm}$ at $t = t \text{ hr}$
 $w_1 = 1 \text{ kg}$ $w_2 = ?$

$$w_2 = \frac{P_2}{P_1} \times w_1 = 1/4 \text{ kg}$$

Hence wt of H_2 diffused = $1 - 1/4 = 3/4 \text{ kg}$

Now, we are to conclude one point as

$$\frac{r_A}{r_B} = \sqrt{\frac{\rho_B}{\rho_A}}, \text{ as per Graham law}$$

$$\frac{\frac{V_A}{t_A}}{\frac{V_B}{t_B}} = \sqrt{\frac{\rho_B}{\rho_A}} \quad \text{or} \quad \frac{V_A}{V_B} \times \frac{t_B}{t_A} = \sqrt{\frac{\rho_B}{\rho_A}} \quad \text{or} \quad \frac{V_A}{V_B} \times \frac{t_B}{t_A} = \frac{\rho_B}{\rho_A} \sqrt{\frac{\rho_A}{\rho_B}}$$

$$\text{or} \quad \frac{V_A \rho_B t_B}{V_B \rho_B t_A} = \sqrt{\frac{\rho_A}{\rho_B}} \quad \text{or} \quad \frac{w_A}{w_B} \times \frac{t_B}{t_A} = \sqrt{\frac{\rho_A}{\rho_B}}$$

For our problem we can write,

$$\frac{w_{\text{H}_2} \times t_{\text{N}_2}}{w_{\text{N}_2} \times t_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{N}_2}}} \quad \text{or} \quad \frac{3/4 \times 1}{21/2 \times t} = \sqrt{\frac{2}{28}} = \sqrt{\frac{1}{14}} \quad \text{or} \quad \frac{6}{21 \times 4} \times \frac{1}{t} = \sqrt{\frac{1}{14}}$$

$$\text{or} \quad \frac{1}{14t} = \frac{1}{\sqrt{14}} \quad \text{or} \quad t = \frac{\sqrt{14}}{14} \text{ hr} = \frac{60}{\sqrt{14}} \text{ mins} = \frac{60}{3.741} \text{ mins} = 16 \text{ mins}$$

\therefore for H_2 , 16 mins are required

Ans.

C-3. Change in pressure = 2000-1500 = 500 torr; time-taken = 40 min

$$\text{rate}_1 = \frac{500}{40} \text{ torr/min}; \text{ similarly } \text{rate}_2 = \frac{500}{80} \text{ torr/min}$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M}{32}}$$

C-4. $\frac{n_{N_2}}{n_x} = \sqrt{\frac{m_x}{M_{N_2}}} \dots\dots(i)$

$$P_T V_T = n_T RT \dots\dots(ii)$$

$$\text{Here } n_T = \frac{2.8 \times 4}{0.0821 \times 273} = 0.5 \quad \text{and} \quad n_x + n_{N_2} = 0.5 \quad \Rightarrow \quad n_x = 0.1$$

From (1)

$$\frac{0.4}{0.1} = \sqrt{\frac{M_x}{28}} \quad \Rightarrow \quad M_x = 448.$$

D-1. $u_{\text{rms}} = \sqrt{\frac{\sum n_i u_i^2}{\sum n}} = \sqrt{\frac{u_1^2 \times n_1 + u_2^2 \times n_2 + u_3^2 \times n_3}{n_1 + n_2 + n_3}}$

$$\therefore u_{\text{rms}} = \sqrt{\frac{2 \times 10^{23} \times (10^4)^2 + 2 \times 10^{23} \times (2 \times 10^4)^2 + 2 \times 10^{23} \times (3 \times 10^4)^2}{6 \times 10^{23}}} = 2.16 \times 10^4 \text{ cm/sec}$$

D-3. $U_{\text{MPS}} \propto \sqrt{T} \quad \Rightarrow \quad \frac{(U_{\text{MPS}})_2}{(U_{\text{MPS}})_1} = \sqrt{\frac{T_2}{T_1}} \quad \Rightarrow \quad \frac{2}{1} = \sqrt{\frac{T_2}{400}}$

$$T_2 = 1600 \text{ K} = 1327^\circ\text{C}.$$

D-4. $U_{\text{rms}} = \sqrt{\frac{3RT}{T_1}} \quad \Rightarrow \quad \sqrt{\frac{3R \times 308}{28}} = \sqrt{\frac{3RT}{2}} \quad \Rightarrow \quad T = 22 \text{ K}.$

E-1. Volume of one mole of given vapour = $\frac{18}{0.36} \text{ L} = 50 \text{ L}$

$$\text{volume of one mole of an ideal gas} = \frac{RT}{P} = \frac{0.082 \times 500}{1} = 41 \text{ L}$$

$$\text{so value of } Z = \frac{V_{\text{m,real}}}{V_{\text{m,ideal}}} = \frac{50}{41}$$

E-3. $T_C = 273 + 31 = 304 \text{ K}, P_C = 728 \text{ atm}$

$$T_C = \frac{8a}{27Rb} \quad \text{and} \quad P_C = \frac{a}{27b^2}$$

$$\therefore \frac{T_C}{P_C} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\text{On substitution } \frac{304}{728} = \frac{8b}{0.082}$$

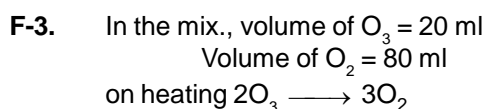
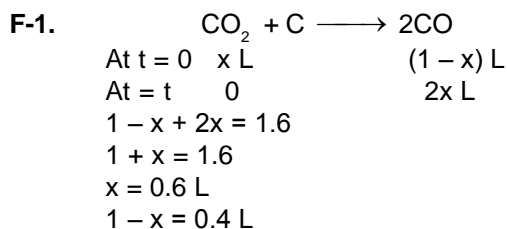
$$\therefore b = \frac{304 \times 0.082}{728 \times 8} = 4.28 \times 10^{-3} \text{ litre/mole}$$

$$\text{Now, } T_C = \frac{8a}{27Rb}$$

$$\therefore a = \frac{27RbT_C}{8} = \frac{27 \times 0.0082 \times 4.28 \times 10^{-3} \times 304}{8} = 0.36 \text{ atm litre}^2 \text{ mole}^{-2} \text{ Ans.}$$

E-5. $\left(P + \frac{n^2 \times 4.2}{(10)^2} \right) (V - nb) = n RT$

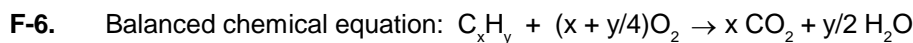
$$\left(P + \frac{(10)^2 \times 4.2}{(10)^2} \right) (10 - 10 \times 0.037) = 10 \times 0.082 \times 300$$



$$20 \text{ ml O}_3 \text{ will give } \frac{3}{2} \times 20 = 30 \text{ ml O}_2$$

$$\text{total volume} = 80 + 30 = 110 \text{ ml}$$

$$\text{increase in volume} = 110 - 100 = 10 \text{ ml.}$$



$$22.4 \text{ Lt of C}_x\text{H}_y \text{ gives} = 44 \text{ a gram CO}_2$$

$$1.12 \text{ Lt of C}_x\text{H}_y \text{ gives} = 44 \text{ a} \times 1.12 / 22.4 \text{ gram CO}_2$$

$$44 \text{ a} \times 1.12 / 22.4 = 2.2$$

$$a = 1$$

$$22.4 \text{ Lt of C}_x\text{H}_y \text{ gives} = 18 \times b/2 \text{ gram H}_2\text{O}$$

$$1.8 \text{ Lt of C}_x\text{H}_y \text{ gives} = 18 \times b/2 \times 1.12 / 22.4 \text{ gram H}_2\text{O}$$

$$18 \text{ b}/2 \times 1.12 / 22.4 = 1.8$$

$$b = 4$$

∴ Hydrocarbon is CH₄

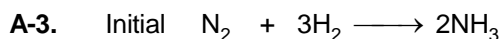
$$\text{wt of } 1.12 \text{ Lt CH}_4 \text{ at NTP} = 16 \times 1.12 / 22.4 = 0.8 \text{ gram}$$

$$\text{mole of O}_2 \text{ used in the } 22.4 \text{ Lt. hydrocarbon combustion} = a + b/4 = 2 \text{ mole}$$

$$\text{mole of O}_2 \text{ used in the } 1.12 \text{ Lt. hydrocarbon combustion} = 2 \times 1.12 / 22.4 = 0.1$$

$$\text{volume of O}_2 \text{ used in the } 1.12 \text{ Lt. hydrocarbon combustion} = 0.1 \times 22.4 = 2.24 \text{ Lt.}$$

PART - II



 1 3
 final - - 2

$$\text{ratio} = \frac{4}{2} = \frac{2}{1}$$

A-6. Two flask initially at 27° and 0.5 atm, have same volume and 0.7 mole thus each flask has 0.35 mole

Let n mole of gas are diffuse from II to I on heating the flask at 127°C

$$\text{Mole in I flask} = 0.35 + n, \quad \text{Mole in II flask} = 0.35 - n$$

If new pressure of flask is P then

$$\text{for I flask } P \times V = (0.35 + n) \times R \times 300 ;$$

$$\text{for II flask } P \times V = (0.35 - n) \times R \times 400$$

$$n = 0.5$$

$$\text{mole in I flask} = 0.40$$

$$\text{mole in II flask} = 0.30$$

$$0.5 \times 2V = 0.7 \times 0.0821 \times 300 \text{ (initially)}$$

$$V = 17.24 \text{ Lt.}$$

$$P \times 17.24 = 0.30 \times 0.0821 \times 400 \text{ (finally)}$$

$$P = 0.57 \text{ atm.}$$

A-7. Let vol. of each flask is 'V' L, Initially
 $0.5 \times 2V = 0.7 \times 0.0821 \times 300$
 $V = 17.24 \text{ L}$

Let T is final temperature of flask when pressure in each flask becomes equal, it happens. when

$$n_{\text{Total}} = n_1 + n_2$$

$$\frac{P \times (2V)}{R \times T} = \frac{PV}{R \times 400} + \frac{PV}{R \times 300} \Rightarrow \frac{2}{T} = \frac{1}{400} + \frac{1}{300} = \frac{3+4}{1200} = \frac{7}{1200}$$

$$T = \frac{2400}{7} = 342.85 \text{ K}$$

$$P \times 2 \times 17.24 = n_1 \times 0.0821 \times 400 \Rightarrow n_1 = 0.3$$

$$0.5714 \times 17.24 = n_2 \times 0.0821 \times 300 \Rightarrow n_2 = 0.4$$

A-12. $P_A = \frac{3RT}{M_A}$; $P_B = \frac{1.5RT}{M_B}$

$$\frac{P_A}{P_B} = \frac{2M_B}{M_A} = \frac{2 \times 2M_A}{M_A} = 4.$$

B-2. (D) Weight of $\text{H}_2 = 20 \text{ g}$ in 100 g mixture ; Weight of $\text{O}_2 = 80 \text{ g}$

$$\therefore \text{Moles of } \text{H}_2 = \frac{20}{2} = 10 ; \quad \therefore \text{Moles of } \text{O}_2 = \frac{80}{32} = \frac{5}{2}$$

$$\therefore \text{Total moles} = 10 + \frac{5}{2} = \frac{25}{2}$$

$$\therefore P_{\text{H}_2} = P_T \times \text{mole fraction of } \text{H}_2 = 1 \times \frac{10}{25/2} = 0.8 \text{ bar}$$

B-3. Since A and A_2 are two states in gaseous phase having their wt ratio 50% i.e. 1 : 1

$$\text{moles of A} = \frac{96}{2} \times \frac{1}{48} = 1 \quad \text{Moles of } \text{A}_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$$\text{Total mole} = 3/2$$

$$P = nRT/V.$$

C-3. $r \propto \frac{1}{\sqrt{M}}$ So, NH_3 diffuses with faster rate.

C-5.*- Given $\frac{r_A}{r_B} = \frac{16}{3}$; $\frac{w_A}{w_B} = \frac{2}{3}$

we have $\frac{r_A}{r_B} = \frac{n_A}{n_B} \sqrt{\frac{M_B}{M_A}}$

$$\frac{16}{3} = \frac{w_A}{M_A} \frac{M_B}{w_B} \sqrt{\frac{M_B}{M_A}}$$

$$\frac{16}{3} = \frac{2}{3} \left(\frac{M_B}{M_A} \right)^{3/2} \Rightarrow \left(\frac{M_B}{M_A} \right)^{3/2} = 8 \Rightarrow \frac{M_B}{M_A} = 4$$

$$\therefore \text{mole ratio} = \frac{8}{3}$$

D-3. $m_A = 2 m_B$
 $u_A = 2 u_B$
 $n_A = n_B$
 $V_A = V_B$

$$\frac{P_A V_A}{P_B V_B} = \frac{\frac{1}{3} m_A n_A u_A^2}{\frac{1}{3} m_B n_B u_B^2}$$

$$\text{D-4. } K.E_{O_2} = \frac{\frac{3}{2} \times \frac{N}{32} \times R \times 150}{\frac{3}{2} \times \frac{N'}{32} \times R \times 300} = \frac{x}{2x} \quad \Rightarrow \quad K.E_{O_2} = \frac{N \times 1}{N' \times 2} = \frac{1}{2}$$

$N = N'$ Therefore, (A) option is correct.

$$\text{D-8. } \frac{(V_{rms})_1}{(V_{rms})_2} = \sqrt{\frac{T_1 M_2}{M_1 T_2}}$$

D-9.* K.E. is a function of temperature. If temperature is constant, K.E. will be constant.

$$\text{E-4. } \left(P + \frac{a}{V^2} \right) (V) = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} = 1 - \frac{a}{VRT}$$

$$\text{E-5. } 4 \times \frac{4}{3} \pi r^3 \times N_A = 24$$

$$\text{E-10.*} \quad P_c = \frac{a}{27b^2}$$

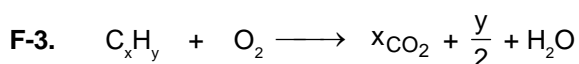
$$T_c^2 = \frac{64 a^2}{27 \times 27 R^2 b^2}$$

$$V_c = 3b$$

$$\frac{T_c^2}{P_c} = \frac{64 a^2}{27 \times 27 R^2 b^2} \times \frac{27 b^2}{a}$$

$$T_c = \frac{8a}{27Rb}$$

$$a = \frac{27 R^2 T_c^2}{64 P_c}$$



$$15 \text{ ml} \quad \frac{357 \times 21}{100} \text{ ml} \\ 75 \text{ ml}$$

$$\left(x + \frac{y}{4} \right) \times 15 = 75$$

$$x + \frac{y}{4} = \frac{75}{15}$$

$$x + \frac{y}{4} = 5$$

$$x + \frac{y}{4} = 5$$

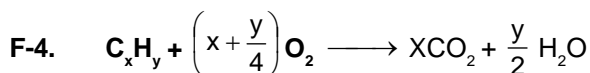
$$3 + \frac{y}{4} = 5$$

$$15x + 15x + 282 = 327$$

$$y = 8$$

$$x = 3$$

$$\text{Formula} = C_3 H_8$$



$$7.5 \text{ ml} \quad 36 \text{ ml}$$

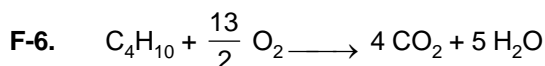
$$36 - 7.5 \left(x + \frac{y}{4} \right) + 7.5x = 28.5$$

$$36 - 7.5 \left(15 + \frac{y}{4} \right) + 7.5x = 28.5$$

$$y = 4$$

$$x = 2$$

So formula = C_2H_4



x ml n-butane

y ml isobutane

$$\text{Volume of } O_2 = x \times \frac{13}{2} + y \times \frac{13}{2}$$

EXERCISE # 2

PATR - I

1. $\left(\frac{P_1 V_1}{T_1} \right)_{\text{Inside cylinder}} = \left(\frac{P_2 V_2}{T_2} \right)_{\text{Outside cylinder}}$

$$\frac{20 \times 2.82}{300} = \frac{1 \times V_2}{273}$$

$$V_2 = 51.324 \text{ L}$$

Volume of gas at STP in cylinder = 51.324 L

Volume of gas left inside cylinder = 2.82 L

Volume of gas available to be filled in balloon = 48.504 L

Let n balloons are filled

$$\therefore \frac{4}{3} \pi \times \left(\frac{21}{2} \right)^3 \times \frac{n}{1000} = 48.504 \quad \Rightarrow \quad n = 10$$

3. $PV = n_{\text{Total}} RT$
 $10^5 \times 0.02 = n_{\text{Total}} \times 8.314 \times 300$
 $n_{\text{Total}} = 0.8$

$$\frac{m_{Ar}}{40} + \frac{m_{Ne}}{20} = 0.8$$

$$m_{Ar} + m_{Ne} = 28$$

$$m_{Ar} = 24; \quad m_{Ne} = 4$$

5. $u_{AV} = \sqrt{\frac{8RT}{\pi M}}$

For He: $4 \times 10^2 = \sqrt{\frac{8RT}{\pi \times 4 \times 10^{-3}}}$ so $RT = \frac{16 \times 10^4 \times \pi \times 1 \times 10^{-3}}{8} = 80\pi$

for Ne: $4 \times 10^2 = \sqrt{\frac{8RT}{\pi \times 20 \times 10^{-3}}}$ so $RT = \frac{16 \times 10^4 \times \pi \times 20 \times 10^{-3}}{8} = 400\pi$

$$\therefore KE = \frac{3}{2} nRT \quad \therefore \text{Total KE of He} = \frac{3}{2} \times \frac{6}{4} \times 80\pi = 565.71 \text{ J/mol}$$

$$\therefore \text{Total KE of Ne} = \frac{3}{2} \times \frac{12}{20} \times 400\pi = 1131.42 \text{ J/mol}$$

$$\text{Total K.E. of mixture} = 565.71 + 1131.42 \text{ J} = 1697.13 \text{ J/mol}$$

$$\text{Total mole in mixture} = \frac{6}{4} + \frac{12}{20} = 1.5 + 0.6 = 2.1.$$

$$KE / \text{mole of mixture} = \frac{1697.13}{2.1} = 808.16 \text{ J/mol}$$

6. For the gaseous mixture

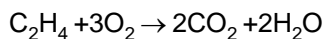
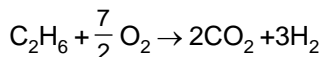
$$PV = nRT \quad 1 \times 40 = n \times 0.0821 \times 400$$

$$n = 1.219$$

Total mole of mix. = 1.219

Suppose moles of C_2H_6 and C_2H_4 are a and b respectively

$$a + b = 1.219 \quad \dots\dots\dots (1)$$



$$a \quad 7a/2$$

$$b \quad 3b$$

moles of O_2 required for the combustion of mix. = $7a/2 + 3b$

$$\frac{7a}{2} + 3b = \frac{130}{32} \quad \dots\dots\dots (2)$$

by solving eq. (1) and (2) we get

$$a = 0.808 \quad b = 0.4115$$

$$\text{mole fraction of } C_2H_6 = \frac{0.808}{1.219} = 0.66$$

$$\text{mole fraction of } C_2H_4 = \frac{0.4115}{1.219} = 0.34$$

7. Before effusion

Moles of CO = 0.5

Moles of CO_2 = 0.5

Total moles diffused out = A

Let moles of CO effused out = a

Let moles of CO_2 effused out = b

$$\therefore a + b = A$$

$$\therefore M_1 = \frac{28a + 44b}{a + b} = \frac{28a + 44b}{A}$$

Mean molar mass of residual gases in the vessel

$$M_2 = \frac{28(0.5 - a) + 44(0.5 - b)}{0.5 - a + 0.5 - b}$$

$$\text{or } M_2 = \frac{14 - 28a + 22 - 44b}{1 - (a + b)} = \frac{36}{1 - A} - \frac{(28a + 44b)}{1 - A}$$

$$\text{or } M_2 = \frac{36}{1 - A} - \frac{(28a + 44b)}{1 - A}$$

$$\text{or } M_2 = \frac{36}{1 - A} - \frac{M_1 A}{1 - A}$$

$$\text{or } M_2 (1 - A) = 36 - M_1 A$$

$$\text{or } M_1 A + M_2 (1 - A) = 36$$

Ans.

9. Let moles of Ar = x

Moles of O_2 = y

Moles of SO_2 = $1 - (x + y)$

$$\text{Total moles of mixture} = \frac{1 \times 22.4}{0.08 \times 273}$$

$$1 - (x + y) = y + x \Rightarrow 1 = 2x + 2y$$

$$y = 2 \times x \quad 1 = 2x + 4x$$

$$x = \frac{1}{6} \quad ; \quad y = \frac{1}{3}$$

$$M_{\text{mix}} = \frac{\frac{1}{6} \times 40 + \frac{1}{3} \times 32 + \frac{1}{2} \times 64}{\frac{1}{6} + \frac{1}{3} + \frac{1}{2}} = 49.33$$

$$f = \frac{\rho M_{\text{mix}}}{RT} = \frac{1 \times 49.33}{0.0821 \times 273} = 2.2 \text{ g/L}$$

10. (a) By Dalton's partial pressure

$$P_{N_2} + P_{H_2O} = 760 \text{ mm}$$

From given data $P_{N_2} = 745 \text{ mm}$

$$\text{So } P_{H_2O} = 760 - 745 = 15 \text{ mm}$$

$$\% \text{ Mole of } N_2 = \% \text{ of pressure of } N_2 = \frac{745}{760} \times 100 = 98.02$$

∴ Mole % of H₂O = 100 – 98.02 = **1.98%** **Ans.**

(b) Increase weight of drying agent due to absorption of water (H₂O).

Hence, Wt. of H₂O = 0.15 g

$$\therefore \text{Mole of H}_2\text{O} = \frac{0.15}{18}$$

$$\text{Pressure of H}_2\text{O} (P_{\text{H}_2\text{O}}) = 15 \text{ mm} = \frac{15}{760} \text{ atm}$$

From gas equation PV = nRT

$$\frac{15}{760} \times V = \frac{0.15}{18} \times 0.0821 \times (273 + 20)$$

$$V = \mathbf{10.156 \text{ litres}} \quad \mathbf{Ans.}$$

12. Based on Dalton law of partial pressure, partial pressure of H₂ is determined hence, its number of moles. Partial pressure of H₂ and water vapour are known, hence, mole fraction can be determined. Since number of moles of dry H₂ is known, mass of dry H₂ can be determined.

$$(a) n_{\text{H}_2\text{O}} (\text{vapour}) = \frac{P_{\text{H}_2\text{O}} V}{RT} = \frac{\frac{19}{760} \times 0.300}{0.0821 \times 294} = 0.31 \text{ m mole}$$

$$(b) X_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{Total}}} = \frac{P_{\text{H}_2}}{P_{\text{Total}}} = \frac{729}{748} = 0.975$$

$$(c) P_{\text{Total}} = P_{\text{H}_2} + P_{\text{H}_2\text{O}} \quad \Rightarrow \quad 748 = P_{\text{H}_2} + 19$$

$$\therefore P_{\text{H}_2} = 748 - 19 = 729 \text{ Torr} = \frac{729}{760} \text{ atm}$$

$$n_{\text{H}_2} = \frac{P_{\text{H}_2} V}{RT} = \frac{\frac{729}{760} \times 0.300}{0.0821 \times 294} = 0.0119 \text{ mol H}_2$$

$$\text{mass of gas (H}_2) = n_{\text{H}_2} \times M_{\text{gas}} = 0.0119 \times 2 = 0.24 \text{ g}$$

14. (a) Under low pressure region, V is high

$$(V - b) \approx V \quad \Rightarrow \quad \left(P + \frac{a}{V^2} \right) V = RT \quad \Rightarrow \quad PV + \frac{a}{V} = RT$$

$$\Rightarrow \quad \frac{PV}{RT} + \frac{a}{RTV} = 1 \quad \therefore \quad Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV} \right)$$

$$Z = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b) Under high pressure region, P is high,

$$\left(P + \frac{a}{V^2} \right) \approx P \quad \therefore \quad P(V - b) = RT$$

$$\Rightarrow \quad PV - Pb = RT \quad \Rightarrow \quad \frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore \quad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{b}{V} \quad \text{by approximation} \quad \left(\because \frac{PV}{RT} = 1, \frac{P}{RT} = \frac{1}{V} \right)$$

$$= 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

15. $\text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\text{Moles of CaCO}_3 \text{ used} = \frac{25}{100}$$

$$\text{Moles of CaO formed} = \frac{25}{100} = \text{moles of CO}_2 \text{ formed}$$

$$\text{Mass of CaO formed} = \frac{25}{100} \times 56 \text{ g} = 14 \text{ g}$$

$$\text{Volume occupied by CaO} = \frac{14}{3.3} \text{ cc} \approx 4.2 \text{ mL}$$

$$\therefore \text{Volume available for CO}_2(\text{g}) = 504.2 - 4.2 \text{ mL} = 0.5 \text{ L}$$

Now applying the van der waals equation of state

$$\left(p + \frac{an^2}{v^2} \right) (v - nb) = nRT$$

$$\left[p + \frac{4 \times (0.25)^2}{(0.5)^2} \right] [0.5 - 0.25 \times 0.04] = 0.25 \times 0.082 \times 1500$$

$$\Rightarrow p = 62.83 - \frac{4 \times (0.25)^2}{(0.5)^2} = 61.83 \text{ atm.}$$

PART - II

$$3. \quad \text{N}_2 \quad \rightarrow \quad 2\text{N}$$

$$\text{at } t = 0 \quad \frac{1.4}{28} = \frac{1}{20} \quad 0$$

$$\text{at } t = t_f \quad \frac{1}{20} - x \quad 2x$$

$$\text{but, } x = 30\% \text{ of } \frac{1}{20} = \frac{3}{200}$$

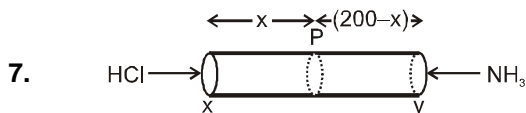
$$\text{Final number of mole} = \frac{1}{20} - x + 2x = \frac{1}{20} + x = \frac{1}{20} + \frac{3}{200} = \frac{13}{200}$$

$$\therefore P = \frac{13}{200} \times \frac{0.0821 \times 1800}{5} = 1.92 \text{ atm.}$$

$$4. \quad \frac{r_{\text{mixture}}}{r_{\text{O}_2}} = \sqrt{\frac{32}{M}} = \frac{20 \times 60}{311}$$

$$M = 2.16$$

$$\text{V.D.} = 4.32$$



$$\frac{r_{\text{HCl}}}{r_{\text{NH}_3}} = \sqrt{\frac{17}{36.5}} \quad \Rightarrow \quad \frac{x}{200-x} = \sqrt{\frac{17}{36.5}} \quad \Rightarrow \quad x = 81.13 \text{ cm}$$

8. Let both gases meet at n^{th} row

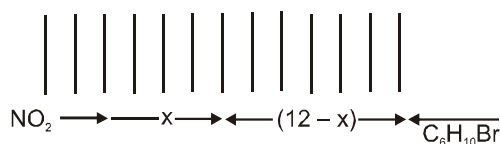
$$\frac{r_{\text{NO}_2}}{r_{\text{C}_6\text{H}_{10}\text{Br}}} = \frac{x}{12-x} = \sqrt{\frac{179}{44}} = 2$$

$$x = 24 - 2x$$

$$3x = 24$$

$$x = 8 = n - 1$$

$$n = 9^{\text{th}} \text{ Row}$$



$$10. \quad PV = nRT$$

$$PV = \frac{1}{M} RT$$

12. Max capacity of balloon = 600 ml

$$P_1 V_1 = P_2 V_2$$

$$500 \times 1 = 600 \times P_2$$

$$P_2 = \frac{5}{6} \times 760 \text{ mm} = 633 \text{ mm}$$

Height above which balloon will burst.

$$= (760 - 633) \times 100 \text{ cm}$$

$$= 127 \times 100 \text{ cm} = 127 \text{ m}$$

14. $76 \times 13.6 = x \times 13.6 + 1 \times 13.6 + 3.4 \times 20 + 6.8 \times 30 + 13.6 \times 15$
 $76 \times 13.6 = x \times 13.6 + 13.6 + 13.6 \times 5 + 13.6 \times 15 + 13.6 \times 15$
 $76 = x + 1 + 5 + 30$
 $x = 40 \text{ cm}$

17. $H_2 + 1/2 O_2 \rightarrow H_2 O_{(l)}$
 a b 0
 a-2b 0 b

Reaction is studied at constant P & T.

$$a + b = 40$$

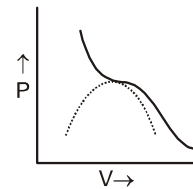
$$a - 2b = 10$$

$$a = 30 \text{ ml}$$

$$b = 10 \text{ ml}$$

mole fraction of H_2 = volume fraction of H_2 = $30/40 = 0.75$.

20. I – Slope of isotherm below critical point < 0.
 Slope of isotherm above critical point < 0.
 Slope of isotherm at critical point = 0.
 So slope of isotherm at critical point is maximum.



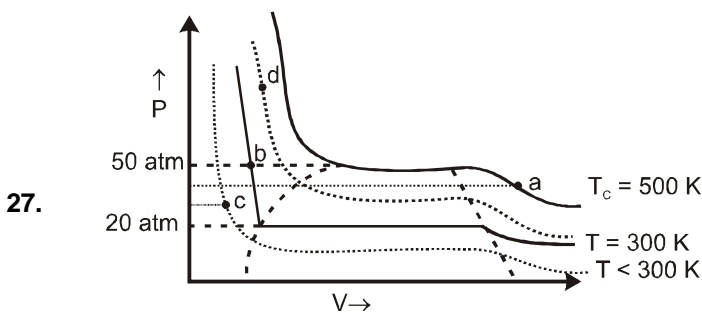
II – $T_c = \frac{8a}{27Rb}$

$$T_c \propto a$$

Larger value of T_c It means less decreases in temperature is required to liquify the gas. Gas will liquify at higher temperature. So, easier'll be liquification.

- III – When gas is below critical temperature. It is 'liquid' so vander waal equation of state is not valid.
 So, Answer (B).

25. $V_c = 3 \times N \times \frac{4}{3} \pi r^3 \times 0.44$



- (a) at $T = 500 \text{ K}$, $P = 40 \text{ atm}$ corresponds to 'a' substance - gas
 (b) at $T = 300 \text{ K}$, $P = 50 \text{ atm}$ corresponds to 'b' substance - liquid
 (c) at $T < 300 \text{ K}$, $P > 20 \text{ atm}$ corresponds to 'c' substance - liquid
 (d) at $T < 500 \text{ K}$, $P > 50 \text{ atm}$ corresponds to 'd' substance - liquid
 So, Answer (D)

28. Suppose the cylinder will burst at $T_2 \text{ K}$

$$T_2 = \frac{P_2 T_1}{P_1} \quad (V_1 = V_2) = \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

29. Clearly from the diagram $(v_{MPS})_B > (v_{MPS})_A \Rightarrow \frac{T_2}{M_B} > \frac{T_1}{M_A} \Rightarrow \frac{T_2}{T_1} > \frac{M_B}{M_A}$
 hence if $T_1 > T_2$, M_A is necessarily greater than M_B
31. With increase in temperature, most probable velocity increases & fraction of molecules with velocity equal to M.P. velocity decreases. Total no. of molecules remain same.

EXERCISE # 3

1. (A) $PV = K$ (Boyle's law)
 $P_1V_1 = P_2V_2 = P_3V_3$
- (B) From charle's law
 $V \propto T \Rightarrow \frac{V}{T} = K$
 $\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$
- (C) From Graham's law
 $r \propto \frac{1}{\sqrt{M}}$ and $d = \frac{PM}{RT} \Rightarrow d \propto M$
 So, $r \propto \frac{1}{\sqrt{d}}$.
- (D) From Dalton's law of partial pressure at constant temperature.
 $P = P_1 + P_2 + \dots$
- (E) Vander Waal's equation (real gas equation)
 $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ (For 1 mole)
- (F) $\frac{R}{N} = K$ (Boltzmann constant)
- (G) Molar volume = 22.4 L at STP
- (I) Constant temperature $P - V$ curve is called isotherm.
- (J) Graph between V and T at constant pressure called isobar.
2. (A) $PV = nRT$
 At constant temperature
 $PV = K$ ($T = \text{constant}$)
 Higher the value of PV , higher the temperature.
 So, $T_3 > T_2 > T_1$
 Since, $P_1 = P_2 = P_3$
 So, $V \propto T \Rightarrow V_3 > V_2 > V_1$
 $d = \frac{PM}{RT}$
 Since, $P_1 = P_2 = P_3$
 $d \propto \frac{1}{T} \Rightarrow d_1 > d_2 > d_3$
- (B) From Graph,
 $V_3 > V_2 > V_1$ and $T_1 = T_2 = T_3$
 Higher the volume, lesser the pressure because temperature is same for all.
 $P_1 > P_2 > P_3$
 $d = \frac{PM}{RT}$
 Since, $T_1 = T_2 = T_3$
 So, $d \propto P \Rightarrow d_1 > d_2 > d_3$
- (C) From the graph,
 $P_3 > P_2 > P_1$ and $T_1 = T_2 = T_3$
 Higher the pressure, lesser the volume because temperature is same for all.
 $V_1 > V_2 > V_3$

$$d = \frac{PM}{RT}$$

Since, $T_1 = T_2 = T_3$

So, $d \propto P \Rightarrow d_3 > d_2 > d_1$

(D) From the graph, $d_3 > d_2 > d_1$ and $P_1 = P_2 = P_3$

$$d = \frac{PM}{RT} \Rightarrow d \propto \frac{1}{T}$$

So, $T_1 > T_2 > T_3$

$$PV = nRT$$

Since, $P_1 = P_2 = P_3$

$$V \propto T$$

So, $V_1 > V_2 > V_3$

3. (A) At low pressure, b is negligible in comparison to V_m .

$$\left(P + \frac{a}{V_m^2} \right) (V_m) = RT$$

$$\Rightarrow \frac{PV_m}{RT} = Z = 1 - \frac{a}{V_m RT} < 1$$

So, gas is more compressible than ideal gas.

(B) At high pressure, $\frac{a}{V_m^2}$ is negligible in comparison to P .

$$\therefore P(V_m - b) = RT$$

$$\Rightarrow \frac{PV_m}{RT} = Z = 1 + \frac{Rb}{RT} < 1.$$

So, gas is less compressible than ideal gas.

(C) Low density of gas means pressure is low so, at low pressure $Z = 1 - \frac{a}{V_m RT} < 1$ and gas is more compressible than ideal gas.

(D) At 0°C H_2 and He have $a \approx 0$.

So, $Z = 1 + \frac{Pb}{RT}$ and gas is less compressible than ideal gas.

5. $P_1 = 75 \text{ cm of Hg}$, $V_1 = 24 \times A$

$$P_2 = 75 + 10 + \frac{20.4 \times 10}{13.6} = 100 \text{ cm of Hg}$$

$$\Rightarrow 75 \times 24 = 100 \times x$$

$$x = 18 \text{ cm}$$



6. **Case I**

$$P_1 = (P_0 + h)$$

$$P_1 V_1 = P_2 V_2$$

Now in both the cases, the gas is the same and temperature is also constant, hence boyles law can be applied.

$$l_1 A (P_0 + h) = l_2 A (P_0 - h)$$

$$P_0 = \frac{h(l_1 + l_2)}{(l_2 - l_1)} \text{ cm of Hg column.}$$

Case II

$$P_2 = (P_0 - h)$$

8. $Z = \frac{PV_m}{RT} > 1$

$$\frac{PV_m}{RT} = \frac{1 \times 22.4}{R \times T}$$

At same pressure = 1 atm.

$$\frac{1 \times V_m}{RT} > \frac{1 \times 22.4}{R \times T} \Rightarrow V_m > 22.4 \text{ L at STP for real gas.}$$

For, $V_m = 22.4 \text{ L}$ of real gas, we have to increase the pressure.

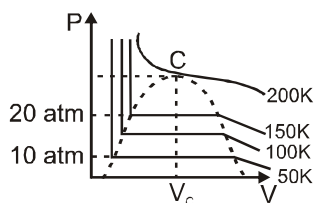
11. P_c , V_c and T_c are given hence 'a' and 'b' should be calculated using P_c and T_c as it is more reliable.

$$P_c = \frac{a}{27b^2}, T_c = \frac{8a}{27Rb}$$

$$\frac{P_c}{T_c} = \frac{R}{8b} \Rightarrow b = \frac{300 \times 1/12}{8 \times 50} = \frac{1}{16}$$

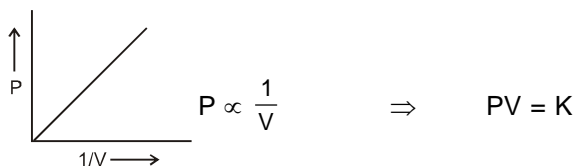
$$4 \times \frac{4}{3} \pi r^3 \cdot N_A = \frac{1}{16} \Rightarrow r = \left(\frac{3}{256\pi N_A} \right)^{1/3}$$

- 12.



At 100 K and pressure below 20 atm it may have liquid or gaseous state depending on the pressure.

- 13.



Pressure is directly proportional to $\frac{1}{V}$.

14. From Charle's law, volume is theoretically zero at 0 K and kinetic energy is directly proportional to absolute temperature. So, it is zero at 0 K.

16. Rate of diffusion $\propto \frac{1}{\sqrt{\text{Molar mass}}}$

$$\text{Total K.E.} = \frac{3}{2} nRT = \frac{3}{2} \frac{w}{M} RT$$

22. On collision, K.E. redistributes, one molecule acquires and other loses the K.E. so, average K.E. remains the same at the same temperature.

24. Rate of diffusion $\propto \frac{1}{\sqrt{\text{Molar mass}}}$

27. Increase in volume per degree rise in Celsius temperature at constant pressure is $V_0/273.15$, where V_0 is the volume of gas at 0°C .

28. Rate of diffusion $\propto \frac{PA}{\sqrt{TM}}$

32. At NTP, $P_T = 1 \text{ atm}$, $T = 0^\circ\text{C}$

$$d_{\text{mix}} = \frac{PM_{\text{mix}}}{RT} \Rightarrow \frac{1.3 \times 0.082 \times 273}{1} \Rightarrow M_{\text{mix}} = 29.1.$$

$$M_{\text{mix}} = 29.1 = \frac{x \times 28 + (100 - x) \times 32}{100} \Rightarrow x = \frac{3200 - 2910}{4} = 72.5\%$$

$$\therefore P_{\text{N}_2} = 0.725 \text{ atm.}$$

$$33. \quad \frac{20 + w_{\text{H}_2}}{11} = 2 \Rightarrow w_{\text{H}_2} = 2 \text{ g.}$$

$$M_{\text{avg}} = \frac{20 + 2}{\frac{20}{2} + \frac{2}{2}} = 11.$$

$$35. \quad \left(P + \frac{an^2}{V^2} \right) (V - b) = nRT$$

$$\text{Unit of } a \text{ will be unit of } \frac{PV^2}{n^2} = \frac{\text{Pa m}^6}{\text{mol}^2}.$$

37. At constant temperature,

$$P_1 V_1 = P_2 V_2$$

$$\frac{875}{760} \times V = P_2 \times \frac{V}{3} \Rightarrow P_2 = \frac{875 \times 3}{760} \text{ atm} = 3.454 \text{ atm.}$$

39. **Case I**

$$P_1 = (P_0 + h)$$

$$P_1 V_1 = P_2 V_2$$

Case II

$$P_2 = (P_0 - h)$$

Now in both the cases, the gas is the same and temperature is also constant, hence boyles law can be applied.

$$l_1 A (P_0 + h) = l_2 A (P_0 - h)$$

$$P_0 = \frac{h(l_1 + l_2)}{(l_2 - l_1)} \text{ cm of Hg column.}$$

40. (i) From KTG assumption, no effect of gravity on motion of molecules.

$$(ii) d = \frac{PM}{RT} \Rightarrow M = \frac{dRT}{P} = \frac{1.8 \times 0.082 \times 300}{1} = 44.3.$$

$$(iii) \frac{U_{27^\circ\text{C}}}{U_{927^\circ\text{C}}} = \sqrt{\frac{300}{1200}} = \frac{1}{2} \Rightarrow \frac{0.25}{U_{927^\circ\text{C}}} = \frac{1}{2} \Rightarrow U_{927^\circ\text{C}} = 0.5 \text{ ms}^{-1}.$$

$$(iv) P_{\text{total}} = P_{\text{H}_2} + P_{\text{O}_2} + P_{\text{CO}_2} = \left(\frac{2}{2} + \frac{8}{32} + \frac{22}{44} \right) \frac{0.082 \times 273}{22.4} = 1.75 \text{ atm.}$$

$$44. \quad d = \frac{PM_{\text{mix}}}{RT} \Rightarrow M_{\text{mix}} = \frac{dRT}{P} = \frac{1.146 \times 0.082 \times 300 \times 760}{740}$$

$$\Rightarrow M_{\text{mix}} = 28.95 = \frac{x \times 28 + (100 - x) \times 32}{100} \Rightarrow x = 76.25\%$$

$$45. \quad n = \frac{PV}{RT} \Rightarrow n = \frac{750 \times 200}{760 \times 1000 \times 0.082 \times 293} = 0.0082 \text{ moles.}$$

$$\text{weight of gas} = x \times 30 + 58 (0.0082 - x) = 0.3846.$$

$$x = \frac{0.091}{28} = 0.00325.$$

$$\text{mole \% of butane} = \frac{(0.0082 - 0.00325)}{0.0082} \times 100 = 60.36\%.$$

EXERCISE # 4

PART - I

1. Compressibility of an ideal gas $(Z) = \frac{P \times V}{nRT}$

For a mole of ideal gas at STP, $(Z) = \frac{P \times 22.4}{RT}$

For other gases $Z < 1$. It is equal to $\frac{P \times V_m}{RT}$

Hence $V_m < 22.4$ litre.

2. Given that : $\sqrt{\frac{3RT_{H_2}}{2}} = \sqrt{7} \sqrt{\frac{3RT_{N_2}}{28}}$ (because $U_{rms} = \sqrt{\frac{3RT}{M}}$)

So $\frac{3RT_{H_2}}{2} = 7 \times \frac{3 \times RT_{N_2}}{28}$ $\therefore T_{N_2} = 2T_{H_2}$ or $T_{N_2} > T_{H_2}$.

3. Mass of steam = $1000 \times 0.0006 = 0.6$ gm
Mass of water (ℓ) = 0.6 gm
Volume of liquid water = 0.6 cm³

4. $U_{rms} = \sqrt{\frac{3RT}{M}}$ using ideal gas equation,

$PV = nRT = \frac{w}{M} RT$; $\frac{RT}{M} = \frac{RV}{w} = \frac{P}{d}$ where d is the density of the gas

$\therefore U_{rms} = \sqrt{\frac{3P}{d}}$ at constant pressure, $U_{rms} \propto \frac{1}{\sqrt{d}}$

5. We know that, Compressibility factor, $Z = \frac{PV}{RT} \Rightarrow 0.5 = \frac{100 \times V}{0.082 \times 273} \therefore V = 0.1119$ L

Further when volume of a gas molecule is negligible, van der Waal's equation becomes $\left(P + \frac{a}{V^2}\right)(V - 0) = RT$

or $PV = RT - \frac{a}{V}$ or $a = RTV - PV^2$

Substituting the values

$a = (0.082 \times 0.1119 \times 273) - (100 \times 0.1119 \times 0.1119) = 1.253$ atm L²mol⁻².

6. (C) At const P,

$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{22.4}{273} = \frac{V_2}{373} \Rightarrow V_2 = 30.6$ litre.

7. (a) (i) $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$ or, $1.33 = \sqrt{\frac{32}{M_1}} \Rightarrow M_1 = 18.09$.

(ii) $V_m = \frac{M_1}{\text{molar density}} = \frac{18.09 \times 10^{-3}}{0.36} = 50.25 \times 10^{-3}$ m³.

(iii) $Z = \frac{PV_m}{RT} = \frac{1 \times 50.25}{0.0821 \times 500} = 1.224$.

(iv) Since $Z > 1$. \Rightarrow Force of repulsion dominates over force of attraction.

(b) Av. translation K.E. = $\frac{3}{2} kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000$ J = 2.07×10^{-20} J.

8. $U_{av} = \sqrt{\frac{8RT}{\pi M}}$ and $U_{rms} = \sqrt{\frac{3RT}{M}}$

$\therefore \frac{U_{av}}{U_{rms}} = \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}} = 0.9216$ or $U_{av} = 0.9216 \times U_{rms}$

Given, $U_{av} = 400$ m/s or $U_{rms} = \frac{400}{0.9216} = 434.02$ m/s

9. $U_{rms} = \sqrt{\frac{3RT}{M}}$

$E = \frac{3}{2} RT$ $\therefore RT = \frac{2E}{3} \Rightarrow U_{rms} = \sqrt{\frac{2E}{M}}$

10. $\frac{\text{rate of diffusion}_2}{\text{rate of diffusion}_1} = \sqrt{\frac{M_1}{M_2}}$ $\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{16}{4}} = 2$

11.* The vander waals equation of state is -
(for 1 mole of gas)

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

When a is negligible, then

$$Z = \frac{pV_m}{RT} = 1 + \frac{b}{RT} P$$

that is Z increases with increase in p.

when b is negligible, then

$$Z = \frac{pV_m}{RT} = 1 - \frac{a}{VRT}$$

increasing p implies decrease in V, which in turn, implies increase in the value of a/VRT and hence decrease in the value of Z.

The curve IV is applicable provided temperature of the gas is near but larger than its critical temperature. Hence, the choice (a), (b) and (c) are correct.

12. (A) For H₂ gas at high pressure Z > 1.
(B) For any gas at P ~ 0, Z ~ 1 i.e. ideal behaviour.
(C) For CO₂ gas at normal pressure and temperature Z < 1.
(D) For any gas at very large molar volume i.e. P ~ 0, Z ~ 1 i.e. ideal behaviour of gas.

13. (A) At very large molar volume

$$P + \frac{a}{V_m^2} \approx P \quad \text{and} \quad V_m - b = V_m$$

- (C) According to van der Waals equation 'a' and 'b' are independent of temp.

14. Correction factor for attractive force in to the real gas is given by $\frac{an^2}{V^2}$.

15. $V_{rms} = V_{mp}$

$$\sqrt{\frac{3RT}{M_X}} = \sqrt{\frac{2RT}{M_Y}} \Rightarrow \sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M_Y}}$$

$M_Y = 4.$

16. (A) Fact (B) $P = MV = M \sqrt{\frac{3RT}{M}} = \sqrt{3MRT}$
(C) Max well distribution (D) Fact

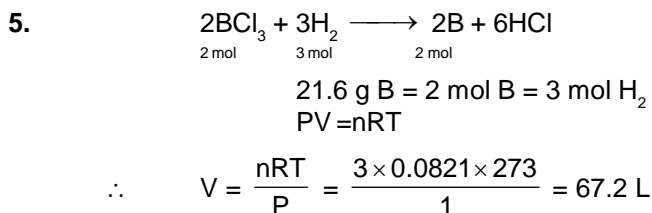
17. $P_{\text{He}} = 1 - 0.68 = 0.32 \text{ atm}$
 $V = ?$
 $n = 0.1$
 $V = \frac{nRT}{P} = \frac{0.1 \times 0.0821 \times 273}{0.32} = 7$

PART - II

1. $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1} = 2 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1} = 0.082 \text{ litre atm K}^{-1} \text{ mol}^{-1}$
 2. Various gas laws can be easily derived from kinetic equation obtained as a result of kinetic theory of gases.

3. $\frac{n}{V} = \frac{P}{RT}$

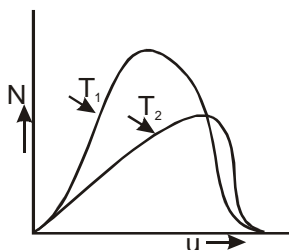
4. It is one of the assumption of kinetic theory of gas.



6. $\text{K.E.} = \frac{3}{2} RT$

$E_1 = \frac{3}{2} R 293$ and $E_2 = \frac{3}{2} R 313 \Rightarrow E_2 = \frac{313}{293} \times E_1$

7. $b = 4N \times v$ i.e., total volume occupied by molecules of one mole of gas in motion.
 8. Helium is not used to produced and sustain powerful superconducting magnets. All others are the uses of helium.
 9. Distribution of molecules (N) with velocity (μ) at two temperature T_1 and T_2 ($T_2 > T_1$) is show below:



At both temperatures, distribution of molecules with increase in velocity first increases, reaches a maximum value and then decreases.

10. Let the mass of methane and oxygen be m gm. Mole fraction of oxygen x_{O_2}

$$= \frac{\frac{m}{32}}{\frac{m}{32} + \frac{m}{16}} = \frac{m}{32} \times \frac{32}{3m} = \frac{1}{3}$$

Let the total pressure be P .

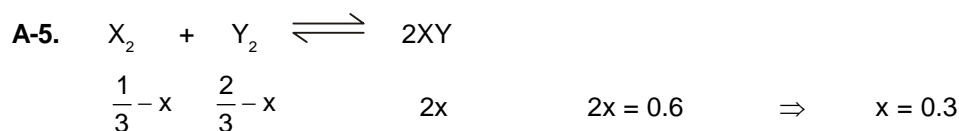
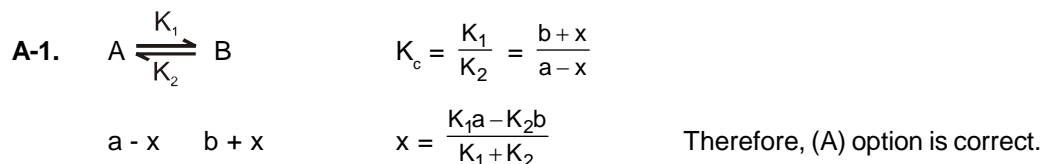
\therefore Partial pressure of O_2 , $P_{\text{O}_2} = P \times x_{\text{O}_2}$

$$P \times \frac{1}{3} = \frac{1}{3} P.$$

CHEMICAL EQUILIBRIUM

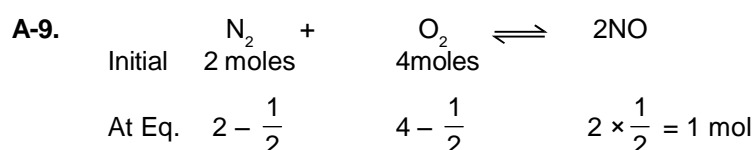
EXERCISE # 1

PART - I

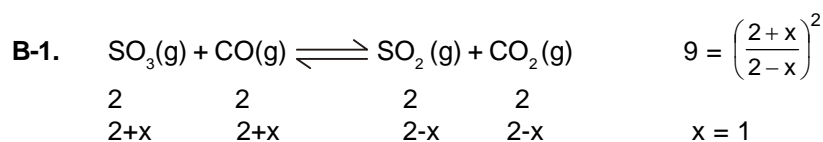


$[x_2] = \frac{1}{3} - 0.3$ $[y_2] = \frac{2}{3} - 0.3$

Therefore, (A) option is correct.

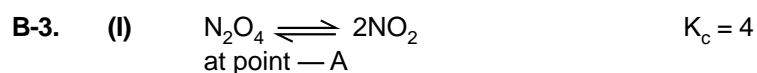


Molar concentration of NO at equilibrium = $\frac{1}{2.5} = 0.4$



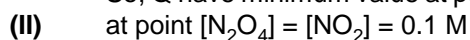
$n_{eq} = 3 + 3 + 1 + 1 = 8$ $n(SO_3) + n(CO_2) = 4$ $\frac{n(SO_2)}{n(CO)} = \frac{1}{2} < 1$

Therefore, (D) option is correct.



$Q = \frac{[\text{Product}]}{[\text{Reactant}]} = 0$

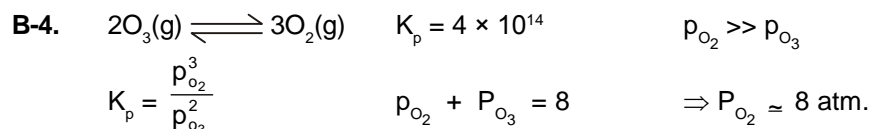
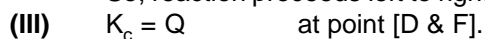
So, Q have minimum value at point A.



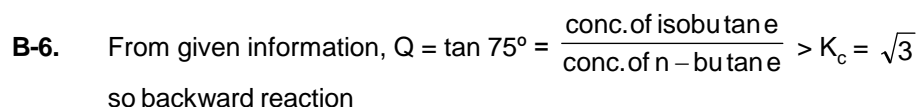
$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.1 \times 0.1}{0.1} = 0.1$

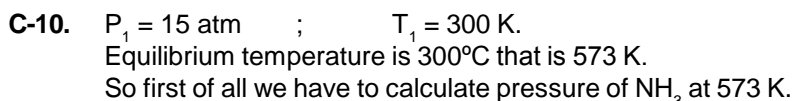
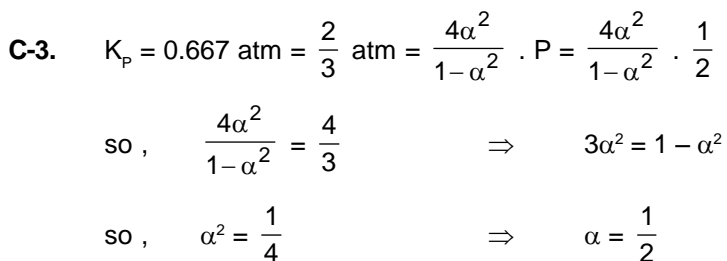
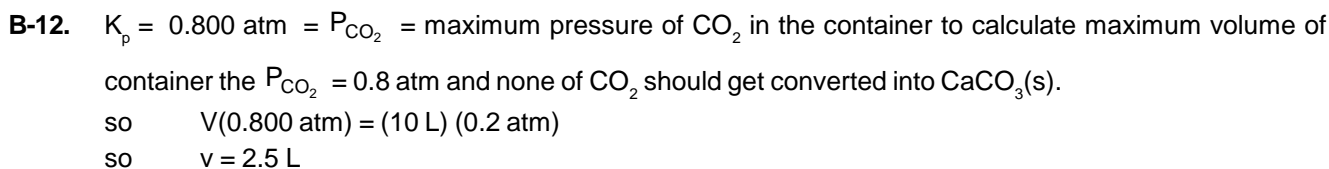
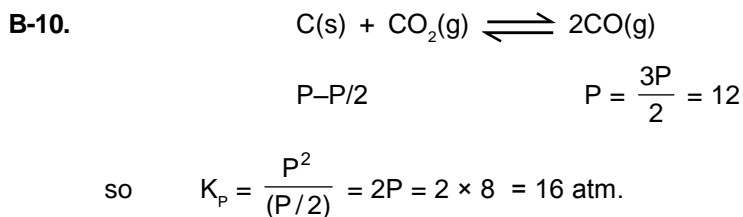
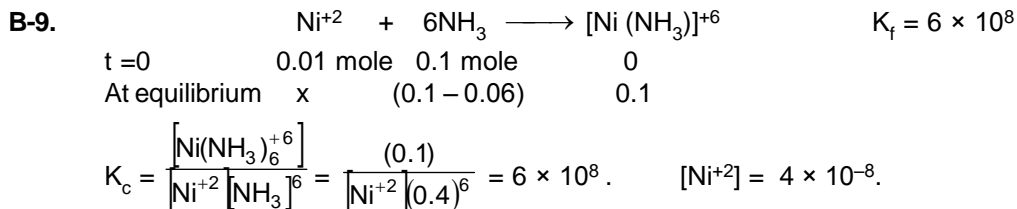
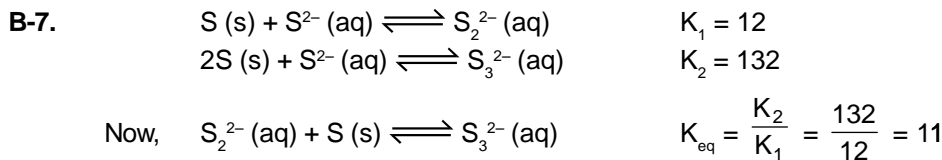
$Q < K_c$

So, reaction proceeds left to right



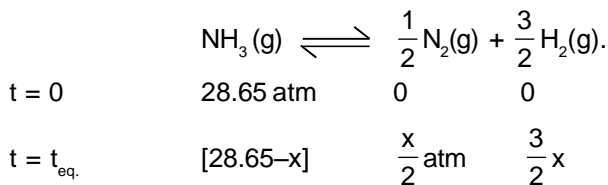
$4 \times 10^{14} = \frac{8^3}{p_{O_3}^2}$ $p_{O_3}^2 = 11.3 \times 10^{-7}$ Therefore, (B) option is correct.





$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{15}{300} = \frac{P_2}{573}$$

$$P_2 = 28.65 \text{ atm at } 300^\circ\text{C}.$$

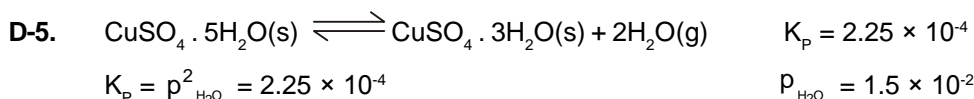


But according to question.

$$P_{total} = 28.65 - x + \frac{x}{2} + \frac{3}{2}x$$

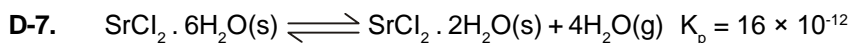
$$\text{or } 28.65 + x = 40.11. \Rightarrow x = 11.46.$$

$$\text{Degree of dissociation of } NH_3 = \frac{11.46}{28.65} = 0.4.$$



$$\text{Vapour Pr} = \frac{22.8}{760} = 3 \times 10^{-2} \quad \text{R.H.} = \frac{P_{\text{H}_2\text{O}}}{\text{V.P.}} \times 100 = 50\%$$

Therefore, (B) option is correct.



$$(P_{\text{H}_2\text{O}})^4 = K_p \quad P_{\text{H}_2\text{O}} = (K_p)^{1/4} = 2 \times 10^{-3} \text{ atm}$$

$$\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g}) \quad P_{\text{H}_2\text{O}} = \frac{7.6}{760} = 1.0 \times 10^{-2}$$

$$n_{\text{H}_2\text{O}} = \frac{PV}{RT} = \frac{10^{-2} \times 1}{0.082 \times 274} = 4.45 \times 10^{-4}$$

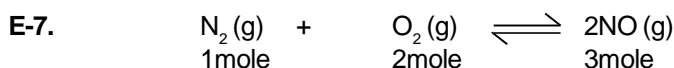
$$n_{\text{H}_2\text{O}} = \frac{2 \times 10^{-3}}{0.082 \times 274} = 8.9 \times 10^{-5} \quad \therefore n_{\text{H}_2\text{O}} \text{ absorbed} = 3.56 \times 10^{-4}$$

\therefore wt absorbed = 6.4 mg. Therefore, (A) option is correct.

D-8. From thermodynamics.

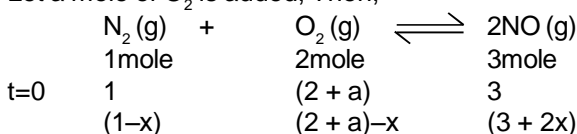
D-12* $10^{-10} \text{ atm} = P_{\text{H}_2\text{O}}^5 \Rightarrow P_{\text{H}_2\text{O}} = 10^{-2} \text{ atm.} \quad n = \frac{PV}{RT} = \frac{10^{-2} \times 2.5}{\frac{1}{12} \times 300} = 10^{-3}$

E-5. Solubility of gas is directly proportional to the pressure of gas above liquid.



$$K_c = \frac{(3)^2}{1 \times 2} = \left(\frac{9}{2}\right)$$

Let a mole of O_2 is added, Then,



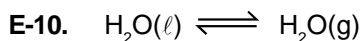
$$[\text{NO}] = \left[\frac{3+2x}{100} \right] = 0.04 \quad ; \quad (3+2x) = 4.$$

$$2x = 1, \quad x = 0.5.$$

$$K_c = \frac{(3+2x)^2}{(1-x)(2+a-x)} = \frac{9}{2} \quad ; \quad K_c = \frac{(4)^2}{0.5[(1.5)-a]} = \frac{9}{2}$$

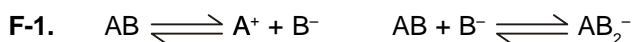
$$= \frac{16}{0.5(1.5+a)} = \frac{9}{2} \quad ; \quad = \frac{35}{4.5} = [1.5+a]$$

$$7.11 = 1.5 + a \quad ; \quad a = \frac{101}{18} = 5.61$$



$$K_p = (P_{\text{H}_2\text{O}})$$

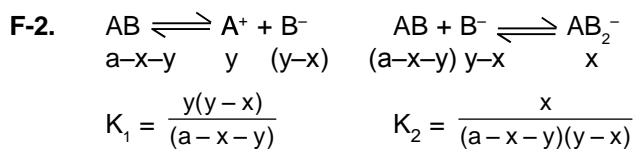
When neon is added at constant pressure, we have to increase volume of the container. So more water will evaporate to maintain equilibrium.



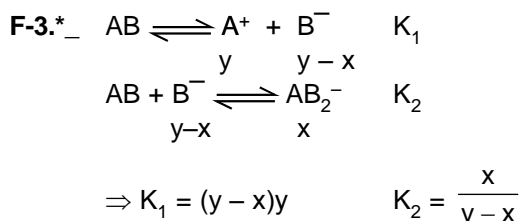
$$K_1 = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} \quad K_2 = \frac{[\text{AB}_2^-]}{[\text{AB}][\text{B}^-]}$$

$$K_1/K_2 = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} \cdot \frac{[\text{AB}][\text{B}^-]}{[\text{AB}_2^-]} = \frac{[\text{A}^+]}{[\text{AB}_2^-]} \cdot [\text{B}^-]^2 \Rightarrow \frac{[\text{A}^+]}{[\text{AB}_2^-]} = \frac{K_1}{K_2} \cdot \frac{1}{[\text{B}^-]^2}$$

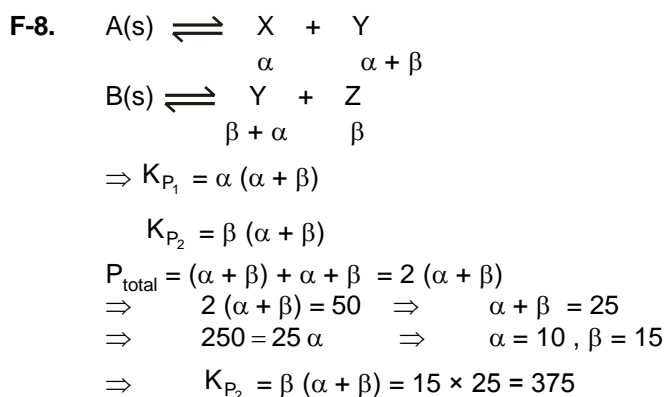
Therefore, (D) option is correct.



$$\frac{K_1}{K_2} = \frac{\frac{y(y-x)}{(a-x-y)}}{\frac{x}{(a-x-y)(y-x)}} \Rightarrow \frac{K_1}{K_2} = \frac{y}{x} (y-x)^2$$

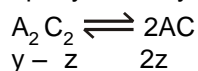
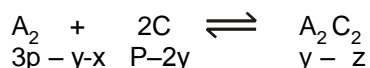
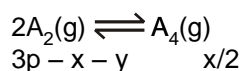


$$\Rightarrow \frac{K_1}{K_2} = \frac{y}{x} (y-x)^2$$



PART - II

(7 to 9)



$$\frac{P_{A_4}}{P_{A_2}^2} = K_{P_1} \Rightarrow (P_{A_2})^2 = \frac{P_{A_4}}{K_{P_1}} = \frac{1}{2/81} = \frac{81}{4}$$

$$\Rightarrow P_{A_2} = \frac{9}{2} \text{ atm.}$$

$$\Rightarrow 3p - x - y = \frac{9}{2} \quad \dots \text{ (i)}$$

$$\frac{x}{2} = \frac{1}{2} \quad \dots \text{ (ii)}$$

$$\Rightarrow x = 1 \text{ atm}$$

$$\text{also given } 2Z = \frac{1}{2} \quad \dots \text{ (iii)}$$

$$Z = \frac{1}{4} \text{ atm}$$

$$P_{\text{total}} = 3p - x - y + x/2 + p - 2y + y - z + 2z = 4p - x/2 - 2y + z$$

$$= 4 \times p - \frac{1}{2} - 2 \times \frac{1}{2} + \frac{1}{4} = \frac{27}{4} \text{ atm.} \quad \Rightarrow \quad P = 2 \text{ atm.}$$

Sol. 7. $3P - x - y = \frac{9}{2}$

$$6 - \frac{1}{2} - y = \frac{9}{2}$$

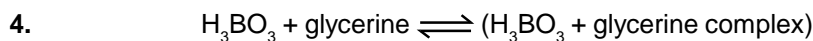
$$y = 1 \text{ atm.}$$

$$P_{A_2C_2} = y - z = 1 - \frac{1}{4} = \frac{3}{4} \text{ atm.}$$

Sol. 8. $\frac{n_{A_2}}{n_{AC}} = \frac{P_{A_2}}{P_{AC}} = \frac{3P - x - y}{2z} = \frac{\frac{9}{2}}{1/2} = 9$

Sol. 9. $K_p = \frac{P_{A_2C_2}}{P_{AC}^2} = \frac{3/4}{\left(\frac{1}{2}\right)^2} = 3$

EXERCISE # 2

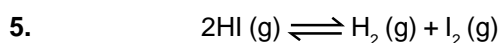


$$\begin{array}{l} t = 0 \quad 0.1 \quad a \quad 0 \\ t = \text{eq} \quad 0.04 \quad (a - 0.06) \quad (0.06) \end{array}$$

$$\text{Given: } \frac{0.06}{(0.04)(a - 0.06)} = 0.9$$

$$\text{so, } (a - 0.06) = \frac{6}{4 \times 0.9} = \frac{1}{0.6}$$

$$\text{Hence, } a = \frac{1}{0.6} + 0.06 = 1.73 \text{ M}$$

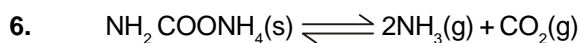


$$\begin{array}{l} t = 0 \quad a \quad 0 \quad 0 \\ t \quad (a - 2x) \quad x \quad x \end{array}$$

$$\text{Given: } \frac{x^2}{(a - 2x)^2} = \frac{1}{54.8}$$

$$\text{so, } \frac{a - 2x}{x} = \sqrt{54.8} \quad \text{and} \quad (a - 2x) = 0.5 \text{ M}$$

$$\text{so, } x = \frac{0.5}{\sqrt{54.8}} = \frac{0.5}{7.40} = 0.0675 \text{ M}$$



$$\begin{array}{cc} 2P_o & P_o \\ 3P_o & P' \end{array}$$

$$K_p = (2P_o)^2 \times P_o = 4P_o^3$$

$$K_p = (3P_o)^2 \times P' = 9P_o^2 \cdot P'$$

$$P' = \frac{4}{9} P_o$$

$$\frac{P^f}{P^i} = \frac{3P_o + \frac{4}{9}P_o}{3P_o} = \frac{31}{27}$$

9.
$$\text{C(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{(g)}$$

$$t = 0 \quad \quad \quad - \quad \quad 1 \quad \quad 2 \quad \quad 3$$
carbon solid will start forming when there will be equilibrium in the container

$$K_p = \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = 3 \text{ atm} = \frac{(2P)(3P)}{P} = 6P = 3 \text{ atm}$$

So $P = \frac{1}{2} \text{ atm}$

So Total pressure in the container will be

$$P_T = P + 2P + 3P = 6P = 3 \text{ atm} \quad \text{Ans. 3}$$

11.
$$\text{LiCl} \cdot 3\text{NH}_3 \text{(s)} \rightleftharpoons \text{LiCl} \cdot \text{NH}_3 \text{(s)} + 2\text{NH}_3 \text{(g)}$$

$$0.1 \quad \quad \quad a \quad \quad \quad \Rightarrow P_{\text{NH}_3} = 3 \text{ atm}$$

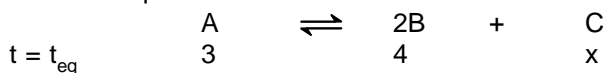
$$K_p = 9 \text{ atm}^2 = p_{\text{NH}_3}^2$$

no. of moles of NH_3 at equilibrium = $\frac{3 \times 5}{0.082 \times 313} = 0.5844$

For 0.1 mol of $\text{LiCl} \cdot \text{NH}_3$ to convert 0.2 mol of NH_3 must be needed.

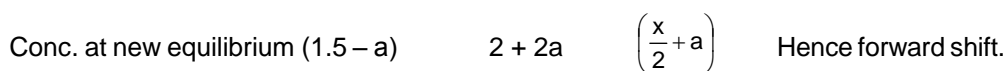
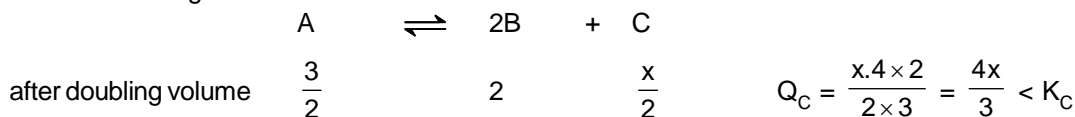
Total number of mol of NH_3 req. = 0.7844.

12. Let initial equilibrium concentration of C = x M



$$K_C = \frac{x \times 4^2}{3} = \frac{16x}{3} \quad \dots\dots\dots(i)$$

Now on doubling the volume concentrations will become half of initial so



Now given that $(2 + 2a) = 3$

so $a = 0.5$

so $[A] = 1\text{M} \quad [B] = 3 \quad [C] = \frac{1}{2}(x + 1)$

so $K_C = \frac{(1+x) \times 9}{2 \times 1} = \frac{16x}{3}$

so $27x + 27 = 32x$

so $x = \frac{27}{5} = 5.4$ and $K_C = \frac{16}{3} \times \frac{27}{5} \times \frac{144}{5} = \mathbf{28.8. Ans.}$

13.
$$2\text{AB}_2 \text{(g)} \rightleftharpoons 2\text{AB (g)} + \text{B}_2 \text{(g)}$$

$$t=0 \quad \quad \quad a \quad \quad \quad 0 \quad \quad \quad 0$$

$$a(1-\alpha) \quad \quad \quad (a\alpha) \quad \quad \quad \frac{(a\alpha)}{2}$$

Total mole = $a[1 - \alpha + \alpha + \frac{\alpha}{2}] \quad \quad \quad \frac{a[2 + \alpha]}{2}$

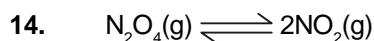
$$P_{\text{AB}_2} = \frac{a(1-\alpha) \times 2}{a(2+\alpha)} \times P \quad ; \quad P_{\text{AB}} = \frac{a\alpha \times 2}{a(2+\alpha)} \times P$$

$$P_{\text{B}_2} = \frac{\left(\frac{a\alpha}{2}\right)}{a(2+\alpha)} = \left[\frac{\alpha}{2+\alpha}\right] \times P.$$

$$K_p = \frac{\left(\frac{2\alpha}{2+\alpha} \times P\right)^2 \left(\frac{\alpha}{2+\alpha} \times P\right)}{\left(\frac{2(1-\alpha)}{2+P} \times P\right)^2}$$

$$\alpha \ll 1.$$

$$K_p = \frac{\alpha^3 P}{2} \quad ; \quad \alpha = \left(\frac{2K_p}{P}\right)^{1/3} \quad \text{i.e. } x = \left(\frac{2K_p}{P}\right)^{1/3}$$



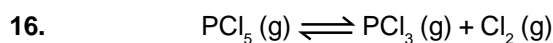
$$a(1-\alpha) \quad 2a\alpha$$

(i) $M_{\text{obs}} = 38.33 \times 2 = 76.66$

(ii) $76.66 = \frac{a(1-\alpha) \times 92 + 2a\alpha \times 46}{a(1+\alpha)}$
 $\alpha = 0.2$

(iii) % of $\text{NO}_2 = \frac{2a\alpha}{a(1+\alpha)} \times 100 = 33.33\%$

(iv) $K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \times 2\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \times 2\right)} = 0.33$



t = 0 $\frac{8.34}{208.5} \quad 0 \quad 0$

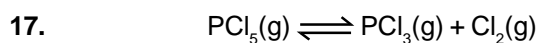
teq. $\left(\frac{8.34}{208.5} - x\right) \quad x \quad x \quad n_T = \left(\frac{8.34}{208.5} + x\right)$

Given, (1 atm) (2.05 L) = $\left(\frac{8.34}{208.5} + x \text{ mole}\right) (0.082 \text{ L atm mole}^{-1} \text{ K}^{-1}) (500 \text{ K})$

so, $\frac{8.34}{208.5} + x = \frac{2.05}{0.082 \times 500} = 0.05 \text{ mole}$
 $x = 0.05 - 0.04 = 0.01$

so, $\alpha = \frac{0.01}{0.04} = 0.25 = 25\%$

$$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P = \left(\frac{1/16}{1-(1/16)}\right) = \frac{16}{15} \text{ atm.}$$



t = 0 $a \quad 0 \quad 0$

teq $0.61 a \quad 0.39 a \quad 0.39 a \quad n_T = 1.39 a$

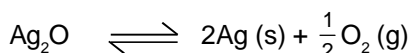
so, $M_{\text{mix}} = \frac{208.5 a}{1.39 a} = 150$

so, density = $\frac{PM_{\text{mix}}}{RT} = \frac{1 \times 150}{0.082 \times 500} = \frac{150}{41} \text{ g/L}$

19. $T = 445^\circ\text{C} = 445 + 273 = 718\text{K}$

$P = 207\text{atm}$

$n = 1 \text{ mole}$



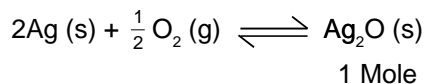
$$K_p = \sqrt{P_{O_2}} = (207)^{1/2} = 14.39$$

$$\Delta G^0 = \Delta G^0 + 2.303 RT \log K_{eq}$$

But at eq. $\Delta G = 0$

$$\Delta G^0 = -2.303 RT \log K_{eq}$$

But for formation



$$K_p = \frac{1}{(P_{O_2})^{1/2}} = \frac{1}{(207)^{1/2}}$$

$$\Delta G^0 = -2.303 \times 8.312 \times 718 \log \frac{1}{(207)^{1/2}}$$

$$\Delta G^0 = \frac{2.303 \times 8.312 \times 718}{2} \times \log 207$$

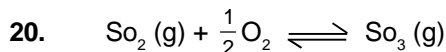
$$\Delta G^0 = 6872.17 \log 207$$

$$\Delta G^0 = 15915.75 \text{ J}$$

$$\Delta G^0 = 3789.46 \text{ Cal}$$

$$\Delta G^0 = 3.789 \text{ KCal}$$

$$\Delta G^0 = 3.8 \text{ KCal}$$



$$\Delta H^0 = -98.32 \text{ KJ/mole} = -98.32 \times 10^3 \text{ J/mole}$$

$$\Delta S^0 = -95.0 \text{ J/mole } ^\circ\text{K}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = -98.32 \times 10^3 - [298 \times (-95)] = -98.32 \times 10^3 + 28.310 \times 10^3$$

$$\Delta G^0 = -70.01 \times 10^3$$

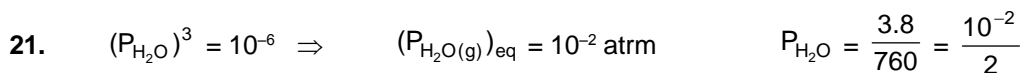
$$\Delta G^0 = -2.303 RT \log K_p$$

$$-70.01 \times 10^3 = -2.303 \times 8.312 \times 298 \log K_p$$

$$70.01 \times 10^3 = 5.705 \times 10^3 \log K_p$$

$$12.27 = \log K_p$$

$$K_p = 1.86 \times 10^{12} \text{ (atm)}^{1/2}$$

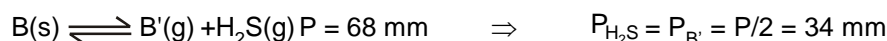
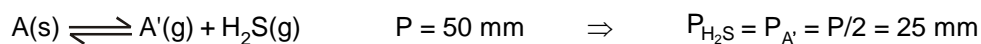


$$\Delta P = 0.01 - \frac{0.01}{2} = 5 \times 10^{-3}$$

$$\text{number of moles of } H_2O(g) \text{ absorbed} = \frac{\Delta PV}{RT} = \frac{5 \times 10^{-3}}{25} \times 15 = 3 \times 10^{-3} \text{ moles}$$

$$\therefore \text{moles of } CuSO_4 \cdot 5H_2O \text{ formed} = \frac{3 \times 10^{-3}}{3} = 10^{-3} = x$$

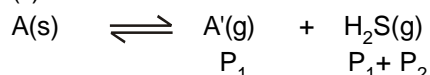
$$\Rightarrow 10^5 x = 10^5 \times 10^{-3} = 100$$

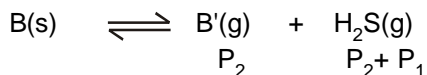


$$(i) K_{p_1} = (25)^2 = 625 \text{ mm}^2$$

$$K_{p_2} = (34)^2 = 1156 \text{ mm}^2$$

(ii) Ratio of moles is same as that of partial pressure so





$$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1 + P_2) \quad \dots\dots\dots (i)$$

$$K_{P_2} = P_B \times P_{H_2S} = P_2(P_1 + P_2) \quad \dots\dots\dots (ii)$$

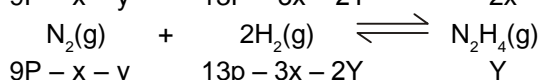
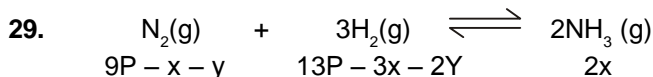
$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

$$(iii) \text{ total pressure} = P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$$

$$(i) + (ii) = (P_1 + P_2)^2$$

$$\sqrt{K_{P_1} + K_{P_2}} = P_1 + P_2$$

$$P_T = 2 \times (\sqrt{K_{P_1} + K_{P_2}}) = 84.4 \text{ mm.}$$



$$\text{given } 9P - x - y + 13P - 3x - 2y + 2x + y = 7P_0$$

$$\Rightarrow 22P - 2x - 2y = 7P_0 \quad \dots\dots\dots(1)$$

$$\text{then } 2x = P_0 \quad \dots\dots\dots(2)$$

$$\text{and } 13P - 3x - 2y = 2P_0 \quad \dots\dots\dots(3)$$

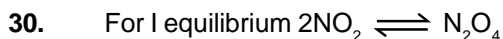
$$\begin{array}{r} 22P - 2y = 5P_0 \\ - 13P - 2y = \frac{7}{2}P_0 \\ \hline 9P = \frac{9}{2}P_0 \end{array} \quad P = \frac{P_0}{2}$$

$$9P - x - y = \frac{9P_0}{2} - \frac{P_0}{2} - \frac{3P_0}{2} = \frac{5P_0}{2} \quad 2y = \frac{13-7}{2}P_0 = 3P_0$$

$$13P - 3x - 2y = \frac{13P_0}{2} - \frac{3P_0}{2} - \frac{6P_0}{2} = 2P_0 \quad y = \frac{3}{2}P_0$$

$$K_1 = \frac{(2x)^2}{(9p - x - y)(13p - 3x - 2y)^3} = \frac{P_0^2}{\frac{5}{2}P_0 \cdot (2P_0)^3} = \frac{1}{20P_0^2}$$

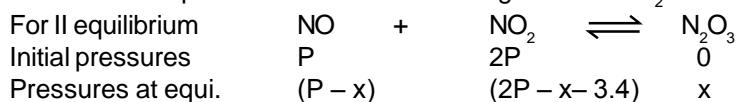
$$K_2 = \frac{\frac{3}{2}P_0}{\left(\frac{5}{2}P_0\right)(2P_0)^2} = \frac{3}{20P_0^2}$$



$$K_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = 6.8 \quad \dots\dots (1)$$

$$\therefore P_{N_2O_4} = 1.7 \text{ atm} \quad \therefore \text{By Eq. (1); } P_{NO_2} = 0.5 \text{ atm}$$

The equilibria are maintained using NO and NO₂ in the ratio 1 : 2



$$\therefore 3.4 \text{ atm of } NO_2 \text{ are used for I equilibrium to have } P_{N_2O_4} = 1.7 \text{ atm}$$

At equilibrium	(P - x)	0.5	x
----------------	---------	-----	---

($\therefore P_{NO_2}$ is same for both the equilibria since both reactions are at equilibrium at a time.)

Total pressure at equilibrium (Given 5.05 atm)

$$= P_{NO} + P_{NO_2} + P_{N_2O_3} + P_{N_2O_4} = P - x + 0.5 + x + 1.7$$

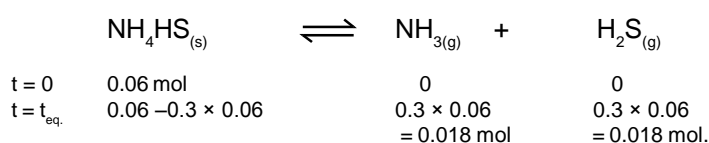
$$\begin{aligned} \therefore & 5.05 = P + 2.20 \\ \therefore & P = 5.05 - 2.20 \\ \therefore & P = 2.85 \text{ atm} \\ \therefore & 2P - x - 3.4 = 0.5 \\ & 2 \times 2.85 - x - 3.4 = 0.5 \\ \therefore & x = 5.70 - 3.90 \\ \therefore & x = \mathbf{1.80 \text{ atm}} \\ \therefore & P_{\text{NO}} = 2.85 - 1.80 = \mathbf{1.05 \text{ atm}} \end{aligned}$$

Now K_p for $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$

$$K_p = \frac{P_{\text{N}_2\text{O}_3}}{P_{\text{NO}} \times P_{\text{NO}_2}} = \frac{1.80}{1.05 \times 0.5} = \mathbf{3.43 \text{ atm}^{-1}}$$

EXERCISE # 3

1. Mole of $\text{NH}_4\text{HS} = \frac{3.06}{18+1+32} = 0.06 \text{ mol}$



$$P_{\text{total}} \times 2 = 2 \times 0.018 \times 0.0821 \times 300$$

$$P_{\text{total}} = 0.4433 \text{ atm}$$

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{0.443}{2} \text{ atm} \quad K_p = \left(\frac{0.443}{2}\right)^2 = 0.049 \text{ atm}^2$$

$$K_c = \frac{k_p}{(RT)^2} = \frac{0.049}{(24.63)^2} = 8.1 \times 10^{-5} \text{ (mol/lit)}^2$$

(ii) No effect of addition of $\text{NH}_4\text{HS}_{(s)}$ on equilibrium as active mass of solid is one.

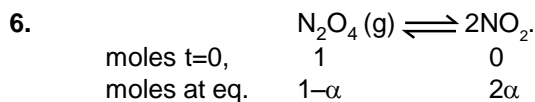
2. Equilibrium is affected by pressure and temperature but not by catalyst.

3. $K_p = K_c (RT)^{\Delta n_g} \Rightarrow K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

4. $Q_c = \frac{[C][D]}{[A][B]}, < K_c$

$\therefore Q_c \uparrow$ with time

5. With change of pressure, x will change in such a way that K_p remains a constant.



$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha} \times P\right)^2}{\frac{1-\alpha}{1+\alpha} \times P} = \frac{4\alpha^2}{1-\alpha^2} \times P.$$

Let total pressure at eq. = P.

or $K_p = \frac{4\alpha^2}{1-\alpha^2} \times P.$

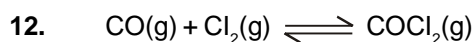
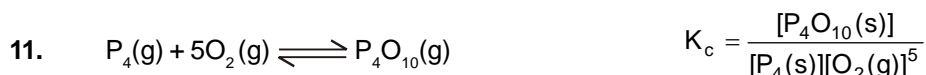
When volume is halved, P is double.

$\therefore \alpha$ will change as K_p is independent of pressure change.

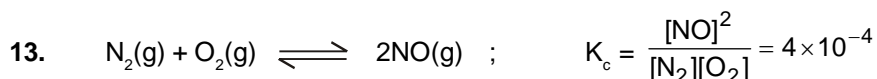
7. In this reaction the ratio of number of moles of reactants to products is same i.e., 2 : 2, hence change in volume will not alter the number of moles .
8. If in the reaction the ratio of number of moles of reactants to products is same i.e., 1 : 1, then change in volume will not alter the number of moles .
9. The conversion of SO_2 to SO_3 is an exothermic reaction, hence there is no need to increase the temperature. There is also a decrease in volume or moles in product side. Thus the reaction is favoured by low temperature and high pressure. (Le-Chatelier's principle).

10. $C_{[\text{N}_2\text{O}_4]} = 4.8 \times 10^{-2} \text{ mol L}^{-1}$, $C_{[\text{NO}_2]} = 1.2 \times 10^{-2} \text{ mol L}^{-1}$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{1.2 \times 10^{-2} \times 1.2 \times 10^{-2}}{4.8 \times 10^{-2}} = 0.3 \times 10^{-2} = 3 \times 10^{-3} \text{ mol L}^{-1}$$



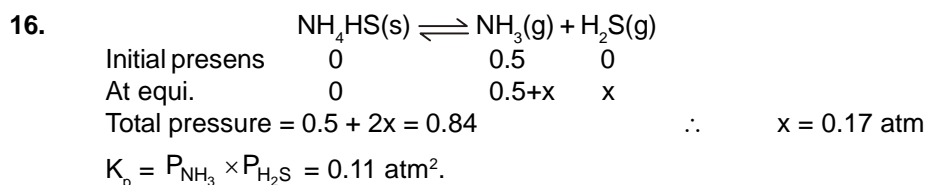
$$\Delta n = 1 - 2 = -1; K_p = K_c(\text{RT})^{\Delta n} \therefore \frac{K_p}{K_c} = (\text{RT})^{-1} = \frac{1}{\text{RT}}$$



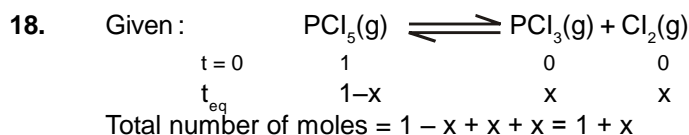
$$\text{NO}(\text{g}) \rightleftharpoons \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}); K_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = \frac{100}{2} = 50$$

14. $K_p = K_c (\text{RT})^{\Delta n}$ $\Delta n = 3 - 2 = 1$.
 $K_p = K_c (0.0821 \times 457)^1$. $K_p > K_c$.

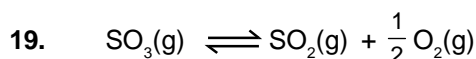
15. $\text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightleftharpoons 2\text{ClF}_3(\text{g})$; $\Delta H = -329 \text{ kJ}$. Favourable conditions:
 (i) Decrease in temperature, (ii) Addition of reactants, (iii) Increase in pressure i.e., decrease in volume.



17. When nitrogen is added at equilibrium condition, the equilibrium will shift according to Le-chatelier principle at equilibrium $\Delta G = 0$ and catalyst changes the rate of forward and backward reactions by equal extent. K_p of reaction is a function of temperature only.



Thus partial pressure of $\text{PCl}_3 = \left(\frac{x}{1+x}\right)P$.



$$\frac{[\text{SO}_2][\text{O}_2]^{1/2}}{[\text{SO}_3]} = K_c = 4.9 \times 10^{-2} \dots\dots\dots(\text{i})$$



$$\frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = K'_c = \frac{1}{4.9 \times 10^{-2}} \text{ For } 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$

$$\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = K_c^2 = \frac{1}{4.9 \times 4.9 \times 10^{-4}} = \frac{10000}{24.01} = 416.49$$

20. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -54.07 \times 1000 - 298 \times 10 = -54070 - 2980 = -57050$
 $\Delta G^\circ = -2.303 RT \log_{10} K$
 $-57050 = -2.303 \times 298 \times 8.314 \log_{10} K = -5705 \log_{10} K$
 $\log_{10} K = 10$

21. At equilibrium ΔG (Gibbs energy) = 0 but ΔG° (standard Gibbs energy) $\neq 0$
 As ΔG (Gibbs energy) is more negative reaction will be more spontaneous.

22. $c = a + b$



$$K_{p_1} = \frac{\left(\frac{2\alpha}{1+\alpha} P_{T_1}\right)^2}{\left(\frac{1-\alpha}{1+\alpha} P_{T_1}\right)} \quad K_{p_2} = \frac{\left(\frac{\alpha}{1+\alpha} P_{T_2}\right) \left(\frac{\alpha}{1+\alpha} P_{T_2}\right)}{\left(\frac{1-\alpha}{1+\alpha} P_{T_2}\right)}$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{\left(\frac{2\alpha}{1+\alpha} P_{T_1}\right)^2}{\left(\frac{1-\alpha}{1+\alpha} P_{T_2}\right)} \times \frac{\left(\frac{1-\alpha}{1+\alpha} P_{T_2}\right)}{\left(\frac{\alpha}{1+\alpha} P_{T_2}\right) \left(\frac{\alpha}{1+\alpha} P_{T_2}\right)}$$

$$\frac{1}{9} = \frac{4P_{T_1}}{P_{T_2}} ; \quad \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36}$$

24. $PV = nRT$
 $V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$
 $P = 3170 \text{ Pa}$
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $T = 300 \text{ K}$
 $3170 \times 10^{-3} = n \times 8.314 \times 300$
 $n = \frac{3170 \times 10^{-3}}{8.314 \times 300} = 1.27 \times 10^{-3} \text{ mol.}$

25.
$$\begin{array}{ccc} \text{CO}_2(\text{g}) + \text{C}(\text{s}) & \rightleftharpoons & 2\text{CO}(\text{g}) \\ 0.5 \text{ atm} & & \\ 0.5-p & & 2p \end{array}$$

 Total pressure = $0.5 - P + 2P = 0.8$
 $P = 0.3$

$$K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(2P)^2}{(0.5-P)} = \frac{(0.6)^2}{(0.5-0.3)}$$

 $K_p = 1.8$

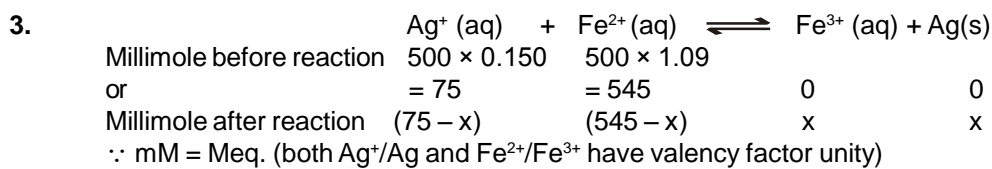
26. $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO} \quad K = 4 \times 10^{-4}$
 $\text{NO} \longrightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 \quad K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$

SOLUTION OF ADVANCED LEVEL PROBLEM

1. (i) $\text{CO(g)} + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH(g)}$
- | | | | | | |
|-------------------------------|----------|---|---------------|---|--|
| 0.15 | a | | | | |
| $0.15 - x$ | $a - 2x$ | x | \Rightarrow | $x = 0.08$ | |
| $0.15 - x + a - 2x + x = 0.5$ | | | | $PV = nRT$ | |
| $a - 2x = 0.35$ | | | | $n = \frac{8.2 \times 2.5}{0.082 \times 500} = 0.5$ | |
- $$K_c = \frac{\frac{0.08}{2.5}}{\frac{0.07}{2.5} \times \left(\frac{0.35}{2.5}\right)^2} = \frac{20000}{343} = 58.3$$
- $$K_p = 58.3 \times (RT)^{-2} = \frac{58.3}{(0.082 \times 500)^2} = \frac{58.3}{41 \times 41} = 0.035$$
- (ii) Total pressure will remain 8.2 atm as catalyst reduces only time taken to achieve equilibrium, does not affect equilibrium condition / concentrations.

2. $2.0 \times 10^{-37} = \frac{(x)^2}{(0.482)^2 \times (0.933)} \Rightarrow x = 6.6 \times 10^{-20}$

$\therefore [\text{N}_2] = 0.0482 \text{ mol L}^{-1}$; $[\text{O}_2] = 0.0933 \text{ mol L}^{-1}$; $[\text{N}_2\text{O}] = 6.6 \times 10^{-21} \text{ mol L}^{-1}$



$$\therefore K_c = \frac{[\text{Fe}^{3+}]}{[\text{Ag}^+][\text{Fe}^{2+}]}$$

$$\therefore K_c = \frac{\frac{x}{1000}}{\left(\frac{75-x}{1000}\right)\left(\frac{545-x}{1000}\right)} \dots (1)$$

$$\therefore \text{Conc.} = \frac{\text{Millimole}}{\text{Total volume}}$$

$$[\text{Ag}^+] = \frac{75-x}{1000} ; \quad [\text{Fe}^{2+}] = \frac{545-x}{1000} ; \quad [\text{Fe}^{3+}] = \frac{x}{1000}$$

Now 25 mL of mixture requires 30 mL of 0.0832 M or $0.0832 \times 5 \text{ N KMnO}_4$.

$\therefore \text{Fe}^{2+}$ is oxidized by KMnO_4 .

$$\begin{aligned} \therefore \text{Milliequivalent of Fe}^{2+} \text{ left at equilibrium in } 1000 \text{ mL} \\ &= \text{Milliequivalent of KMnO}_4 \text{ for } 1000 \text{ mL} \\ &= \frac{30 \times 0.0832 \times 5 \times 1000}{25} = 499.2 \end{aligned}$$

$$\therefore 545 - x = 499.2$$

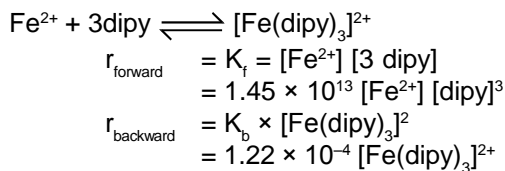
$$\therefore x = 545 - 499.2 = 45.8$$

Thus, by Eq. (1),

$$K_c = \frac{\frac{45.8}{1000}}{\left(\frac{75-45.8}{1000}\right)\left(\frac{545-45.8}{1000}\right)} = \frac{45.8 \times 1000}{29.2 \times 499.2}$$

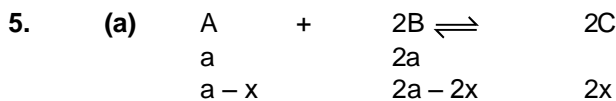
$$K_c = \mathbf{3.1420.}$$

4. For the reaction,



At equilibrium $r_f = r_b$ and $K_c = \frac{K_f}{K_b} = \frac{[\text{Fe}(\text{dipy})_3]^{2+}}{[\text{Fe}^{2+}] [\text{dipy}]^3}$

Also, stability constant of complex = Equilibrium constt. of reaction = $\frac{K_f}{K_b} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.188 \times 10^{17}$



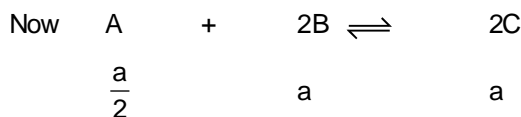
Total moles at equilibrium $3a - x$

$$\text{Mole fraction of C} = \frac{2x}{3a - x} = 0.4$$

$$2x = 1.2a - 0.4x$$

$$x = \frac{1.2a}{2.4}$$

$$x = \frac{a}{2}$$

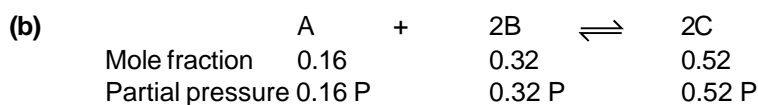


$$\text{Total moles} = \frac{5a}{2}$$

$$P_A = \frac{\frac{a}{2}}{\frac{5a}{2}} \times 8 = \frac{8}{5} \text{ atm} ; \quad P_B = \frac{a}{5a/2} \times 8 = \frac{16}{5} \text{ atm}$$

$$P_C = \frac{a}{5a/2} \times 8 = \frac{16}{5} \text{ atm} ; \quad K_p = \frac{(P_C)^2}{(P_B)^2 \cdot P_A} = \frac{5}{8}$$

$$K_p = 0.625 \text{ atm}^{-1}$$



$$K_p = \frac{(0.52P)^2}{0.16P \times (0.32P)^2} = \frac{5}{8}$$

$$P = \frac{0.52 \times 0.52 \times 8}{0.16 \times 0.32 \times 0.32 \times 5} = 26.4 \text{ atm}$$

6. (i) From the graph $0.3 \times n = 0.6$

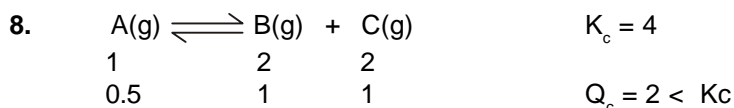
$$n = 2$$

(ii) $K = (0.6)^2 / 0.3 = 1.2 \text{ mol / L}$

(iii) initial rate of conservation of A = $\frac{0.6 - 0.5}{1} = 0.1 \text{ M hr}^{-1}$

$$7. \quad Q_c = \frac{\left(\frac{3}{10}\right)^4 \left(\frac{3}{10}\right)}{\left(\frac{2}{10}\right) \left(\frac{4}{10}\right)^2} = \frac{243}{32} \times 10^{-2} = 7.59 \times 10^{-2} > K_c$$

so, reaction will proceed in backward direction.

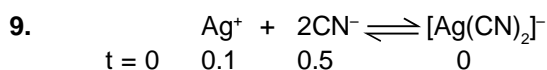


$$Q_c = 2 < K_c$$

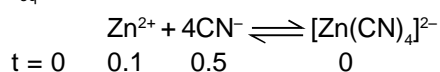
$$0.5 - x \quad 1 + x \quad 1 + x \quad 4 = \frac{(1+x)^2}{0.5-x}$$

$$x = 0.162 \quad [A] = 0.338$$

$$[B] = [C] = 1.162$$



$$t_{eq} \quad 10^{-6} \quad 0.3 \quad 0.1 \quad K_1 = \frac{10}{9} \times 10^6$$



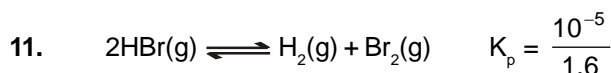
$$eq. \quad 10^{-12} \quad 0.1 \quad 0.1 \quad K_2 = \frac{0.1}{(0.1)^4 \times 10^{-12}} = 10^{15}$$

Subtracting two times Ist reaction from IInd reaction, we will get the required reaction, so

$$K_{eq} = \frac{10^{15}}{\left(\frac{10}{9}\right)^2 \times 10^{12}} = \frac{10^3 \times 81}{100} = 810 \quad \text{Ans. 810}$$

$$10. \quad K_p = \left(\frac{0.55}{0.45}\right)^2 = 1.49 \quad ; \quad K_p = \left(\frac{0.76}{0.24}\right)^2 = 10.03$$

Higher temperature ($\because K_p > K_p$).



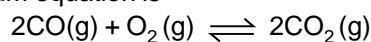
$$10 - 2p \quad p \quad p$$

$$\left(\frac{p}{10-2p}\right)^2 = \frac{10^{-5}}{1.6} \quad p = 2.5 \times 10^{-2}$$

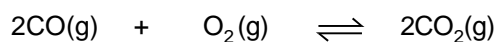
$$(p_{H_2})_{eq} = (p_{Br_2})_{eq} = 2.5 \times 10^{-2} \text{ bar} \quad ; \quad (p_{HBr})_{eq} = 10.0 \text{ bar}$$

12. The equilibrium reaction would involve 2 moles of CO, 1 mole of O₂ and 2 moles of CO₂ as the unit of K_c is lit/mole.

So the equilibrium equation is



The equation, $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ would have an equilibrium constant with units (lit/mole)^{1/2}.



$$\text{Initial conc.} \quad \frac{1}{2} = 0.5 \quad \frac{1}{2} = 0.5 \quad 0$$

$$\text{Conc. at equil.} \quad 0.5 - x \quad 0.5 - \frac{x}{2} \quad x$$

$$\therefore K_c = \frac{[CO_2]^2}{[CO]^2 [O_2]} = 5 \times 10^3$$

$$\therefore 5 \times 10^3 = \frac{x^2}{(0.5-x)^2 \left(0.5 - \frac{x}{2}\right)}$$

Since, the value of equilibrium constant is pretty high so we can assume that almost entire CO goes to CO₂. Thus, value of x would be close to 0.5. But concentration of CO, (0.5 - x) would not be zero but would be a small value. Let this value be y. Then the concentration of O₂ at equilibrium would be $\left(0.25 + \frac{y}{2}\right)$.

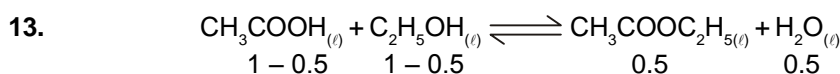
$$\therefore 5 \times 10^3 = \frac{(0.5)^2}{y^2 \left(0.25 + \frac{y}{2}\right)}$$

As value of y is very small, $\frac{y}{2}$ can be easily ignored with respect to 0.25

$$5 \times 10^3 = \frac{(0.5)^2}{y^2 \times 0.25}$$

$$y = 1.4 \times 10^{-2}$$

$$[\text{CO}] = y = 1.4 \times 10^{-2} \text{ M.}$$



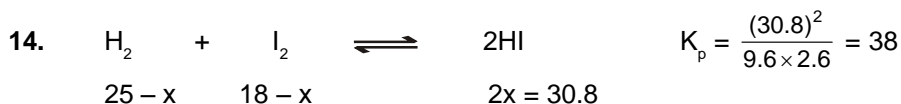
So,
$$K_c = \frac{0.5 \times 0.5}{0.5 \times 0.5} = 1$$

Now let a moles of CH₃COOH and b moles of C₂H₅OH are taken :

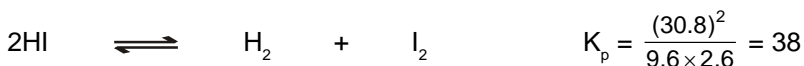
$$a - \frac{a}{3} \quad b - \frac{a}{3} \quad \frac{a}{3} \quad \frac{a}{3}$$

$$K_c = \frac{(a/3) \times (a/3)}{2a/3 \times (b - \frac{a}{3})} \quad \text{or} \quad 2\left(b - \frac{a}{3}\right) = \frac{a}{3}$$

or $2b = a$ or $\frac{a}{b} = \frac{2}{1}$

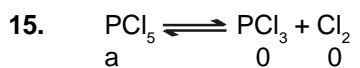


$$K_p = \frac{(30.8)^2}{9.6 \times 2.6} = 38$$



$$K_p = \frac{(30.8)^2}{9.6 \times 2.6} = 38$$

$$1 - \alpha \quad \frac{\alpha}{2} \quad \frac{\alpha}{2} \quad \frac{1}{38} = \frac{\alpha^2}{4(1-\alpha)^2} \Rightarrow \alpha = 0.245$$

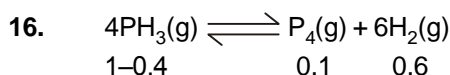


Total moles at equilibrium = $a(1+\alpha)$ (i)

From $n = \frac{PV}{RT} = \frac{1 \times 1.7}{0.0821 \times 523} = 0.03959$ (ii)

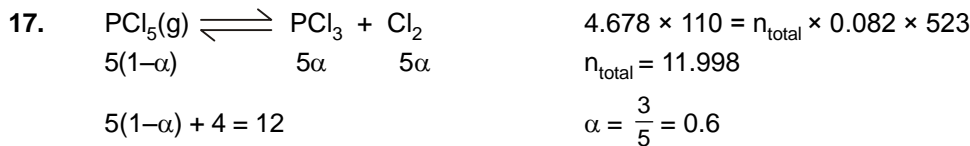
From (i) and (ii) $a(1+\alpha) = 0.03959$

Here $a = \frac{4.5}{208.5}$ Hence $\alpha = 0.8329$



$$M_{\text{eq.}} = \frac{0.6 \times 34 + 0.1 \times 124 + 0.6 \times 12}{1.3} = 30.76$$

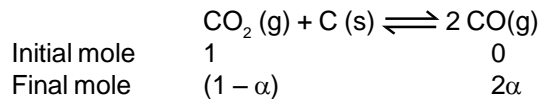
Vapour density = 15.38



$$P_{\text{eq mix.}} = \frac{4.768}{12} \times 8 = 3.18$$

$$K_p = \frac{\alpha^2 P}{1-\alpha^2} = \frac{0.6^2 \times 3.18}{1-0.6^2} = \mathbf{1.78}$$

18. (a) The given equilibrium is ,



$$K_p = \frac{(n_{\text{CO}})^2}{n_{\text{CO}_2}} \times \left[\frac{P}{\Sigma n} \right]^1 = \frac{(2\alpha)^2}{(1-\alpha)} \times \left[\frac{5}{1+\alpha} \right]$$

$$10 = \frac{20\alpha^2}{(1-\alpha)}$$

or $10 - 10\alpha^2 = 20\alpha^2$.

$$\therefore \alpha^2 = \frac{10}{30}$$

$$\therefore \alpha = \sqrt{\frac{1}{3}} = 0.577$$
 .

Thus, mole of CO_2 at equilibrium = $1 - \alpha = 1 - 0.577 = 0.423$.

and mole of CO at equilibrium = $2\alpha = 2 \times 0.577 = 1.154$

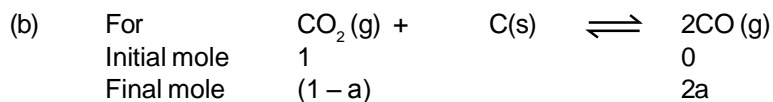
Total mole present at equilibrium = $0.423 + 1.154 = 1.577$.

At equilibrium, $PV = nRT$
 $P = 5 \text{ atm}$; $n = 1.577$, $T = 817 + 273 = 1090$.
 $5 \times V = 1.577 \times 0.0821 \times 1090$.

$\therefore V = 28.22 \text{ litre}$.

$$\therefore [\text{CO}] \text{ at equilibrium} = \frac{1.154}{28.22} = \mathbf{0.041 \text{ mol litre}^{-1}}$$

$$\therefore [\text{CO}_2] \text{ at equilibrium} = \frac{0.423}{28.22} = \mathbf{0.015 \text{ mol litre}^{-1}}$$



Total mole at equilibrium = $1 - a + 2a = 1 + a$.

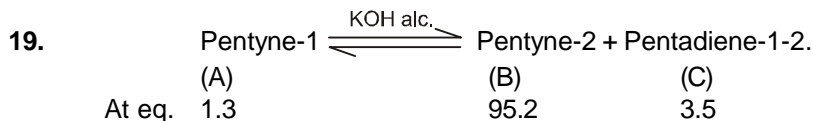
Given $\frac{1-a}{1+a} = \frac{5}{100}$

$$\therefore a = \frac{95}{100}$$

$$K_p = \frac{(n_{\text{CO}})^2}{(n_{\text{CO}_2})} \times \left[\frac{P}{\Sigma n} \right]^1$$

$$10 = \frac{\left(\frac{2 \times 95}{100} \right)^2}{\left(\frac{5}{100} \right)} \times \left[\frac{P}{\frac{105}{100}} \right]^1$$

$\therefore P = \mathbf{0.145 \text{ atm}}$.



$$K_{\text{eq.}} = \frac{[\text{B}][\text{C}]}{[\text{A}]} = \frac{95.2 \times 3.5}{1.3} = 256.31 \quad \dots(i)$$

Now, for $\text{B} \rightleftharpoons \text{A}$

$$K_1 = \frac{[\text{A}]}{[\text{B}]}$$

then from Eqs. (i) and (ii), $K_1 = \frac{[\text{C}]}{K_{\text{eq.}}} = \frac{3.5}{256.31} = 0.013$.

$$\therefore \Delta G^\circ = -2.303 RT \log_{10} K = -2.303 \times 8.314 \times 448 \log 0.013 = 16178 \text{ J} = \mathbf{16.178 \text{ kJ.}}$$

Stability order for A and B is $\text{B} > \text{A}$.

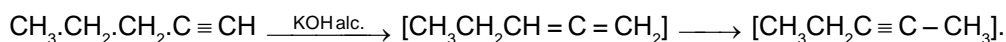
Similarly for $\text{B} \rightleftharpoons \text{C}$

$$K_2 = \frac{[\text{C}]}{[\text{B}]} = \frac{K_{\text{eq.}}[\text{A}]}{[\text{B}]^2} = \frac{256.31 \times 1.3}{95.2 \times 95.2} = 0.037.$$

$$\therefore \Delta G^\circ = -2.303 R \log_{10} K = -2.303 \times 8.314 \times 448 \log 0.037 = 12282 \text{ J} = \mathbf{12.282 \text{ kJ.}}$$

Thus, stability order for B and C is $\text{B} > \text{C}$.

Given the values of ΔG°_1 and ΔG°_2 , the total stability order is $\text{B} > \text{C} > \text{A}$.



20. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; $K = e^{-\Delta G^\circ / RT}$

At 300 K, $\Delta G^\circ = (-41.16 - 300 \times -0.0424) \times 1000 = -28440 \text{ J/mol}$

At 1200 K, $\Delta G^\circ = (-32.93 - 1200 \times -0.0296) \times 1000 = -2590 \text{ J/mol}$

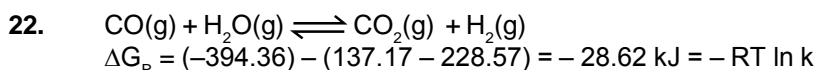
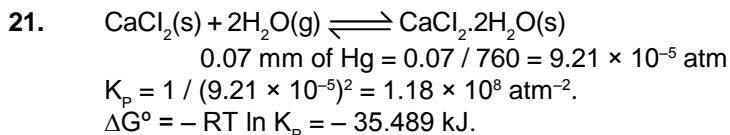
$K_p(300 \text{ K}) = 8.935 \times 10^4$

$K_p(1200 \text{ K}) = 0.37753$

$Q = 1$

at 300 K: $Q < K$, Hence forward direction.

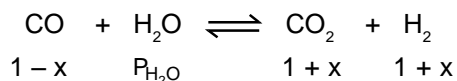
at 1200 K: $Q > K$, Hence backward direction.



$$\log K = \frac{28.62}{8.314 \times 248 \times 2.303} = 5$$

$$K = 10^5$$

$$K = \frac{P_{\text{CO}_2} \times P_{\text{H}_2}}{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}$$



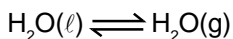
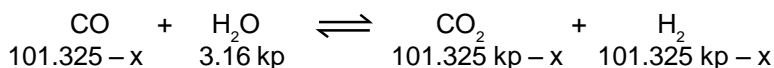
$$10^5 = \frac{(1+x)^2}{(1-x)P_{\text{H}_2\text{O}}} = \frac{(1+x)^2}{(1-x)1.22 \times 10^{-3}}$$

$$122 = \frac{(1+x)^2}{(1-x)}$$



$$\Delta G^\circ_{\text{rxn.}} = -28.62 \text{ kJ}$$

$$k_p = 10^5$$



$$\Delta G = -8.56$$

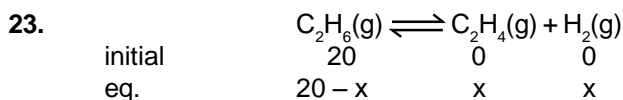
$$-8.56 = -2.303 RT \log kp$$

$$\log kp = 1.5$$

$$kp = 3.16 = P_{\text{H}_2\text{O}}$$

$$kp = 10^5 = \frac{(101.325 + x)(101.325 + x)}{(3.16)(101.325 + x)}$$

$$x = 101.201 \text{ kPa}; \quad P_{\text{CO}} = 0.124 \text{ kPa}; \quad P_{\text{CO}_2} = 202.65 \text{ kPa}$$



$$0.5 \frac{\left(\frac{x}{20+x}\right)^2}{\left(\frac{20-x}{20+x}\right)} = 0.05 \quad \Rightarrow \quad x = 6.02$$

$$\text{mole percentage} = \frac{26.02}{106.02} \times 100 = 24.5$$

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = 144.01 \text{ kJ}$$

From the equation,

$$\log\left(\frac{0.05}{K_2}\right) = \frac{144.01 \times 1000}{2.303R} \left(\frac{1}{300} - \frac{1}{900}\right)$$

$$\Delta G^\circ (300 \text{ K}) = -R \times 300 \times 2.303 \log K_2 = 103.47 \text{ kJ/mol.}$$

24. (a) Because Fe_2O_3 is a solid, its "concentration" doesn't change when more Fe_2O_3 is added. Therefore, there is no concentration stress, and the original equilibrium is undisturbed.

(b) Le Chatelier's principle predicts that the concentration stress of removed CO_2 will be relieved by reaction from left to right to replenish the CO_2 .

(c) Le Chatelier's principle predicts that the concentration stress of removed CO will be relieved by reaction from right to left to replenish $Q_c = [\text{CO}_2]^3 / [\text{CO}]^3$.

When the equilibrium is disturbed by reducing [CO], Q_c increases, so that $Q_c > K_c$. For the system to move to a new state of equilibrium, Q_c must decrease—that is, $[\text{CO}_2]$ must decrease and $[\text{CO}]$ must increase. Therefore the reaction goes from right to left, as predicted by Le Chatelier's principle.

25. (a) Because the forward reaction is endothermic, an increase in temperature favours the formation of NF_2 .

$$\text{The equilibrium constant } K_c = \frac{[\text{NF}_2]^2}{[\text{N}_2\text{F}_4]}$$

will therefore increase with increasing temperature.

(b) The stress here is the removal of NF_2 gas. To offset it, more N_2F_4 will decompose to form NF_2 . The equilibrium constant K_c remains unchanged, however.

(c) A decrease in pressure (which is accompanied by an increase in gas volume) favors the formation of more gas molecules, that is, the forward reaction. Thus, more NF_2 gas will be formed. The equilibrium constant will remain unchanged.

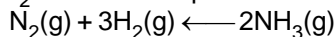
(a) Adding helium to the equilibrium mixture of constant volume will not shift the equilibrium.

26. (a) Consider only the gaseous molecules. In the balanced equation there are 3 mol of gaseous reactants and 2 mol of gaseous product. Therefore the net reaction will shift toward the products (to the right) when the pressure is increased.

(b) The number of moles of products is 2 and that of reactants is 1; therefore the net reaction will shift to the left, toward the reactants.

(c) The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

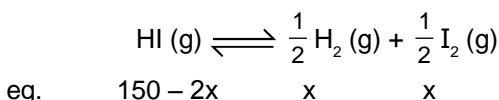
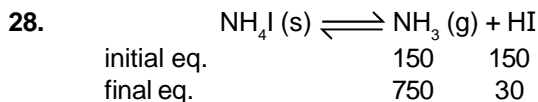
27. (a) The stress applied to the system is the addition of NH_3 . To offset this stress, some NH_3 reacts to produce N_2 and H_2 until a new equilibrium is established. The net reaction therefore shifts from right to left that is:



- (b) At the instant when some of the NH_3 is added, the system is no longer at equilibrium. The reaction

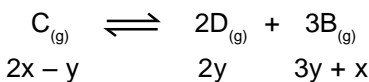
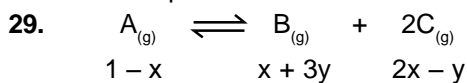
$$\text{quotient is given by } Q_c = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(3.65)^2}{(0.683)(8.80)^3} = 2.86 \times 10^{-2}$$

Because this value is greater than 2.37×10^{-3} , the net reaction shifts from right to left until Q_c equals K_c .



$$\frac{\sqrt{x}\sqrt{x}}{150 - 2x} = 2 \Rightarrow x = 60$$

Final pressure = $750 + 30 + 60 + 60 = 900$ mm of Hg.



$$n_{\text{eq}} = 1 - x + x + 3y + 2x - y + 2y$$

$$\frac{n_{\text{eq}}}{n_i} = \frac{1 + 2x + 4y}{1} = \frac{13}{6} \Rightarrow 2x + 4y = \frac{7}{6}$$

$$\frac{1 + 2x + 4y}{1} = \frac{13}{6}$$

$$2x + 4y = \frac{7}{6}$$

$$12x + 24y = 7 \quad \text{.....(i)}$$

$$\frac{2x + y}{1 - x} = \frac{4}{9}$$

$$18x - 9y = 4 - 4x$$

$$\frac{8}{3}(22x - 9y = 4) \quad \text{.....(ii)}$$

$$\frac{176}{3}x - 24y = \frac{32}{3} \quad \text{.....(iii)}$$

(1) + (3)

$$12x + \frac{176}{3}x = \frac{32}{3} + 7$$

$$\frac{212}{3}x = \frac{53}{3}$$

$$x = \frac{53}{212}$$

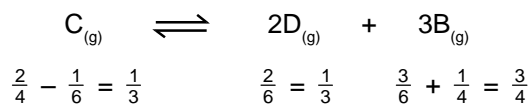
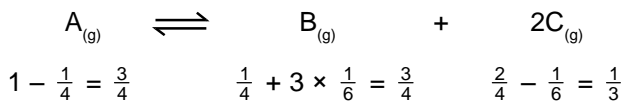
$$x = 0.25 = \frac{1}{4}$$

use in eq. (1)

$$312 \times \frac{1}{4} + 24y = 7$$

$$24y = 4$$

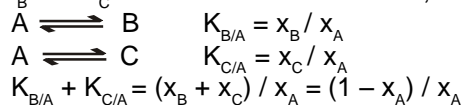
$$y = \frac{1}{6}$$



$$K_{C_1} = \frac{\frac{3}{4} \times \left(\frac{1}{3}\right)^2}{\frac{3}{4}} = \frac{1}{9} = 0.111$$

$$K_{C_2} = \frac{\left(\frac{1}{3}\right)^2 \times \left(\frac{3}{4}\right)^2}{\frac{1}{3}} = \frac{1}{3} \times \frac{27}{64} = 0.14$$

30. Let x_A , x_B and x_C are the mole fractions of A, B and C respectively.



$$\Rightarrow x_A = \frac{1}{1 + K_{B/A} + K_{C/A}}$$

$$x_B = \frac{K_{B/A}}{1 + K_{B/A} + K_{C/A}}, \quad x_C = \frac{K_{C/A}}{1 + K_{B/A} + K_{C/A}}$$

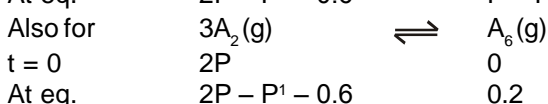
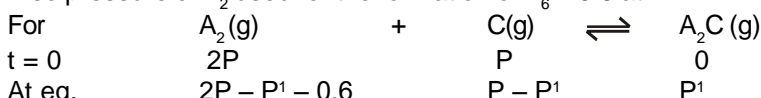
31.



$$K_p = 1.6 = \frac{P_{A_6}}{(P_{A_2})^3}$$

$$P_{A_2} = \sqrt[3]{\frac{0.2}{1.6}} = 0.5 \text{ atm}$$

Also pressure of A_2 used for the formation of $A_6 = 0.6 \text{ atm}$



$$2P - P^1 - 0.6 = 0.5$$

(since P_{A_2} at eq. is 0.5 for simultaneous equilibria)

$$\begin{aligned} \text{Also pressure of } A_2 + C + A_2C + A_6 \\ = (2P - P^1 - 0.6) + (P - P^1) + P^1 + 0.2 \\ = 1.4 \end{aligned}$$

$$0.5 + P + 0.2 = 1.4$$

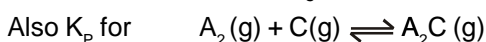
$$P = 0.7 \text{ atm}$$

$$\therefore 2P - P^1 - 0.6 = 0.5$$

$$\therefore P^1 = 2 \times 0.7 - 0.6 - 0.5$$

$$P^1 = 0.3 \text{ atm}$$

$$\therefore P_{A_2} = 0.5 \text{ atm}, P_C = 0.7 - 0.3 = 0.4 \text{ atm}, P_{A_2C} = 0.3 \text{ atm}$$

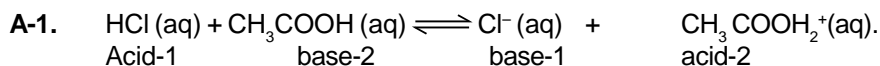


$$K_p = \frac{P_{A_2C}}{P_{A_2} \times P_C} = \frac{0.3}{0.5 \times 0.4} = 1.5 \text{ atm}^{-1}$$

IONIC EQUILIBRIUM

EXERCISE # 1

PART - I



A-7.* $\text{p}K_w = -\log K_w = -\log 1 \times 10^{-12} = 12$.
 $K_w = [\text{H}^+][\text{OH}^-] = 10^{-12}$.
 $[\text{H}^+] = [\text{OH}^-]$
 $\Rightarrow [\text{H}^+]^2 = 10^{-12}$; $[\text{H}^+] = 10^{-6}$; $\text{pH} = -\log[\text{H}^+] = -\log 10^{-6} = 6$.
 H_2O is neutral because $[\text{H}^+] = [\text{OH}^-]$ at 373 K even when $\text{pH} = 6$.
 (D) is not correct at 373 K. Water cannot become acidic.

- B-1.** (A) At 25°C, $[\text{H}^+]$ in a solution of 10^{-8} M HCl $> 10^{-7}$ M.
 (B) $[\text{H}^+] = 10^{-8}$ M.
 (C) $[\text{OH}^-] = 4 \times 10^{-6}$ M $\Rightarrow [\text{H}^+] = 2.5 \times 10^{-9}$ M.
 (D) $[\text{H}^+] = 10^{-9}$ M.

B-3. Inital	Final
pH = 12	pH = 11
$[\text{H}^+] = 10^{-12}$ M	$[\text{H}^+] = 10^{-11}$ M
$[\text{OH}^-] = 10^{-2}$ M	$[\text{OH}^-] = 10^{-3}$ M
Inital No. of mole of $\text{OH}^- = 10^{-2}$	Final No. of mole of $\text{OH}^- = 10^{-3}$
So no. of mole of OH^- removed = $[.01 - 0.001] = 0.009$	

- B-8.** In this solution, source of OH^- is water
 $\therefore C\alpha = [\text{OH}^-]$

$$\alpha = \frac{10^{-9}}{1000/18} = 1.8 \times 10^{-11} \text{ M}$$

% ionisation = $1.8 \times 10^{-9} \text{ M}$

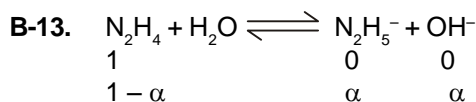
- B-11.** Given density of formic acid = 1.15 g/cm^3
 \therefore Weight of formic acid in 1 litre solution = $1.15 \times 10^3 \text{ g}$

$$\text{Thus, } [\text{HCOOH}] = \frac{1.15 \times 10^3}{46} = 25 \text{ M}$$

Since in case of auto ionisation

$$[\text{HCOOH}_2^+] = [\text{HCOO}^-] \text{ and } [\text{HCOO}^-][\text{HCOOH}_2^+] = 10^{-6} \Rightarrow [\text{HCOO}^-] = 10^{-3}$$

$$\text{Now \% dissociation of HCOOH} = \frac{[\text{HCOO}^-] \times 100}{[\text{HCOOH}]} = \frac{10^{-3}}{25} \times 100 = 0.004\%$$



$$K_b = C\alpha^2.$$

$$\therefore a = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{4 \times 10^{-6}}{0.16 \times \frac{1000}{32} \times \frac{1000}{500}}} = 0.02 \text{ or } 2\%.$$

C-2. Relative strengths of weak acids = $\sqrt{\frac{K_{a1}}{K_{a2}}}$

Assume C_1 and C_2 are same (Although not given).

$$\therefore \text{Relative strength} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \sqrt{\frac{2.1 \times 10^{-4}}{1.1 \times 10^{-5}}}$$

Relative strength for HCOOH to $\text{CH}_3\text{COOH} = 4.37 : 1$.

C-3 to C-5

Final volume of solution become double and concentration becomes half.

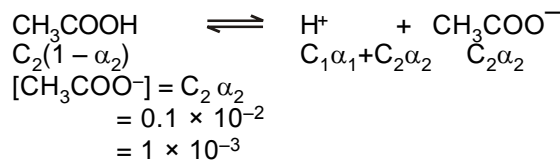
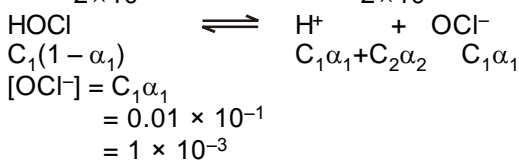
$$C_1 = 0.01, \quad C_2 = 0.1$$

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$= \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$pH = 3 - \log 2 = 3 - 0.3 = 2.7$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1}; \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}$$

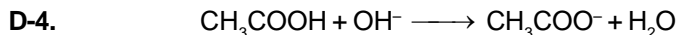
$$[\text{HOCl}] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 10^{-1}(1 - 0.01) \approx 10^{-1}$$

C-7. Initial pH = $\frac{1}{2}(\text{p}K_b - \log C) = \frac{1}{2}(5 - \log 2 - \log 0.1) = 2.85$

After adding NaOH, pOH of solution = 1

Change in pOH = 1.85



$$\begin{array}{l} t = 0 \qquad 20 \qquad 20 \\ t = \text{eq} \qquad - \qquad - \qquad 20 \end{array}$$

So, $[\text{CH}_3\text{COO}^-] = \frac{20}{200} = 0.1 \text{ M}$

$$pH = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C = 7 + 2.37 + \frac{1}{2} \log 10^{-1} = 7 + 2.37 - 0.5 = 8.87$$

D-7.* Let BA be this salt $\text{BA} \rightarrow \text{B}^+ + \text{A}^-$

A^- does not undergo hydrolysis because HA is strong acid. B^+ undergoes hydrolysis

$$h = \sqrt{\frac{K_h}{C}} \quad h = \text{degree of hydrolysis where } K_h = \text{Hydrolysis constant} = \frac{K_w}{K_b}$$

$$h \propto \sqrt{K_h} \quad \text{greater the hydrolysis constant greater the } h(\text{degree of hydrolysis}).$$

$$h \propto \frac{1}{\sqrt{K_b}} \quad \text{greater the } K_b \text{ lesser the } h.$$

Hydrolysis is endothermic, K_h increases with temperature and h also increase with temperature.

$$h \propto \sqrt{V} \quad V = \text{volume of salt solution hence } h \text{ increases with dilution. } K_h = \frac{K_w}{K_b}$$

Both K_w and K_b change with temperature, hence K_h changes with temperature.

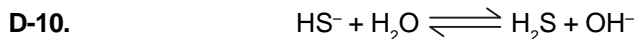
Hence, statement(B) is correct. h increases if K_b decreases, statement(C) correct.

It is found that as temperature increase, K_w and K_b increase but increase in K_w is greater than increase in K_b .

Hence, h increases with increase in temperature. or h decrease in temperature., hence statement.

(D) is correct.

(D) is not correct from explanation of (B).



$$\therefore [\text{OH}^-] = Ch = \sqrt{\frac{K_w C}{K_a}} \quad \therefore [\text{H}^+] = \frac{K_w}{\sqrt{\frac{K_w C}{K_a}}} = \sqrt{\frac{K_w K_a}{C}}$$

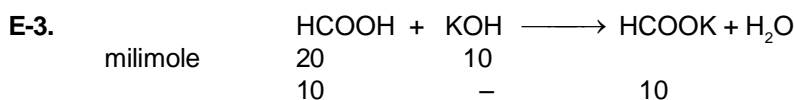
or $\text{pH} = 1/2[\text{p}K_w + \text{p}K_a + \log C]$

E-2. $K_a = 5 \times 10^{-10}$ $\text{p}K_a = 10 \log 5 = 9.3$

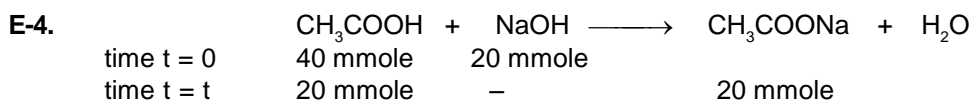
$$\text{pH} = \text{p}K_b + \log \left[\frac{\text{CN}^-}{\text{HCN}} \right]$$

$$9 = 9.3 + \log \left[\frac{5 \times V_{\text{ml}}}{10 \times 2} \right] \quad \Rightarrow \quad -0.3 = \log \left[\frac{V_{\text{ml}}}{4} \right]$$

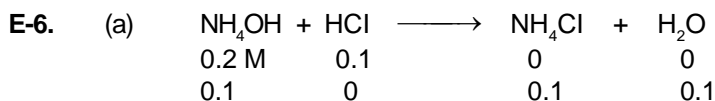
$$0.3 = \log \left[\frac{4}{V_{\text{ml}}} \right] \quad \Rightarrow \quad \frac{4}{V_{\text{ml}}} = 2 \quad \Rightarrow \quad V_{\text{ml}} = 2 \text{ ml}$$



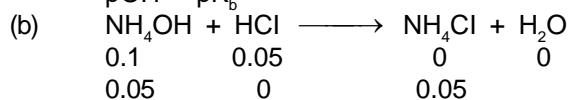
$$\text{pH} = \text{p}K_a + \log \left[\frac{[\text{HCOO}^-]}{[\text{HCOOH}]} \right] = 3.74 + \log \left(\frac{10}{10} \right) \quad \Rightarrow \quad \text{pH} = 3.74$$



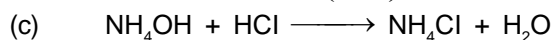
$$\text{pH} = \text{p}K_a + \log \left(\frac{20}{20} \right) \quad \Rightarrow \quad \text{pH} = \text{p}K_a \quad \Rightarrow \quad [\text{H}^+] = K_a = 1.8 \times 10^{-5} \text{ M}$$



$$\text{pOH} = \text{p}K_b$$



$$\text{pOH} = \text{p}K_b + \log \left(\frac{0.05}{0.05} \right) = \text{p}K_b$$



$$\text{pOH} = \text{p}K_b$$

So all solution have same pH

E-9. Maximum buffer capacity of a solution is given by, buffer capacity = $2.303 \left(\frac{ab}{a+b} \right)$. Hence the result.

and $a = b = 0.5$, $\text{BC} = 2.303 \times \frac{(0.5)^2}{1} = 0.57$

E-10. Mole of NaOH is required for 1 lit solution = x
 \therefore Mole of NaOH is required for 100 ml of solution = 0.1 x
 Now, $0.1x = 1 \times V \Rightarrow V = 0.1x \text{ Lt} = 100x \text{ ml}$.

F-4. $\text{p}K_a = 5.45$

$$\text{pH} = \text{p}K_{\text{Hin}} + \log \left[\frac{\text{[Base form]}}{\text{[Acid form]}} \right] \quad \Rightarrow \quad \text{pH} = \text{p}K_{\text{Hin}} = 5.45$$

For a Buffer solution

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \Rightarrow 5.45 = 4.75 + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$0.7 = \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \Rightarrow \frac{5}{1} = \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

F-7. $K_b = \frac{[\text{OH}^-][\text{In}^+]}{[\text{InOH}]}$; The colour is provided when indicator 50% dissociated. Also indicator giving coloured cation in base InOH.

$$\begin{aligned} \therefore [\text{OH}^-] &= K_b = 1 \times 10^{-5} \\ \therefore \text{pOH} &= 5 \\ \therefore \text{pH} &= 9. \end{aligned}$$

F-8. $K_a = \frac{[\text{H}^+][\text{In}^+]}{[\text{HIn}]}$

$$1 \times 10^{-5} = \frac{[\text{H}^+] \times 80}{20} \Rightarrow [\text{H}^+] = \frac{1}{4} \times 10^{-5}$$

$$\therefore \text{pH} = 5.6.$$

G-2. (a) Initially pH will decrease fast, then slowly due to buffer formation and then will decrease fast as buffer action diminishes.

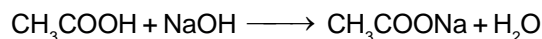
(b) For a weak electrolyte

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

$$\text{when } \alpha \ll 1 \text{ then } \alpha = \sqrt{\frac{K_a}{C}}$$

as C increases \Rightarrow α decreases
as C is tending to zero \Rightarrow α will be unity

(c) At 1/4th neutralisation



$$\left(0.1 \times \frac{3}{4}\right) \qquad \qquad \qquad \left(0.1 \times \frac{1}{4}\right)$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{p}K_a + \log \left(\frac{1}{3}\right)$$

At 3/4th neutralisation

$$\text{pH} = \text{p}K_a + \log 3$$

$$\text{so difference in pH} = \Delta(\text{pH}) = \log 3 - \log \frac{1}{3} = 2 \log 3$$

G-9. Initial decrement is due to consumption of free OH⁻ ions, then slow decrement in pH is due to basic buffer solution and minimum slope will be there when there is best buffer action ([salt] / [base] = 1)

H-2. K_{sp} of Mg(OH)₂ = 2.56×10^{-13}

$$4s_1^3 = 2.56 \times 10^{-13} \Rightarrow s_1 = 4 \times 10^{-5} \text{ M}$$

$$K_{sp} \text{ of Al(OH)}_3 = K_{sp} = 4.32 \times 10^{-34}$$

$$27s_2^4 = 4.32 \times 10^{-34} \Rightarrow s_2 = 2 \times 10^{-9} \text{ M}$$

$$\frac{s_1}{s_2} = \frac{4 \times 10^{-5}}{2 \times 10^{-9}} = 2 \times 10^4$$

H-6. Let K_{sp} of AgCl = x

(a) solubility of AgCl in pure water = $s_1 = \sqrt{x}$ (b) solubility of AgCl in 0.01 M $\text{CaCl}_2 = s_2 = \frac{x}{0.02}$

(c) solubility of AgCl in 0.01 M NaCl = $s_3 = \frac{x}{0.01}$ (d) solubility of AgCl in 0.05 M $\text{AgNO}_3 = s_4 = \frac{x}{0.05}$

So $s_1 > s_3 > s_2 > s_4$

H-8. Solubility of $\text{BaSO}_4 = \sqrt{K_{sp}} = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5} \text{ M}$

\therefore wt. of $\text{BaSO}_4 = 1.05 \times 10^{-5} \times 233 = 244.37 \times 10^{-5} \text{ g/litre.}$

\therefore Volume of water needed to dissolve 1g BaSO_4 is equal to $\frac{1}{244.37 \times 10^{-5}} = 410 \text{ litre}$

H-10. $\text{Ca}_3(\text{PO}_4)_2 + 6\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_3\text{PO}_4$
soluble

I-2. $K_{sp}(\text{BaCrO}_4) = 2.4 \times 10^{-10} \text{ M}^2$
 $[\text{CrO}_4^{2-}] = 6 \times 10^{-4}$ $K_{sp}(\text{BaCrO}_4) = [\text{Ba}^{2+}] [\text{CrO}_4^{2-}] = 2.4 \times 10^{-10}$
 $\Rightarrow [\text{Ba}^{2+}] \times 6 \times 10^{-4} = 2.4 \times 10^{-10}$
 $[\text{Ba}^{2+}] = 4 \times 10^{-7} \text{ M Ans.}$

I-3. $\text{pH} = 4 \Rightarrow [\text{H}^+] = 10^{-4} \text{ M} \Rightarrow [\text{OH}^-] = 10^{-10} \text{ M}$

$\text{Al}(\text{OH})_3 \rightleftharpoons \text{Al}^{3+} + 3 \text{OH}^-$

$K_{sp}(\text{Al}(\text{OH})_3) = [\text{Al}^{3+}] [\text{OH}^-]^3$

$[\text{Al}^{3+}] [\text{OH}^-]^3 = 1 \times 10^{-33}$

$[\text{Al}^{3+}] (10^{-10})^3 = 1 \times 10^{-33} \Rightarrow [\text{Al}^{3+}] = 10^{-3} \text{ M}$

I-7. $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ $\text{AgCNS} \rightleftharpoons \text{Ag}^+ + \text{CNS}^-$
 $(x+y) \quad x$ $(x+y) \quad y$

$\frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgCNS})} = \frac{x}{y} = \frac{[\text{Cl}^-]}{[\text{CNS}^-]}$ So $\frac{[\text{Cl}^-]}{[\text{CNS}^-]} = \frac{x}{y} = \frac{1.8 \times 10^{-10}}{1.6 \times 10^{-11}}$
 $= 1.125 \times 10 = 11.25$

$\Rightarrow \frac{x}{y} = 11.25 \quad x = 11.25 y$

$K_{sp}(\text{AgCl}) = [\text{Ag}^+] [\text{Cl}^-] = (x+y)x = 1.8 \times 10^{-10}$
 $12.25 y \times 11.25 y = 1.8 \times 10^{-10}$

$$y^2 = \frac{1.8 \times 10^{-10}}{12.25 \times 11.25}$$

$$y^2 = \frac{180 \times 10^{-12}}{12.25 \times 11.25}$$

$$y^2 = 1.3 \times 10^{-12}$$

$$y = 1.14 \times 10^{-6}$$

$x = 11.25 \times 1.14 \times 10^{-6} = 12.83 \times 10^{-6}$

$[\text{Ag}^+] = [x+y] = 12.83 \times 10^{-6} + 1.14 \times 10^{-6} = 13.97 \times 10^{-6} = 1.4 \times 10^{-5} \text{ M}$

I-8.* $[\text{Ag}^+] \text{ ion required to precipitate } \text{Cl}^- \text{ ion} = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{10^{-10}}{0.05} = 2 \times 10^{-9} \text{ mol/L.}$

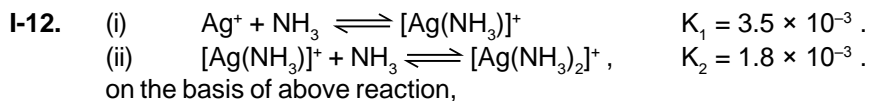
$[\text{Ag}^+] \text{ ion required to precipitate } \text{I}^- \text{ ion} = \frac{K_{sp}}{[\text{I}^-]} = \frac{4 \times 10^{-16}}{0.05} = 8 \times 10^{-15} \text{ mol/L.}$

Since $[\text{Ag}^+]$ ion conc. required to precipitate AgI is less than the $[\text{Ag}^+]$ ion conc. required to precipitate AgCl, AgI precipitates first.

Hence choices (A),(B) and (D) are correct while (C) is incorrect.

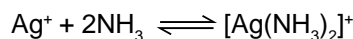
I-10. For precipitation of Ag_2CO_3 . $[\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Ag}^+]^2} = \frac{6.9 \times 10^{-12}}{[10^{-5}]^2} = 6.9 \times 10^{-2}$

and for precipitation of BaCO_3 . $[\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]} = \frac{8.1 \times 10^{-9}}{10^{-4}} = 8.1 \times 10^{-5}$



$$K_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} \quad ; \quad K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}$$

For the formation of



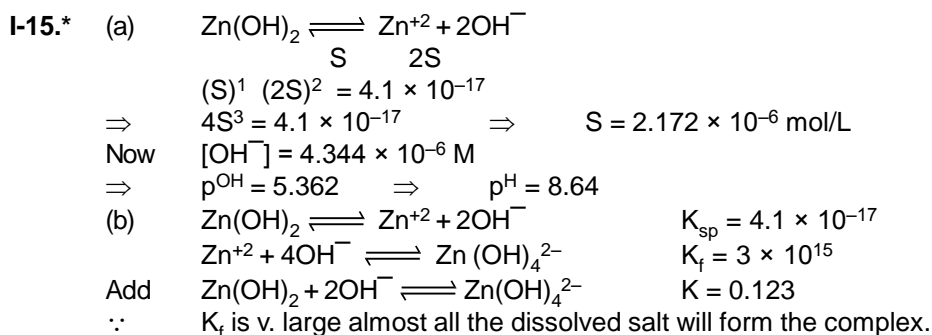
Formation constant

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$K_f = K_1 \times K_2 = 3.5 \times 10^{-3} \times 1.8 \times 10^{-3} = 6.3 \times 10^{-6}$$

I-13.* In AgNO_3 solution, the solubility of AgCN will decrease as compared to pure water because of common ion effect of Ag^+ ion.

In NH_3 solution and buffer of $\text{pH} = 5$, the solubility of AgCN will increase due to complex formation in case of NH_3 solution and hydrolysis of CN^- ions in case of buffer of $\text{pH} = 5$.



Hence $\frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{OH}^-]^2} = 0.123 \Rightarrow \frac{x}{(0.1 - x)^2} = 0.123$ (if x is the solubility)

i.e. $x^2 - 8.33x + 0.01 = 0 \Rightarrow x = 1.2 \times 10^{-3} \text{ mol/L}$

PART - II

4. For SrF_2 in pure water

$$4s_1^3 = K_{\text{sp}}$$

For SrF_2 in 0.1 M NaF solution

$$s_2 (0.1)^2 = K_{\text{sp}} \Rightarrow 4s_1^3 = s_2 (0.01)$$

$$\Rightarrow 4s_1^3 = s_1 \times \frac{256}{10^6} (0.01) \Rightarrow s_1 = 8 \times 10^{-4} \text{ M}$$

$$\therefore K_{\text{sp}} = 4s_1^3 = 2.048 \times 10^{-9}$$

5. $[\text{Sr}^{2+}]_i = 0.0011 = 11 \times 10^{-4} \text{ M}$

$$[\text{Sr}^{2+}]_f = 2 \times 10^{-4} \text{ M}$$

$$\therefore [\text{Sr}^{2+}] \text{ precipitated} = (11 - 2) \times 10^{-4} \text{ M} = 9 \times 10^{-4} \text{ M}$$

$$[\text{F}^-] \text{ needed for this precipitation} = 2 \times 9 \times 10^{-4} = 18 \times 10^{-4} \text{ M}$$

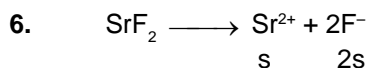
Also, $[\text{Sr}^{2+}]_f [\text{F}^-]_f^2 = K_{\text{sp}} = 2.048 \times 10^{-9}$

But, $[\text{Sr}^{2+}]_f = 2 \times 10^{-4} \text{ M}$

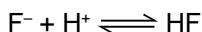
$$\therefore [\text{F}^-]_f = 3.2 \times 10^{-3} \text{ M}$$

$$\therefore \text{Total } [\text{F}^-] \text{ needed} = 3.2 \times 10^{-3} + 18 \times 10^{-4} = 5 \times 10^{-3} \text{ M}$$

$$\therefore \text{NaF needed for 100 ml solution} = \frac{5 \times 10^{-3} \times 42}{10} = 0.021 \text{ g}$$



F^- will react with H^+ to produce HF



$$K = \frac{1}{K_a} = \frac{[\text{HF}]}{[\text{H}^+][\text{F}^-]} = \frac{7}{10^{-5}}$$

$$\therefore [\text{HF}] = 7 \times 10^5 [\text{F}^-] [\text{H}^+] \qquad (\because [\text{H}^+] = 10^{-5}; \text{pH}=5)$$

$$= 7 \times 10^5 [\text{F}^-] \times 10^{-5} = 7 [\text{F}^-]$$

Here $[\text{F}^-] + [\text{HF}] = 2s$

$$\therefore [\text{F}^-] = \frac{s}{4}$$

$$K_{sp} = s \left(\frac{s}{4}\right)^2 = 2.048 \times 10^{-9}$$

$$\therefore s = 3.2 \times 10^{-3} \text{ mol/L}$$

11. (A) $[\text{H}^+]$ in HCl solution = 10^{-5} M

$$[\text{H}^+]$$
 in H_2S solution = $\sqrt{K_a \times C} = 10^{-4}$ M

so $[\text{H}^+]$ in HCl solution < $[\text{H}^+]$ in H_2S solution

& $[\text{OH}^-]$ in HCl solution > $[\text{OH}^-]$ in H_2S solution

& degree of dissociation of water in HCl solution > degree of dissociation of water in H_2S solution

pH of HCl solution > pH of H_2S solution.

(B) At pH = 4.74 in CH_3COOH solution, $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$

$$\therefore \text{degree of dissociation of } \text{CH}_3\text{COOH} = \frac{1}{2}$$

At pH = 9.26 i.e. pOH = 4.74 in NH_4OH solution, $[\text{NH}_4^+] = [\text{NH}_4\text{OH}]$

\therefore degree of dissociation of CH_3COOH = degree of dissociation of NH_4OH

degree of dissociation of water in CH_3COOH solution > degree of dissociation of water in NH_4OH solution.

(C) $[\text{H}^+]$ in CH_3COOH solution = $\sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8} \times 10^{-3}$ M

$$[\text{H}^+]$$
 in HCOOH solution = $\sqrt{1.8 \times 10^{-4} \times 1} = \sqrt{1.8} \times 10^{-2}$ M

so, degree of dissociation of CH_3COOH = degree dissociation of HCOOH.

(D) $[\text{H}^+]$ in HA_1 solution = $\sqrt{10^{-5} \times 0.1} = 10^{-3}$ M

$$[\text{H}^+]$$
 in HA_2 solution = $\sqrt{10^{-6} \times 0.01} = 10^{-4}$ M

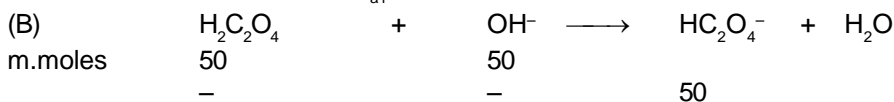
so $[\text{OH}^-]$ in solution of HA_1 < $[\text{OH}^-]$ in solution of HA_2

pH in solution of HA_1 < pH in solution of HA_2

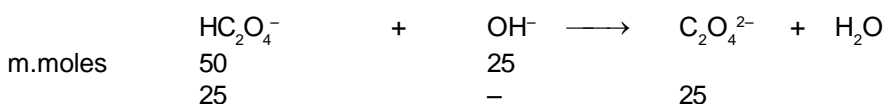
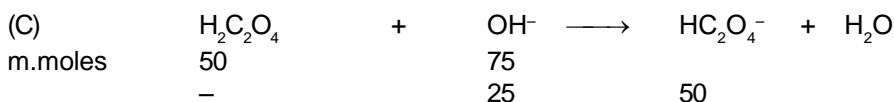
& degree of dissociation of water HA_1 < degree of dissociation of water HA_2 .



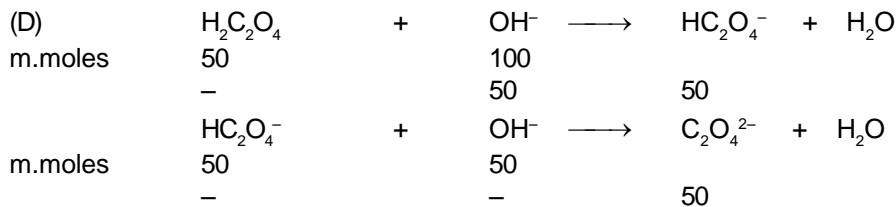
Buffer solution pH = pK_{a1}



$$\text{Amphiprotic, pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} = \frac{13}{2} = 6.5.$$

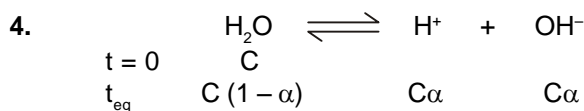


Buffer solution pH = pK_{a2} .



Salt hydrolysis, $\text{pH} > 7$.

EXERCISE # 2



So, $[\text{H}^+] = [\text{OH}^-] = \text{C}\alpha = \frac{1000}{18} \times 3.6 \times 10^{-9}$

∴ $\text{pH} = 7 - \log 2 = 6.7$ and $K_w = [\text{H}^+][\text{OH}^-] = 4 \times 10^{-14}$

6. (i) $[\text{TIOH}] = \frac{2.21}{221 \times 2} = 5.0 \times 10^{-3}$. (mol. wt. TIOH = 221).

∴ $\text{pOH} = \log[\text{OH}^-] = -\log 5.0 \times 10^{-3} = 2.3$;
∴ **pH = 11.7.**

(ii) $[\text{Ca}(\text{OH})_2] = \frac{0.37 \times 1000}{74 \times 500} = 0.01 \text{ M}$.

∴ $[\text{OH}^-] = 2 \times 0.01 \text{ M} = 0.02 \text{ M}$

∴ $\text{pOH} = -\log[\text{OH}^-] = 1.7$;

∴ **pH = 12.3.**

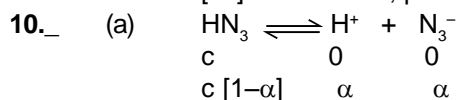
(iii) $[\text{NaOH}] = \frac{0.32 \times 1000}{40 \times 200} = 0.04 \text{ M}$.

∴ $[\text{OH}^-] = 0.04 \text{ M}$; $\text{pOH} = 1.4$;

∴ **pH = 12.6.**

(iv) $[\text{HCl}] \text{ formed} = \frac{1 \times 12}{1000} = 12 \times 10^{-3} \text{ M}$. ($M_1V_1 = M_2V_2$)

∴ $[\text{H}^+] = 12 \times 10^{-3}$; **pH = 1.92.**



$$\frac{c\alpha^2}{1-\alpha} = K_a \quad \because \alpha \ll 1 \quad \therefore \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{2 \times 10^{-5}}{0.1}} = 1.4 \times 10^{-3}$$

$[\text{H}^+] = c\alpha = 1.41 \times 10^{-4}$.

$\text{pH} = 3.85$

$\text{pOH} = 10.15$

(b) $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = 0.141 > 0.1$

α cannot be neglected.

$$\frac{c\alpha^2}{1-\alpha} = K_a$$

$$c\alpha^2 + K_a\alpha - K_a = 0$$

$$\alpha = \frac{-K_a + \sqrt{K_a^2 + 4cK_a}}{2c}$$

$\alpha = 0.13$.

$[\text{H}^+] = c\alpha = 1.3 \times 10^{-2}$.

$$14. \quad C = \frac{1.725}{138} \left(\frac{\alpha^2}{1-\alpha} \right) = 10^{-3}$$

$$12.5 \times 10^{-3} \left(\frac{\alpha^2}{1-\alpha} \right) = 10^{-3}$$

$$\alpha = 0.245$$

$$[H^+] = 12.5 \times 10^{-3} \times 0.245 = 3.07 \times 10^{-3}$$

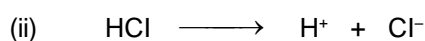
$$pH = 3 - \log 3.07 = \mathbf{2.52}$$

$$15. \quad (i) \quad CH_3COOH = 0.2 \text{ M}$$

$$[H^+] = \sqrt{K_a \times C} = \sqrt{2 \times 10^{-5} \times 0.2} = \sqrt{4 \times 10^{-6}} = 2 \times 10^{-3}$$

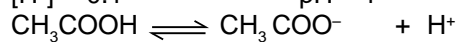
$$pH = 3 - \log 2 = \mathbf{2.7}$$

$$C \alpha = [H^+] \Rightarrow \alpha = \frac{2 \times 10^{-3}}{2 \times 10^{-1}} \Rightarrow \alpha = \mathbf{0.01}$$



$$0.1 \qquad \qquad 0.1 \qquad 0.1$$

$$[H^+] = 0.1 \qquad \qquad pH = 1$$



$$0.2 \qquad \qquad 0 \qquad 0.1$$

$$0.2(1-\alpha) \qquad \qquad 0.2\alpha \qquad 0.1 + 0.2\alpha = 0.1$$

$$K_a = \frac{0.2\alpha \times 0.1}{0.2} = 2 \times 10^{-5} \qquad \qquad \alpha = 2 \times 10^{-4}$$

$$(iii) \quad [CH_3COO^-] = 0.2 \times 2 \times 10^{-4} = \mathbf{4 \times 10^{-5}}$$

$$(iv) \quad \% \text{ change in } \alpha = \frac{1 \times 10^{-2} - 2 \times 10^{-4}}{1 \times 10^{-2}} \times 100 = \left[1 - \frac{2}{100} \right] \times 100 = \mathbf{98 \%}$$

$$21. \quad C_5H_5NH^+ Cl^- \qquad \text{It is salt of SAWB}$$

$$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C \quad \Rightarrow \quad pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log 0.25$$

$$\Rightarrow \quad pK_b = 9.1$$

$$K_b = \text{Antilog}(-9.1) = 8 \times 10^{-10}$$

$$24. \quad (a) \quad \text{We have } pH = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore \quad pH = -\log 1.8 \times 10^{-5} + \log \frac{4.1 \times 60}{82 \times 4} = 4.74 + \log \frac{3}{4} = \mathbf{4.62}$$

$$(b) \quad pOH = -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

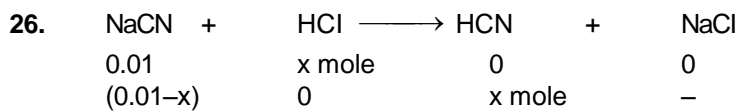
$$\therefore \quad pOH = -\log 1.8 \times 10^{-5} + \log \frac{2.5}{0.5} = 4.74 + \log 5 = 5.43$$

$$\therefore \quad pH = 14 - pOH = \mathbf{8.57}$$

$$(c) \quad pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Base}]} = -\log 1.8 \times 10^{-4} + \log \frac{0.4}{0.25} = 4.74 + \log \frac{8}{5} = \mathbf{4.94}$$

$$25. \quad pH = pK_a + \log \left[\frac{50 \times C}{50 \times 0.2} \right] \quad \Rightarrow \quad 4 = 5 + \log \frac{50 \times C}{50 \times 0.2}$$

$$\Rightarrow \quad \log \frac{C}{0.2} = -1 \quad \Rightarrow \quad \frac{C}{0.2} = 0.1 \quad \Rightarrow \quad C = \mathbf{0.02 \text{ M}}$$

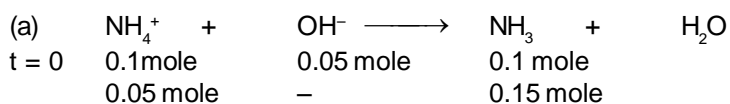


$$\text{pH} = \text{pK}_a + \log \left[\frac{0.01-x}{x} \right] \Rightarrow 8.5 = 9.4 + \log \frac{0.01-x}{x}$$

$$\Rightarrow \log \left(\frac{x}{0.01-x} \right) = 0.9 \Rightarrow \frac{x}{0.01-x} = 8 \Rightarrow x = 8.9 \times 10^{-3} \text{ mole}$$

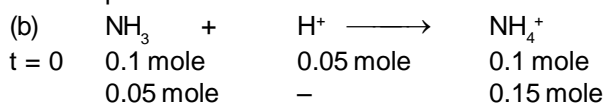
28. $\text{pOH} = 4.74 + \log \frac{0.1}{0.1} = 4.74$

$\therefore \text{pH} = 9.26$



$$\text{pOH} = 4.74 + \log \frac{0.05}{0.15} = 4.26$$

$\therefore \text{pH} = 9.74$



$$\text{pOH} = 4.74 + \log \frac{0.15}{0.05} = 5.22$$

$\therefore \text{pH} = 8.78$

29. A buffer solution show best buffering action when the pH of solution is near to K_a of acid component of buffer solution

There for the above buffer can be best prepared by taking H_2PO_4^- and HPO_4^{2-}

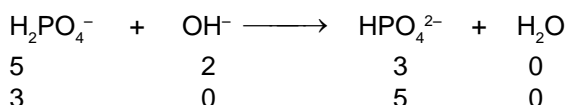
(a) $\text{pH} = \text{pK}_{a2} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 7$

$$\Rightarrow \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = -0.22 \Rightarrow \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.6$$

(b) In 50 ml buffer solution

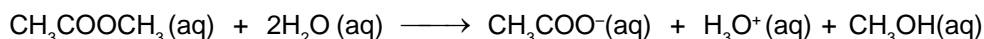
$$[\text{H}_2\text{PO}_4^-] = 0.1 \text{ M} = 5 \text{ milimole}, \quad [\text{HPO}_4^{2-}] = 0.06 = 3 \text{ milimole}$$

$$\text{milimole of NaOH added} = 20 \times 0.01 = 2$$



$$\text{pH} = \text{pK}_{a2} + \log \left(\frac{5}{3} \right) = 7.44.$$

30. $\text{K}_b(\text{NH}_3) = 1.8 \times 10^{-5}$

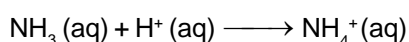


$$[\text{NH}_4^+]_0 = 0.1 \text{ M}, [\text{NH}_3] = 0.06 \text{ M}, [\text{CH}_3\text{COOCH}_3]_0 = 0.02 \text{ M}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.74 + \log \left(\frac{0.1}{0.06} \right)$$

$$(\text{pOH})_{\text{initial}} = 4.74 + 0.22 = 4.96$$

$$\therefore (\text{pH})_{\text{initial}} = 9.04$$



0.06	0.02	0.1	mole
0.04	-	0.12	mole

$$(\text{pOH})_{\text{final}} = 4.74 + \log \frac{0.12}{0.04} = 4.74 + \log \left(\frac{0.12}{0.04} \right) = 4.74 + \log 3 = 4.74 + 0.48 = 5.22$$

$$\therefore (\text{pH})_{\text{final}} = 8.78$$

$$\Delta\text{pH} = 9.04 - 8.78 = 0.26$$

Yes this is satisfactory buffer.

33. For this indicator, $\text{pH} = \text{pK}_{\text{in}} = 2$
Now, at $[\text{H}^+] = 4 \times 10^{-3} \text{ M}$,

$$K_{\text{in}} = \frac{(4 \times 10^{-3})[\text{In}^-]}{[\text{HIn}]} \Rightarrow \frac{[\text{HIn}]}{[\text{In}^-]} = 0.4$$

$$\therefore \% \text{ of HIn} = \frac{[\text{HIn}]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{0.4}{1.4} \times 100 = 28.57 \%$$

37. $\text{NH}_4\text{OH} + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}$
Milimole $\begin{array}{cccc} & 2.25 & 2.25 & 2.25 \end{array}$
at mid point

$$\text{Milimole} = N_1 \times V_{\text{HCl}} = 2.25 \quad V_{\text{HCl}} = \frac{2.25}{0.1} = 22.5$$

$$[\text{NH}_4\text{Cl}] = \left[\frac{2.25}{37.5} \right] = 0.06\text{M} \quad \text{and} \quad \text{pK}_{\text{b}} = 5 - \log 1.8 = 4.74$$

$$\therefore \text{pH} = 7 - \frac{1}{2} \text{pK}_{\text{b}} - \frac{1}{2} \log C = 7 - \frac{4.74}{2} - \frac{1}{2} \log 0.06 = 5.24$$

38. $\text{HCOOH} + \text{OH}^- \longrightarrow \text{HCOO}^- + \text{H}_2\text{O}$
 $t = 0$ $\begin{array}{cccc} 20 \text{ mmol} & 10 \text{ mmol} & & \\ 10 & 0 & 10 & \end{array}$
 $\text{pH} = \text{pK}_{\text{a}} = 3.7$

$$\text{At end point } [\text{HCOONa}] = \left[\frac{20}{40} \right] = \frac{1}{2} \text{ M}$$

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_{\text{a}} + \frac{1}{2} \log 1/2 = 7 + \frac{3.7}{2} - \frac{1}{2} \times 0.30 = 8.7$$

40. (a) At eq. point
No. of milieq. of Base = No. of milieq. of HCl

$$\frac{0.252 \times 1000}{\text{Molarmass}} = 0.14 \times 40$$

\therefore Molar mass of base = 45



$$t = 0 \quad \begin{array}{cccc} 5.6 & 0.14 \times 20 & & \\ 5.6 & 2.8 & 0 & 0 \\ 2.8 & 0 & 2.8 & \end{array}$$

Basic buffer

$$\text{pH} = 10.7 \quad \text{So } \text{pOH} = 3.3$$

$$\text{pOH} = \text{pK}_{\text{b}} = 3.3$$

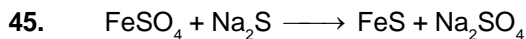
$$K_{\text{b}} = \text{Anti log } (-3.3) = \text{Anti log } (1 - 0.3) \times 10^{-4} = 5 \times 10^{-4}$$

44. Let V ml of each is mixed.

$$[\text{Cu}^{2+}] = \frac{0.002 \times V}{2V} = 0.001 \quad \text{and} \quad [\text{IO}_3^-] = \frac{0.002 \times V}{2V} = 0.001$$

$$K_{\text{sp}} = (0.001) (0.001)^2 = 10^{-3} \times 10^{-6} = 10^{-9}$$

$K_{\text{IP}} < K_{\text{sp}} \longrightarrow \text{NO PPT formation}$

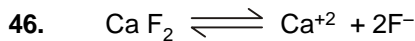


a a

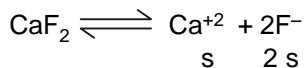
$$K_{\text{sp}} = \left[\frac{a}{2} \right] \left[\frac{a}{2} \right] = 6.25 \times 10^{-18}$$

$$a^2 = 4 \times 6.25 \times 10^{-18} = 4 \times 625 \times 10^{-20}$$

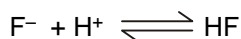
$$a = 2 \times 25 \times 10^{-10} = \mathbf{5 \times 10^{-9} \text{ M}}$$



Let Solubility is s mole/lit



The F^- react with H^+ to produce HF



$$K_1 = \frac{1}{K_a} = \frac{[\text{HF}]}{[\text{F}^-][\text{H}^+]} \Rightarrow [\text{HF}] = \frac{[\text{F}^-][\text{H}^+]}{K_a} = \frac{[\text{F}^-][\text{H}^+]}{3.45 \times 10^{-4}}$$

$$[\text{HF}] = 2.9 \times 10^3 [\text{F}^-][\text{H}^+]$$

(A) at pH = 7 $[\text{HF}] = 2.9 \times 10^{-4} [\text{F}^-]$

But the solution contain $[\text{HF} + \text{F}^-] = 2 [\text{Ca}^{+2}]$

$$[2.9 \times 10^{-4} + 1] [\text{F}^-] = 2s \quad [\text{F}^-] = 2s$$

$$K_{\text{sp}} = 4s^3 = 0.4 \times 10^{-11} \quad s = (10 \times 10^{-12})^{1/3} = 2.15 \times 10^{-4}$$

(b) At pH = s

$$[\text{HF}] = 2.9 \times 10^3 [\text{F}^-] \times 10^{-5} = 2.9 \times 10^{-2} [\text{F}^-]$$

$$[\text{F}^-] + \text{HF} = 2s \Rightarrow [\text{F}^-] + 0.029 [\text{F}^-] = 2s$$

$$[\text{F}^-] [1.029] = 2s \Rightarrow [\text{F}^-] = \left(\frac{1}{1.029} \right) \times 2s$$

$$K_{\text{sp}} = 4s^3 \left(\frac{1}{1.029} \right)^2 = 4 \times 10^{-11} \Rightarrow s^3 = (1.29)^2 \times 10^{-11}$$

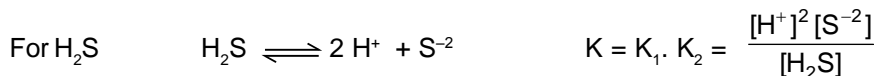
$$s = (10.6 \times 10^{-12})^{1/3} = 2.2 \times 10^{-4}$$

48. concentration of $\text{H}_2\text{S} = 0.1 \text{ M}$
So concentration of $\text{M}^{+2} = 0.05$

concentration of $\text{MBr}_2 = 0.05 \text{ M}$
 K_{sp} of (MS) = $[\text{M}^{+2}] [\text{S}^{-2}] = 6 \times 10^{-21}$

$$[\text{S}^{2-}] = \frac{100 \times 6 \times 10^{-21}}{5} = 120 \times 10^{-21} = 1.2 \times 10^{-19} \text{ M}$$

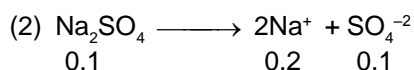
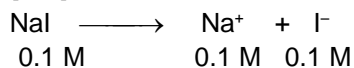
Precipitation of MS will start when H_2S provide $1.2 \times 10^{-19} \text{ M}$ ion of S^{-2}



$$10^{-7} \times 1.2 \times 10^{-19} = \frac{[\text{H}^+]^2 \times 1.2 \times 10^{-19}}{0.1} \quad [\text{H}^+]^2 = 10^{-2}$$

So $[\text{H}^+] = 0.1 \text{ M}$ $\therefore \text{pH} = 1$

49. (1) $[\text{NaI}] = 0.1 \text{ M}$



For precipitation of PbI_2

$$K_{\text{sp}} (\text{PbI}_2) = [\text{Pb}^{+2}] [\text{I}^-]^2 = 9 \times 10^{-9} \Rightarrow [\text{Pb}^{+2}] \times (0.1)^2 = 9 \times 10^{-9}$$

$$\Rightarrow [\text{Pb}^{+2}] = 9 \times 10^{-7}$$

For Precipitation of PbSO_4

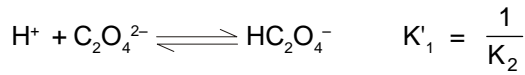
$$K_{\text{sp}} (\text{PbSO}_4) = [\text{Pb}^{+2}] [\text{SO}_4^{-2}] = 1.8 \times 10^{-8} \Rightarrow [\text{Pb}^{+2}] \times 0.1 = 1.8 \times 10^{-8}$$

$$\Rightarrow [\text{Pb}^{+2}] = 1.8 \times 10^{-7}$$

For Precipitation of PbSO_4 required conc. of Pb^{+2} is less **So PbSO_4 is Precipitate first.**

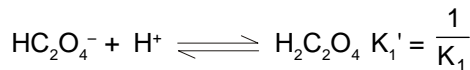
where PbI_2 (more soluble compound) start precipitating conc of $[\text{Pb}^{2+}] = 9 \times 10^{-7}$
 conc. of anion of less soluble salt
 $K_{sp}(\text{PbSO}_4) = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.8 \times 10^{-8} = (9 \times 10^{-7})[\text{SO}_4^{2-}] = 1.8 \times 10^{-8}$
 $[\text{SO}_4^{2-}] = \mathbf{0.02 \text{ M}}$

50. Let solubility of CaC_2O_4 is s mole/lit
 $\text{CaC}_2\text{O}_4 (s) \rightleftharpoons \underset{s}{\text{Ca}^{2+}} (aq) + \underset{s}{\text{C}_2\text{O}_4^{2-}} (aq)$
 $\text{C}_2\text{O}_4^{2-}$ react with H^+ to produce HC_2O_4^- & $\text{H}_2\text{C}_2\text{O}_4$



$$\frac{1}{K_2} = \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]} \Rightarrow [\text{HC}_2\text{O}_4^-] = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{K_2}$$

Again this HC_2O_4^- react with H^+ as.



$$\frac{1}{K_1} = \frac{[\text{H}_2\text{C}_2\text{O}_4]}{[\text{HC}_2\text{O}_4^-][\text{H}^+]} \Rightarrow [\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{HC}_2\text{O}_4^-][\text{H}^+]}{K_1}$$

Putting the value of $[\text{HC}_2\text{O}_4^-] \Rightarrow [\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}^+]^2 [\text{C}_2\text{O}_4^{2-}]}{K_1 K_2}$

Now $[\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] = s$

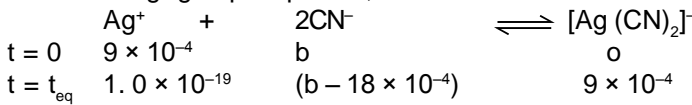
$$[\text{C}_2\text{O}_4^{2-}] \left[1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right] = s \quad ; \quad [\text{C}_2\text{O}_4^{2-}] \left[1 + \frac{10^{-4}}{5 \times 10^{-5}} + \frac{10^{-8}}{25 \times 10^{-7}} \right] = s$$

$$[\text{C}_2\text{O}_4^{2-}] = \left(\frac{s}{3} \right) \Rightarrow K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.7 \times 10^{-9}$$

$$\frac{s^2}{3} = 2.7 \times 10^{-9} \Rightarrow s = \mathbf{9 \times 10^{-5} \text{ M}}$$

52. $K_a[(\text{Ag}(\text{CN})_2)^-] = 1 \times 10^{-21}$ $K_f[\text{Ag}(\text{CN})_2^-] = 1 \times 10^{21}$
 Initial $[\text{Ag}^+]_i = 9 \times 10^{-4} \text{ M}$ $[\text{Ag}^+]_f = 1 \times 10^{-19} \text{ M}$

Almost all Ag^+ get precipitated,

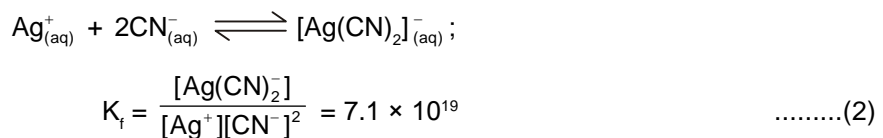


$$K_f = \frac{9 \times 10^{-4}}{(1 \times 10^{-19})(b - 18 \times 10^{-4})^2} = 1 \times 10^{21}$$

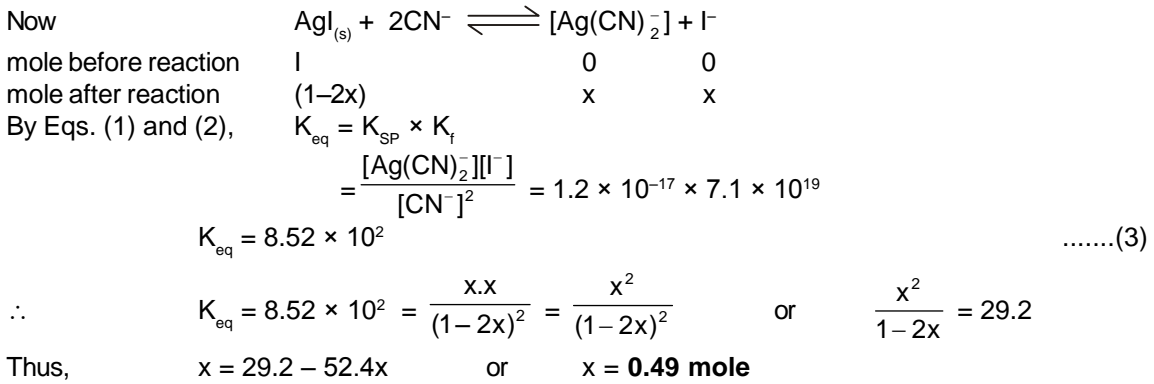
$$\Rightarrow b = 4.8 \times 10^{-3}$$

So Amount of CN^- added = $\mathbf{4.8 \times 10^{-3} \text{ mole}}$

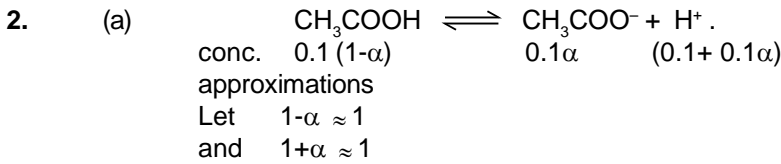
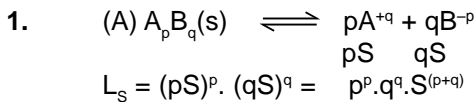
54. Given,



Let x mole of AgI be dissolved in CN⁻ solution then,



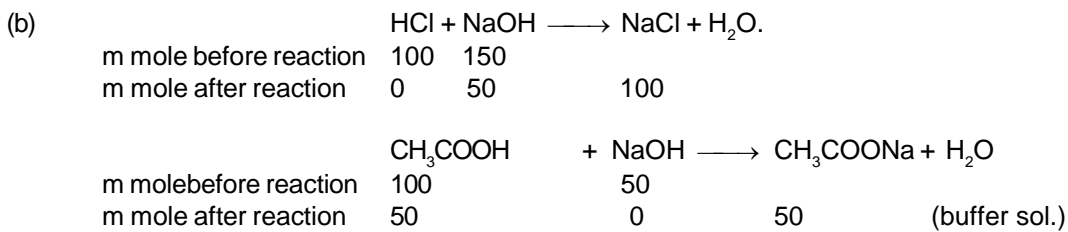
EXERCISE # 3



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

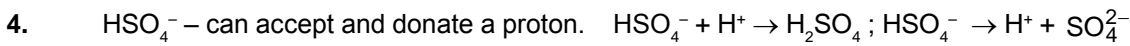
or $1.75 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^-] \times 0.1}{0.1}$

or $[\text{CH}_3\text{COO}^-] = 1.75 \times 10^{-5}$.	;	or $C\alpha = 1.75 \times 10^{-5}$.
or $0.1 \alpha = 1.75 \times 10^{-5}$.	;	or $\alpha = 1.75 \times 10^{-4}$.
or $\alpha = 0.0175\%$.		
or $\text{pH} = -\log[\text{H}^+] = -\log(0.1)$.	;	or pH = 1 .



$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = -\log(1.75 \times 10^{-5}) = 4.757 \text{ Ans.}$$

3. Solution is acidic in nature but not a buffer solution.

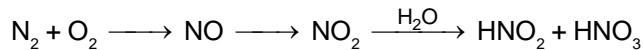


6. At 25°C, Ionic product of water (K_w)
= 1×10^{-14} , So $\text{p}K_w = 14$
 $\therefore [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$
or $-\log [\text{H}^+] - \log [\text{OH}^-] = 14$
 $\text{pH} + \text{pOH} = 14$
It is neutral compound, so in it $\text{pH} = \text{pOH} = 7$ at 25°C. On decreasing the temperature, K_w decreases, so $\text{p}K_w$ increases. Hence at 4°C $\text{p}K_w$ is higher than 25°C and at higher $\text{p}K_w$, pH will be higher i.e., at 4°C pH of water is higher than 7.

7. Lesser the K_{sp} , more is the precipitation.
8. $AB_2 \rightleftharpoons A^{2+} + 2B^-$ $s = 1.0 \times 10^{-5} \text{ mol L}^{-1}$
 $K_{sp} = [A^{2+}][B^-]^2 = 1.0 \times 10^{-5} \times (2.0 \times 10^{-5})^2 = 4.0 \times 10^{-15}$

9. We know for acids, pH must be less than 7.

10. When rain is accompanied by a thunderstorm,



11. $NaX + H_2O \rightleftharpoons NaOH + HX$

In it HX is weak acid, so NaX is a salt of weak acid and strong base.

$$\therefore \text{Hydrolysis constant of NaX is } K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}} = 1 \times 10^{-9}$$

For this type of salt $K_h = Ch^2$

C = molar concentration

h = degree of hydrolysis

$$\therefore 1 \times 10^{-9} = 0.1 \times h^2$$

$$\text{or } h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8} \quad h = 1 \times 10^{-4}$$

$$\therefore \text{percentage hydrolysis of NaX salt} = 1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01 \%$$

12. $HA + OH^- \longrightarrow A^- + H_2O$

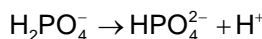
0.1 V	0.1 V		0.1 V	
-	-		-	

m. moles

$$[A^-] = \frac{0.1V}{2V} = \frac{0.1}{2} M,$$

$$pH = 7 + \frac{1}{2} (pK_a + \log c) = 7 + \frac{1}{2} (6 - \log 5.6) + \frac{1}{2} \log \left(\frac{0.1}{2} \right) \approx 9$$

13. Congugate base is formed by the removal of H⁺ from acid



14. $MX_4 (\text{solid}) \rightleftharpoons M^{4+} (\text{aq}) + 4X^- (\text{aq})$ Solubility product, $K_{sp} = s \times (4s)^4 = 256 s^5$

$$\therefore s = \left(\frac{K_{ps}}{256} \right)^{1/5}$$

15. $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$

Initial moles	0.1	0.08	
moles after reaction	0.02	0	0.08 mole in 1 lt

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

$$\text{or, } 5 \times 10^{-4} = \frac{[OH^-] \times 0.08}{0.02}$$

$$\text{or, } [OH^-] = \frac{5}{4} \times 10^{-4}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]}$$

$$\text{or, } [H^+] = \frac{10^{-14} \times 4}{5 \times 10^{-4}} = 8 \times 10^{-11} \text{ M.}$$

16. Conjugate base of OH⁻ $OH^- \rightleftharpoons O^{2-} + H^+$

17. $MX_{2(s)} \rightleftharpoons M^{2+} (\text{aq}) + 2X^- (\text{aq})$

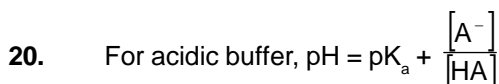
$$K_{sp} = s \cdot (2s)^2 = 4s^3 \Rightarrow 4 \times 10^{-12} = 4s^3 \Rightarrow s^3 = 1 \times 10^{-12}$$

$$\Rightarrow s = 1 \times 10^{-4} \text{ M} \Rightarrow [M^{2+}] = 1 \times 10^{-4} \text{ M}$$

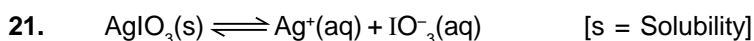
18. $pH = -\log[H^+] \Rightarrow [H^+] = \text{antilog}(-pH) = \text{antilog}(-5.4) = 3.98 \times 10^{-6}$



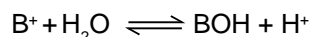
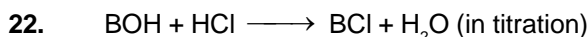
$$K = \frac{[H^+]^2 [A^{2-}]}{[H_2A]} = K_1 \times K_2 = 1 \times 10^{-5} \times 5 \times 10^{-10}$$



when the acid is 50% ionised, $[A^-] = [HA]$ or $pH = pK_a + \log 1$ or $pH = pK_a$
 given $pK_a = 4.5$ $\therefore pH = 4.5$ $\therefore pOH = 14 - 4.5 = 9.5$



$K_{sp} = s^2$
 or $s = 1.0 \times 10^{-4} \text{ mol/lit} = 1.0 \times 10^{-4} \times 283 \text{ g/lit} = 2.83 \times 10^{-3} \text{ gm/100 ml}$



For titration

$$N_{acid} V_{acid} = N_{base} V_{base}$$

$$\frac{2}{15} \times V = 2.5 \times \frac{2}{5}$$

$$V = 3 \times 2.5 = 7.5 \text{ mL}$$

In resulting solution

$$[B^+] = \frac{\frac{2}{5} \times 2.5}{10} = \frac{2}{20} = 0.1$$

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

or $K_h = \frac{0.1 h^2}{(1-h)} = 10^{-2}$ (solve quadratic equation to get 'h', as we can't write $1-h \approx 1$ since h is > 0.1)

or $h = 0.27$

$$[H^+] = 0.1 \times 0.27 = 2.7 \times 10^{-2}$$

23.

MX

$$s_1^2 = 4 \times 10^{-8}$$

$$s_1 = 2 \times 10^{-4}$$

MX_2

$$4s_2^3 = 3.2 \times 10^{-14}$$

$$s_2^3 = 8 \times 10^{-15}$$

$$s_2 = 2 \times 10^{-5}$$

M_3X

$$27s_3^4 = 2.7 \times 10^{-15}$$

$$s_3^4 = 10^{-16}$$

$$s_3 = 10^{-4}$$

$$\Rightarrow s_1 > s_3 > s_2$$

$$\Rightarrow MX > M_3X > MX_2$$

24. $pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b = 7 + \frac{4.8}{2} - \frac{4.78}{2} = 7.01$

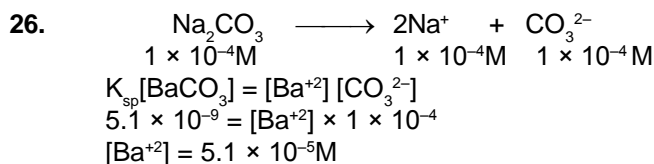
25.

Given $K_a = 10^{-4}$

$$pK_a = 4$$

$$C = 0.01 \text{ M}$$

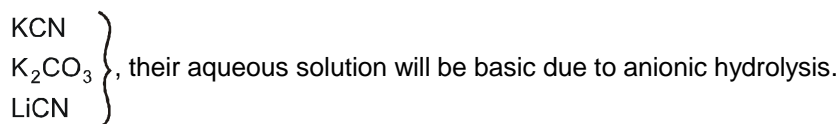
$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \frac{1}{2} (4) + \frac{1}{2} (-2) = 8 \quad \text{Ans.}$$



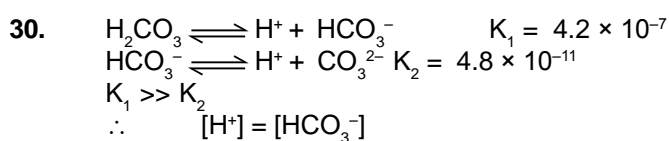
- 27.* (C) $\text{HNO}_3 + \text{CH}_3\text{COONa}$ mixture can act as buffer solution if volume of HNO_3 solution taken is lesser than volume of CH_3COONa solution because of following reaction :

$$\text{CH}_3\text{COONa} + \text{HNO}_3 \longrightarrow \text{CH}_3\text{COOH} + \text{NaNO}_3$$
(D) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ - mixture will act as buffer.

28. Basic solutions will convert red litmus blue.



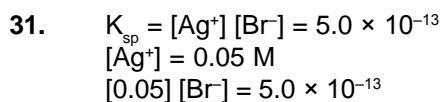
29. In IInd equation H_2PO_4^- give H^+ ion to the H_2O therefore in the IInd equation it act as an acid.



$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

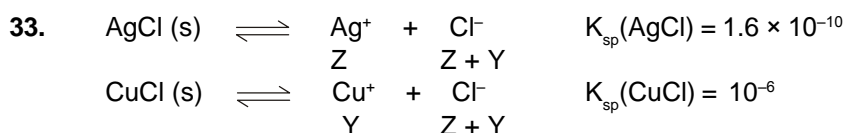
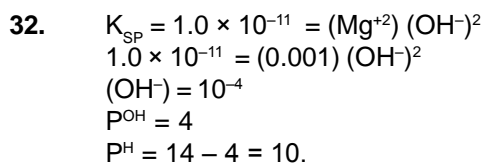
but $[\text{H}^+] = [\text{HCO}_3^-]$

$$[\text{CO}_3^{2-}] = K_2 = 4.8 \times 10^{-11}$$



$$[\text{Br}^-] = \frac{5.0 \times 10^{-13}}{0.05} = 1 \times 10^{-11} \text{ M}$$

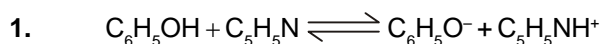
moles of KBr = $M \times V = 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$
weight of KBr = $1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9} \text{ g}$



$$\begin{aligned} Z(Z+Y) &= 1.6 \times 10^{-10} \\ Y(Z+Y) &= 10^{-6} \\ \Rightarrow (Z+Y)^2 &= 1.6 \times 10^{-10} + 10^{-6} & \Rightarrow (Z+Y)^2 &\approx 10^{-6} \\ \Rightarrow Z+Y &= 10^{-3} & \Rightarrow Z(Z+Y) &= 1.6 \times 10^{-10} \\ \Rightarrow Z \times 10^{-3} &= 1.6 \times 10^{-10} & \Rightarrow Z &= 1.6 \times 10^{-7} \\ \Rightarrow 1.6 \times 10^{-x} &= 1.6 \times 10^{-7} \\ \Rightarrow x &= 7 \end{aligned}$$

34. O^{2-} (base) + H_2O (acid) $\longrightarrow \text{OH}^-$ (C.B) + OH^- (C.A.)
 O^{2-} acts as Lewis base.

SOLUTION OF ADVANCED LEVEL PROBLEM



$$K_n = \frac{K_a K_b}{K_w} = 2.34 \times 10^{-5}$$

K_n being small and thus neutralisation does not proceed very far towards completion.

2. Since $[H^+] = \sqrt{K_w}$, therefore

$$pH = -\log [H^+] = -\frac{1}{2} \log K_w$$

Thus, the calculated values of pH at the given temperatures are as follows.

Temperature	pH
0°C	$-\frac{1}{2} \log (0.114 \times 10^{-14}) = 7.472$
10°C	$-\frac{1}{2} \log (0.292 \times 10^{-14}) = 7.267$
25°C	$-\frac{1}{2} \log (1.008 \times 10^{-14}) = 7.002$
40°C	$-\frac{1}{2} \log (2.919 \times 10^{-14}) = 6.767$
50°C	$-\frac{1}{2} \log (5.474 \times 10^{-14}) = 6.631$

3. For a solution to have twice alkalinity, we have

$$[OH^-] = 2.0 \times 10^{-7} \text{ M}$$

Thus, $pOH = -\log \{[OH^-]/M\} = -\log (2.0 \times 10^{-7}) = 7 - 0.301 = 6.699$

and hence $pH = 14 - pOH = 7.301$

4. (a) meq. of H^+ = $10 \times 0.1 + 40 \times 0.2 \times 2 = 17$.

$$[H^+] = \frac{17}{50} = 0.34.$$

$$pH = 0.47$$

$$(b) [H^+] = \frac{10 - 9.9}{109.9} = \frac{0.1}{109.9} = 9.1 \times 10^{-4}$$

$$pH = 4.0 - \log 9.1 = 3.04$$

$$(c) pV = nRT$$

$$n = \frac{(740 - 23.7)}{760} \times 100 \times \frac{1}{0.0821 \times 298} \times 10^{-3} = 3.85 \times 10^{-3} \text{ M}$$

$$[HCl] = 3.85 \times 10^{-3} \text{ M} = [H^+].$$

$$pH = 3 - \log 3.85 = 2.41$$

(d) pH of Final Solution = 1

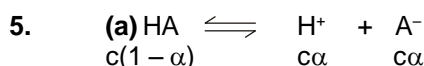
$$pH = 1$$

$$[H^+] = 10^{-1}$$

$$\text{Initial} \rightarrow M = \frac{P \times d \times 10}{\text{M.W.}} = \frac{36.5 \times 10 \times 1.25}{36.5} \quad M = 12.5$$

$$N_1 V_1 = N_2 V_2 \quad \Rightarrow 12.5 \times V_1 = 10^{-1} \times 2.5$$

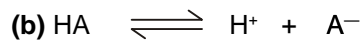
$$V_1 = \frac{2.5}{125} \quad V_1 = .02 \text{ lit} \quad = 20 \text{ ml}$$



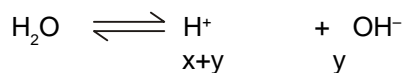
$$pH = pK_a + \log \frac{[A^-]}{[HA]} = pK_a + \log \frac{c\alpha}{c(1 - \alpha)}$$

$$\Rightarrow \text{pH} = \text{p}K_a + \log \left(\frac{\alpha}{1-\alpha} \right) = \text{p}K_a - \log \left(\frac{1-\alpha}{\alpha} \right)$$

$$\Rightarrow \log \left(\frac{1-\alpha}{\alpha} \right) = \text{p}K_a - \text{pH} \quad \Rightarrow \quad \left(\frac{1-\alpha}{\alpha} \right) = 10^{(\text{p}K_a - \text{pH})} \quad \Rightarrow \quad \alpha = \frac{1}{1 + 10^{(\text{p}K_a - \text{pH})}}$$



$$C_0 - x \qquad \qquad x+y \qquad \qquad x$$



$$x+y \qquad \qquad y$$

$$K_a = \frac{[\text{H}^+]x}{C_0 - x}, \quad [\text{H}^+]y = 10^{-14} = K_w \quad \text{Where } [\text{H}^+] = x + y.$$

$$y = \frac{K_w}{[\text{H}^+]}, \quad x = \frac{K_a C_0}{K_a + [\text{H}^]}.$$

$$[\text{H}^+] = x + y = \frac{K_w}{[\text{H}^]} + \frac{K_a C_0}{K_a + [\text{H}^]}.$$

$$10^{-3} = 10^{-11} + \frac{0.1 K_a}{K_a + 10^{-3}}$$

$$K_a + 10^{-3} = 100 K_a$$

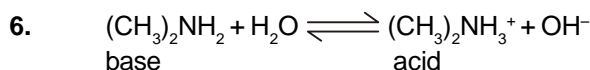
$$K_a = \frac{10^{-3}}{99} \approx 10^{-5}.$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{C^2 \alpha^2}{C(1-\alpha)}$$

$$\text{with in an error of 10\% } \begin{matrix} C(1-\alpha) \\ \text{or} \\ C\alpha = 0.10 C. \end{matrix} \quad \text{or} \quad C - C\alpha = 0.90 C.$$

$$K_a = \frac{(0.10C)^2}{0.90C} = \frac{C}{90} \quad \text{or} \quad C = 90 K_a.$$



base

acid

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_3^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}_2]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

$$5.4 \times 10^{-4} = 0.02 \times \alpha^2.$$

$$\therefore \alpha = 0.164.$$

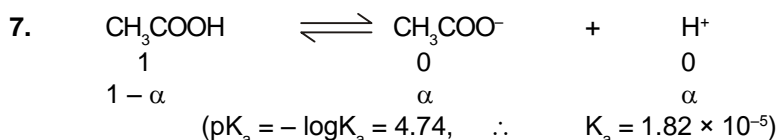
$$\text{Since } \alpha > 0.1, \text{ we will use } K_b = \frac{c\alpha^2}{(1-\alpha)} \quad \text{or} \quad 5.4 \times 10^{-4} = \frac{0.02 \times \alpha^2}{(1-\alpha)}$$

$$\text{Now } \alpha = 0.151$$

In presence of NaOH, the dissociation of diethylamine will decrease due to common ion effect. Thus $0.1 + c\alpha = 0.1 + c\alpha \approx 1$ and $0.1 \& (1-\alpha) \approx 1$

$$\text{Thus } K_b = 5.4 \times 10^{-4} = \frac{c\alpha \times (0.1 + c\alpha)}{c(1-\alpha)} = \alpha \times 0.1.$$

$$\text{or } \alpha = 5.4 \times 10^{-3} = \mathbf{0.0054}.$$



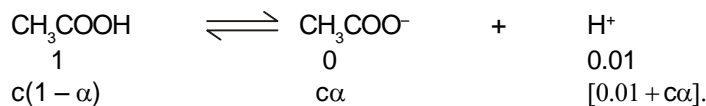
$$K_a = \frac{c\alpha^2}{(1-\alpha)} = c\alpha^2 \quad (1-\alpha \approx 1).$$

$$\therefore \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = \mathbf{0.019 \text{ or } 1.9\%}.$$

Always calculate a first by $K_b = c\alpha^2$, if $\alpha > 10\%$ then use again.

$$K = \frac{c\alpha^2}{(1-\alpha)}$$

(a) If H^+ are already present (due to HCl)



$$K_b = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha \times (0.01 + c\alpha)}{c(1-\alpha)}$$

Since presence of H^+ will favour the reverse reaction or α will decrease.

i.e., $0.01 + c\alpha = 0.01$ and $1 - \alpha = 1$ (due to common ion effect).

$$\therefore 1.82 \times 10^{-5} = \frac{0.05 \times \alpha \times 0.01}{0.05}.$$

$$\therefore \alpha = 1.82 \times 10^{-3} = \mathbf{0.0018}.$$

(b) Similarly solve for 0.1 M HCl

$$\alpha = \mathbf{0.00018}.$$

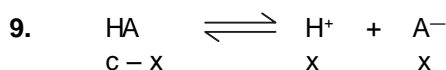
8. $K_a = \frac{C\alpha^2}{1-\alpha}$

$$40\alpha^2 + \alpha - 1 = 0$$

$$\alpha = 0.146$$

$$[H^+] = C\alpha = 1.75 \times 10^{-3} \text{ M}$$

$$\text{pH} = \mathbf{2.76}$$

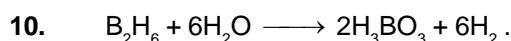


$$[H^+] = x = 1.5 \times 10^{-3} \text{ M}$$

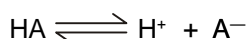
$$K_a = \frac{x^2}{c-x}$$

$$2.5 \times 10^{-3} = \frac{(1.5 \times 10^{-3})^2}{c - 1.5 \times 10^{-3}}.$$

$$c = \mathbf{2.4 \times 10^{-3} \text{ M}}.$$



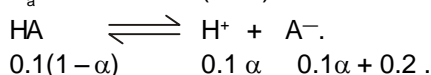
$$\text{concentration } \text{H}_3\text{BO}_3 = c = 2 \times \frac{1}{27.6} \times \frac{1000}{100} = 0.725$$



$$[H^+] = \sqrt{K_a c} = \sqrt{7.3 \times 10^{-10} \times 0.725} = 2.3 \times 10^{-5}.$$

$$\text{pH} = -\log[H^+] = \mathbf{4.64}.$$

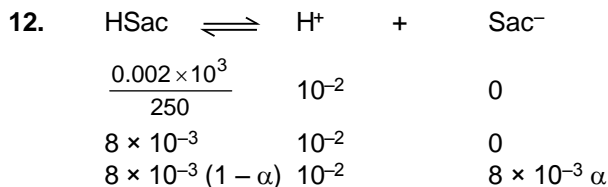
11. $K_a = c\alpha^2 = 0.1 \times (0.01)^2 = 10^{-5}.$



$$10^{-5} = \frac{0.1\alpha \times (0.1\alpha + 0.2)}{0.1}$$

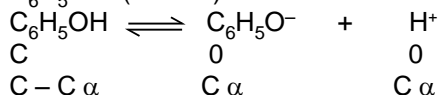
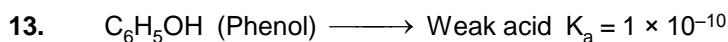
$$\alpha = 5 \times 10^{-5}$$

(Therefore, 0.1α is neglected).



$$K_a = \frac{10^{-2} [8 \times 10^{-3} \alpha]}{8 \times 10^{-3} (1 - \alpha)} = 2 \times 10^{-12} \Rightarrow \alpha = 2 \times 10^{-10}$$

$$[\text{Sac}^-] = 8 \times 10^{-3} \times 2 \times 10^{-10} = 16 \times 10^{-13} = 1.6 \times 10^{-12} \text{ M}$$

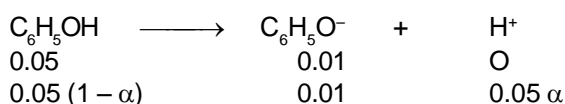
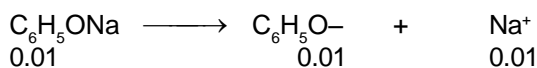


$$K_a = C \alpha^2 = 1 \times 10^{-10}$$

$$\alpha = \sqrt{\frac{1 \times 10^{-10}}{0.05}} = \sqrt{20 \times 10^{-10}} \quad \alpha = 4.47 \times 10^{-5}$$

$$[\text{C}_6\text{H}_5\text{O}^-] = 4.47 \times 10^{-5} \times 0.05 = 2.42 \times 10^{-6}$$

$$[\text{C}_6\text{H}_5\text{ONa}] = 0.01 \text{ M}$$



$$\frac{[0.05\alpha] 0.01}{0.05} = 1 \times 10^{-10} \quad \alpha = 10^{-8}$$

14. $[\text{H}^+] = \sqrt{(3 \times 10^{-8} \times 10^{-6}) + (2 \times 10^{-9} \times 10^{-5}) + 10^{-14}}$

$$= \sqrt{6} \times 10^{-7} = 2.44 \times 10^{-7} \text{ M}$$

for HA, $[\text{H}^+] = [\text{A}^-] = 3 \times 10^{-3} \text{ M}$

for HB, $K_a = 10^{-10} = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]}$

$$\therefore [\text{B}^-] = 3.33 \times 10^{-9} \text{ M}$$

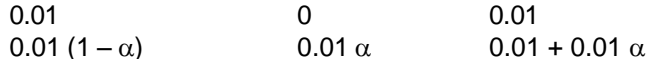
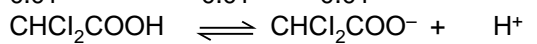
15. $[\text{H}^+] = \sqrt{(0.1 \times 2.4 \times 10^{-4}) + (0.1 \times 4 \times 10^{-4})} = 8 \times 10^{-3} \text{ M}$

for HCOOH, $K_a = 2.4 \times 10^{-4} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$

$$\therefore [\text{HCOO}^-] = 3 \times 10^{-3} \text{ M}$$

for HOCN, $K_a = 4 \times 10^{-4} = \frac{[\text{H}^+][\text{OCN}^-]}{[\text{HOCN}]}$

$$\therefore [\text{OCN}^-] = 5 \times 10^{-3} \text{ M}$$



$$K_a = \frac{0.01\alpha [0.01 + 0.01\alpha]}{0.01(1 - \alpha)} = 2 \times 10^{-2}$$

$$0.01 \alpha^2 + 0.01 \alpha = 2 \times 10^{-2}$$

$$10^{-2} \alpha^2 + 10^{-2} \alpha = 2 \times 10^{-2}$$

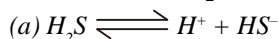
$$\alpha^2 + \alpha - 2 = 0$$

$$\alpha = \frac{-2 \pm \sqrt{1+8}}{2} = \frac{-2+3}{2} \Rightarrow \alpha = 0.56$$

$$[H^+] = 10^{-2} + 10^{-2} \times 0.56 = 1.56 \times 10^{-2} \text{ M}$$

$$[CHCl_2COO^-] = 0.01 \alpha = 5.6 \times 10^{-3} \text{ M}$$

17. Dissociation of H_2S can be represented as



$$\text{From the first ionisation of } H_2S = \frac{[H^+][HS^{-1}]}{[H_2S]} = K_{a1}$$

Since H_2S is weakly ionised and its ionisation is further decreased in presence of highly ionised HCl, concentration of H^+ in solution will be mainly due to HCl. Thus $[H^+] = 0.2 \text{ M}$.

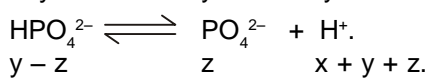
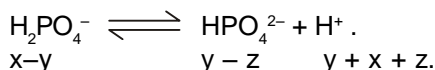
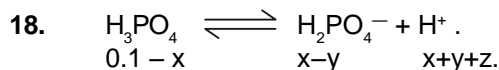
Substituting the value in the above reaction

$$\frac{0.2[HS^-]}{0.1} = 1 \times 10^{-7} \quad ; \quad [HS^-] = 5 \times 10^{-8} \text{ M}$$

From the second ionisation of H_2S ,

$$\frac{[H^+][S^{2-}]}{[HS^-]} = K_{a2} \text{ or } \frac{0.2 \times [S^{2-}]}{5 \times 10^{-8}} = 1.3 \times 10^{-13}$$

$$[S^{2-}] = 3.25 \times 10^{-20} \text{ M}$$



$$K_{a1} = \frac{(x-y)(x+y+z)}{0.1-x} = \frac{x^2}{0.1-x} \quad (y+z \text{ are very small compared to } x)$$

$$7.5 \times 10^{-3} = \frac{x^2}{0.1-x} \Rightarrow x = 0.024 \text{ M}$$

$$K_{a2} = \frac{(y-z)(x+y+z)}{x-y} = \frac{y \cdot x}{x} = y \Rightarrow y = 6.2 \times 10^{-8} \quad (\text{here } z < y)$$

$$K_{a3} = \frac{z(x+y+z)}{y-z} = \frac{z \cdot x}{y} \Rightarrow z = K_{a3} \cdot \frac{y}{x} = 9.3 \times 10^{-19} \text{ M}$$

$$\therefore [H_3PO_4] = 0.1 - x = 0.076 \text{ M}$$

$$[H^+] = [H_2PO_4^-] = x = 0.024 \text{ M}$$

$$[HPO_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$$

$$[PO_4^{3-}] = z = 9.3 \times 10^{-19} \text{ M}$$

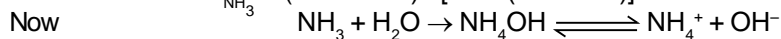
$$[OH^-] = \frac{K_w}{[H^+]} = 4.17 \times 10^{-13} \text{ M}$$

19. Given, $\frac{\text{wt. of } NH_3}{\text{wt. of solution}} = \frac{10}{100}$

$$\therefore 100 \text{ g dsolution contains } 10 \text{ g } NH_3$$

$$\therefore M_{NH_3} = (10 \times 1000) / [17 \times (100/0.99)]$$

$$(\therefore V = \text{mass} / \text{density})$$



$$\text{Before dissociation} \qquad \qquad 1 \qquad \qquad 0 \qquad \qquad 0$$

$$\text{After dissociation} \qquad \qquad (1-\alpha) \qquad \qquad \alpha \qquad \qquad \alpha$$

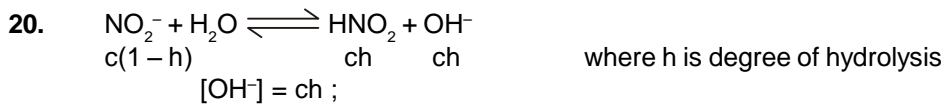
$$\therefore [OH^-] = C \cdot \alpha = C \sqrt{(K_b / C)} = \sqrt{(K_b \cdot C)}$$

$$[\therefore C = 5.82 \text{ M and } K_b = k_w / K_a = 10^{-14} / (5 \times 10^{-10}) = 2 \times 10^{-5}]$$

$$\therefore [\text{OH}^-] = \sqrt{[2 \times 10^{-5} \times 5.82]} = 1.07 \times 10^{-2} \text{ M}$$

$$\therefore [\text{H}^+] = 10^{-14}/1.07 \times 10^{-2} = 0.9268 \times 10^{-12} \text{ M}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log 0.9268 \times 10^{-12} = 12.0330$$



Also; $h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a \cdot c}} = \sqrt{\frac{10^{-14}}{4.5 \times 10^{-4} \times 0.04}} = 2.36 \times 10^{-5}$

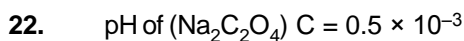
$\therefore [\text{OH}^-] = 0.04 \times 2.36 \times 10^{-5}$ or $\text{pOH} = 6.025$
 $\therefore \text{pH} = 14 - \text{pOH} = 7.975$



$\therefore [\text{OH}^-] = C \cdot h = C \sqrt{\frac{K_h}{C}} = \sqrt{K_h \cdot C} = \sqrt{\frac{K_w}{K_a} \cdot C} = \sqrt{\frac{10^{-14} \times 0.02}{5 \times 10^{-5}}} = 2 \times 10^{-6}$

$\therefore [\text{H}^+] = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9} \text{ M}$

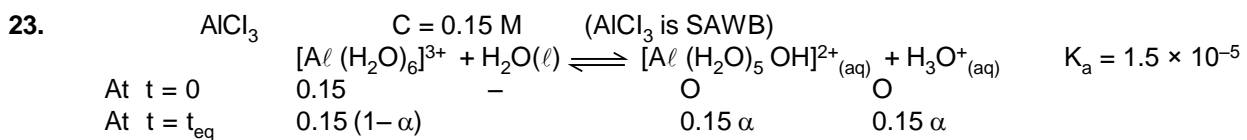
Also $h = \sqrt{\left[\frac{K_h}{C}\right]} = \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-5} \times 0.02}} = 10^{-4}$ or **0.01 %**



$\text{pH} = 7 + \frac{1}{2} \text{p}K_{a2} + \frac{1}{2} \log C$ Here $\text{p}K_{a2} = [6 - \log 5]$

$\text{pH} = 7 + \frac{1}{2} [6 - \log 5] + \frac{1}{2} [\log 5 \times 10^{-4}] = 7 + \frac{1}{2} [6 - \log 5] + \frac{1}{2} [\log 5 - 4] = 8$

$[\text{H}^+] = 10^{-8}$ So $[\text{OH}^-] = 10^{-6} \text{ M}$

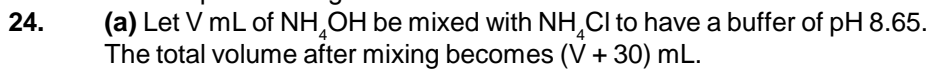


$K_a = \frac{0.15\alpha \times 0.15\alpha}{0.15[1-\alpha]} = 1.5 \times 10^{-5}$

$\Rightarrow 1.5 \times 10^{-1} \alpha^2 = 1.5 \times 10^{-5} \Rightarrow \alpha^2 = 10^{-4} \Rightarrow \alpha = 10^{-2}$

$[\text{H}_3\text{O}^+] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3} \text{ M}$

$\Rightarrow \text{pH} = 3 - \log 1.5 = 3 - 0.18 = 2.82$



m mole of $\text{NH}_4\text{OH} = 0.3 \times V$ $\therefore [\text{NH}_4\text{OH}] = \frac{0.3 \times V}{(V + 30)}$

m mole of $\text{NH}_4\text{Cl} = 0.2 \times 30$ $\therefore [\text{NH}_4\text{Cl}] = \frac{0.2 \times 30}{(V + 30)}$

Also pOH of buffer mixture is given by :

$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

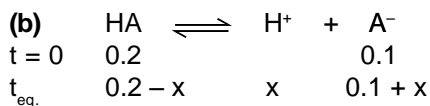
or $14 - 8.65 = 4.74 + \log \frac{(0.2 \times 30)/(V + 30)}{(0.3 \times V)/(V + 30)}$ (pOH = 14 - pH).

$$0.6 = \log \frac{6}{0.3V}$$

$$\therefore V = 5 \text{ mL.}$$

Similarly calculate $\left(14 - 10 = 4.74 + \log \frac{0.2 \times 30 / (V_1 + 30)}{0.3 \times V_1 / (V_1 + 30)} \right)$ for pH = 10 ;

$$V = 111.11 \text{ mL.}$$



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x(0.1+x)}{(0.2-x)}$$

$$\Rightarrow 0.05 = \frac{x^2 + 0.1x}{0.2-x}$$

$$\Rightarrow 0.01 - 0.05x = x^2 + 0.1x$$

$$x^2 + 0.15x - 0.01 = 0$$

$$x = 0.05 \text{ M}$$

(c) Let V mL of 0.1 M HCOONa be mixed to 50 mL of 0.05 M HCOOH.

$$\therefore \text{In mixture } [\text{HCOONa}] = \frac{0.1 \times V}{(V + 50)}$$

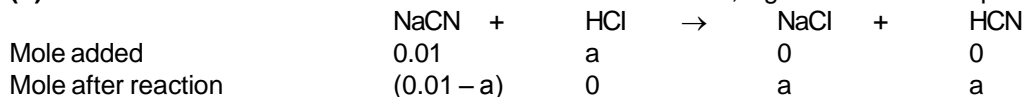
$$[\text{HCOOH}] = \frac{50 \times 0.05}{V + 50}$$

$$\therefore \text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore 4.0 = 3.7 + \log \frac{(0.1 \times V) / (V + 50)}{2.5 / (V + 50)}$$

$$\therefore V = 50 \text{ mL}$$

(d) NaCN + HCl is not a buffer but if HCl is in less amount then, it gives a buffer as it produces HCN.



This is buffer of HCN + NaCN

Let a mole of HCl be used for this purpose

$$\therefore \text{pH} = -\log K_a + \log \frac{0.01 - a}{a}$$

$$8.5 = -\log (4 \times 10^{-10}) + \log \frac{0.01 - a}{a}$$

$$\therefore a = 8.89 \times 10^{-3} \text{ mole of HCl}$$

(e) We know,

$$\text{pOH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$5 = 4.7 + \log \frac{a}{b}$$

$$\frac{a}{b} = 2 \quad \therefore a = 2b$$

Given $a + b = 0.6$

$$2b + b = 0.6$$

$$\therefore 3b = 0.6$$

or $b = 0.2 \text{ mole}$ or $0.2 \times 17 = 3.4 \text{ g/L}$

$\therefore a = 0.4 \text{ mole}$ or $0.4 \times 53.5 = 21.4 \text{ g/L}$

Thus, $[\text{Salt}] = 0.4 \text{ M}$ and $[\text{Base}] = 0.2 \text{ M}$

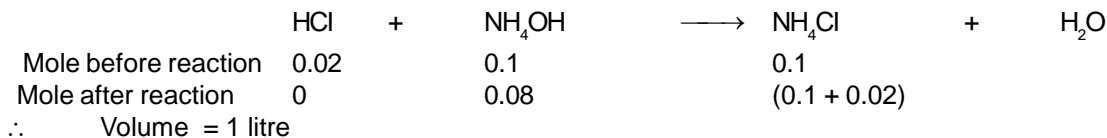
25. (a) initial pH of solution when,

$$[\text{NH}_3] = \frac{0.1}{1} \quad \text{and} \quad [\text{NH}_4\text{Cl}] = \frac{0.1}{1}$$

$$\text{pOH} = -\log 1.8 \times 10^{-5} + \log \frac{[\text{Salt}]}{[\text{Base}]} = -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.74$$

$$\therefore \text{pH} = 9.26$$

(i) Now 0.02 mole of HCl are added then



∴ Volume = 1 litre

$$\therefore [\text{NH}_4\text{OH}] = \frac{0.08}{1} \quad \text{and} \quad [\text{NH}_4\text{Cl}] = \frac{0.12}{1}$$

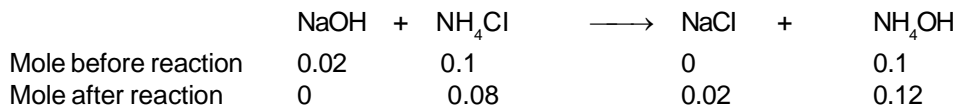
$$\therefore \text{pOH}_1 = -\log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08} = 4.92$$

$$\therefore \text{pH}_1 = 9.08$$

$$\text{Change in pH} = \text{pH} - \text{pH}_1 = 9.26 - 9.08 = +0.18$$

∴ Change in pH = 0.18 and pH decreases

(ii) Now 0.02 mole of NaOH are added

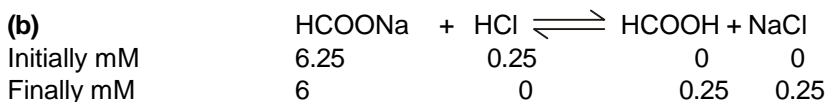


$$\therefore \text{pOH}_2 = -\log 1.8 \times 10^{-5} + \log \frac{0.08}{0.12} = 4.57$$

$$\therefore \text{pH}_2 = 9.43$$

$$\text{Change in pH} = \text{pH} - \text{pH}_2 = 9.26 - 9.43 = -0.18$$

∴ Change in pH = 0.18 unit i.e., pH increases



$$\therefore \text{pH} = 3.75 + \log \frac{6}{0.25} = 3.75 + \log 24 = 5.13$$

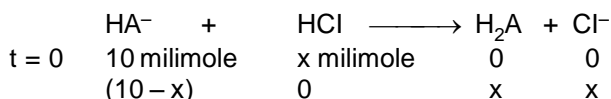
$$\text{Also } [\text{HCOOH}] = \frac{0.25}{60} = 4.17 \times 10^{-3} \text{ M}$$

(c) Let Acid is H₂A



For HA⁻, pK_{a2} = 9.7

and pK_b = 11.7 So pK_{a1} = 14 - 11.7 = 2.3



This solution Act as Buffer solution

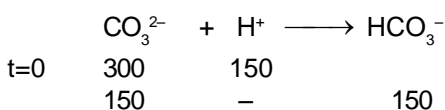
$$\text{So } \text{pH} = \text{pK}_{a1} + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]} \Rightarrow 2.6 = 2.3 + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]}$$

$$0.3 = \log \frac{(10-x)}{x} \Rightarrow 2 = \left[\frac{10-x}{x} \right] \Rightarrow 2x = 10 - x$$

$$3x = 10 \Rightarrow x = 3.33 \text{ milimole}$$

26. (a) m. mole of $\text{CO}_3^{2-} = \frac{31.8}{106} \times 1000 = 300$

m. mole of $\text{H}^+ = 150 \times 1 = 150$



so $\text{pH} = \text{pK}_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10.3.$

(b) Mole balance equation

$$[\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] + \frac{K_{a1}[\text{H}_2\text{CO}_3]}{[\text{H}^+]} + \frac{K_{a1}K_{a2}[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2}$$

$$\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] \left(1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}^+]^2} \right)$$

$$\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] \left(1 + \frac{4.9 \times 10^{-7}}{10^{-8}} + \frac{4.9 \times 10^{-7} \times 10^{-12}}{(10^{-8})^2} \right)$$

$$\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] (1 + 49 + 4.9 \times 10^{-3})$$

$$\therefore [\text{H}_2\text{CO}_3] = \frac{[\text{HCO}_3^-]_0}{50}$$

$$\Rightarrow n_{\text{H}_2\text{CO}_3} = \frac{0.0005}{50} = 10^{-5} \text{ mole.}$$

$$[\text{HCO}_3^-] = \frac{K_{a1}[\text{H}_2\text{CO}_3]}{[\text{H}^+]}$$

$$\Rightarrow n_{\text{HCO}_3^-} = \frac{4.9 \times 10^{-7} \times 10^{-5}}{10^{-8}} = 4.9 \times 10^{-4} \text{ mole}$$

$$[\text{CO}_3^{2-}] = \frac{K_{a1}K_{a2}[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2}$$

$$n_{\text{CO}_3^{2-}} = \frac{4.9 \times 10^{-7} \times 10^{-12} \times 10^{-5}}{(10^{-8})^2} = 4.9 \times 10^{-8} \text{ mole}$$

27. $\text{pH}_1 = \text{pK}_a + \log \frac{x}{a}$

$$\text{pH}_2 = \text{pK}_a + \log \frac{y}{a}.$$

$$\text{pH}_2 - \text{pH}_1 = 0.6 = \log \frac{y}{x}.$$

$$y = x 10^{0.6} = 4x.$$

$$x : y = 1 : 4.$$

28. $\text{pK}_a = 11 - \log 4.7 = 11 - \log 4.7 = 11 - 0.672 = 10.328$

$$\text{pH} = \text{pK}_a + \log \left(\frac{n_{\text{Na}_2\text{CO}_3}}{0.3} \right) \quad 10 = 10.328 + \log \left(\frac{n_{\text{Na}_2\text{CO}_3}}{0.3} \right)$$

$$\log \frac{0.3}{n_{\text{Na}_2\text{CO}_3}} = 0.328 \Rightarrow \frac{0.3}{n_{\text{Na}_2\text{CO}_3}} = 2.13$$

$$W_{\text{Na}_2\text{CO}_3} = \left[\frac{0.3}{2.13} \right] \times 106 = 14.94 \approx 15 \text{ gram}$$

29. For sodium butyrate

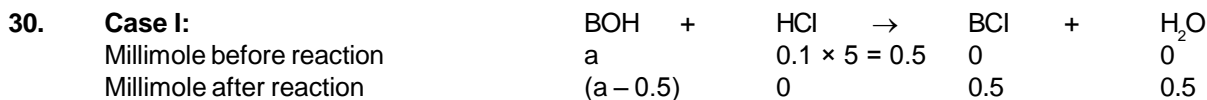
$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C = 7 + \left(\frac{5 - \log 1.5}{2} \right) + \frac{1}{2} \log (0.1)$$

$$= 7 + 2.41 - 0.5 = 8.91$$

For Indicator

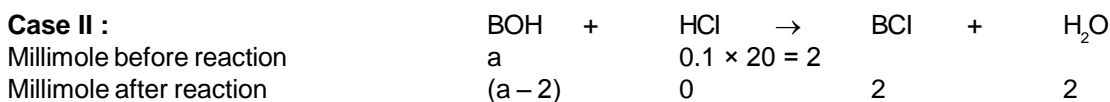
$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$\Rightarrow \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_{\text{In}}}{[\text{H}^+]} = \frac{3.16 \times 10^{-10}}{10^{-8.91}} = 0.257$$



$$\therefore \text{pH} = 10.04 \qquad \therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \qquad \dots(1)$$

$$\therefore \text{pOH} = 3.96 \qquad \therefore 3.96 = -\log K_b + \log \frac{0.5}{(a - 0.5)} \qquad \dots(2)$$



$$\therefore \text{pH} = 9.14 \qquad \therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \qquad \dots(3)$$

$$\therefore \text{pOH} = 4.86 \qquad \therefore 4.86 = -\log K_b + \log \frac{2}{a - 2} \qquad \dots(4)$$

$$K_b = 1.81 \times 10^{-5}$$

31. $\text{pH of CH}_3\text{COOH} = \frac{1}{2} (\text{p}K_a - \log c)$

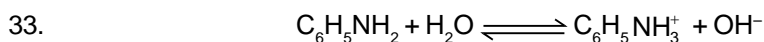
$$3 = \frac{1}{2} (\text{p}K_a - \log 0.1) \qquad \therefore \text{p}K_a = 5$$

$$\frac{1}{4} \text{ stage of neutralisation : } \text{pH} = 5 + \log \frac{1/4}{3/4} = 4.52$$

$$\frac{3}{4} \text{ stage of neutralisation : } \text{pH} = 5 + \log \frac{3/4}{1/4} = 5.48$$

32. We know that pH of a mixture of solution containing weak acid and strong base can be calculated as below

$$\begin{aligned} \text{pH} &= 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c \\ &= 7 + \frac{1}{2} \times 4.72 + \frac{1}{2} \log 0.05 \\ &= 7 + 2.36 - 0.65 = 8.71 \end{aligned}$$



Thus,

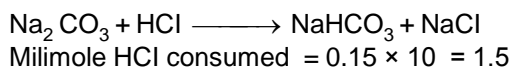
$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$\frac{10^{-14}}{2.4 \times 10^{-5}} = \frac{10^{-8} \times [\text{OH}^-]}{0.24}$$

$$\therefore [\text{OH}^-] = 10^{-2} \text{ M}$$

34. Let $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3 + \text{KCl}$
 $x\text{g} \quad y\text{g}$

At Ist equivalent point



$$\left[\frac{Y}{106} \right] \times 1 \times 10^3 = 1.5 \quad y = \frac{1.5 \times 106}{1000} = 0.159 \text{ g}$$

At IInd equivalent point

m. eq. of $\text{Na}_2\text{CO}_3 + \text{m. eq. of NaHCO}_3 = \text{m. eq. of HCl} = 35 \times 0.15$

$$\Rightarrow \left[\frac{x}{84} \right] + \left[\frac{y}{106} \right] \times 2 = 0.15 \times 35 \times 10^{-3}$$

$$\Rightarrow \frac{x}{84} + (1.5 \times 10^{-3}) \times 2 = 5.25 \times 10^{-3} \quad \Rightarrow \quad x = \frac{(2.25 \times 84)}{1000} = 0.189 \text{ g}$$

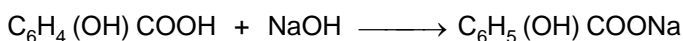
mass of KCl = 0.152 g

$$\text{mass \% of Na}_2\text{CO}_3 = \frac{0.159 \times 100}{0.5} = 31.8 \%$$

$$\text{mass \% of NaHCO}_3 = \frac{0.189 \times 100}{0.5} = 37.8 \%$$

$$\text{mass \% of KCl} = \frac{0.152 \times 100}{0.5} = 30.4 \%$$

35. Let Molarity of $\text{C}_6\text{H}_4(\text{OH})\text{COOH} = M_1$

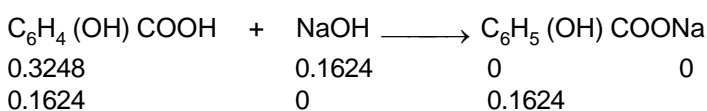


At end point

No. of eq. of $\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{No. of eq. of NaOH} = 16.24 \times .02$

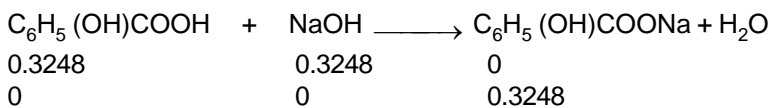
$$25 \times M_1 = 0.3248 \quad \Rightarrow \quad M_1 = \frac{0.3248}{25} = 0.013$$

Half neutralization



$$\text{pH} = \text{pK}_{a1} + \log \frac{[\text{C}_6\text{H}_5(\text{OH})\text{COONa}]}{[\text{C}_6\text{H}_5(\text{OH})\text{COOH}]} \quad \Rightarrow \quad 4.7 = \text{pK}_{a1} \quad \Rightarrow \quad \text{K}_{a1} = 2 \times 10^{-5}$$

Complete Neutralization



$$[\text{C}_6\text{H}_5(\text{OH})\text{COONa}] = \frac{0.3248}{41.24} = 7.88 \times 10^{-3}$$

$\text{C}_6\text{H}_5(\text{OH})\text{COONa}$ This species is amphoteric species.

$$\text{So } \text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} \quad \Rightarrow \quad 7.5 = \frac{4.7 + \text{pK}_{a2}}{2}$$

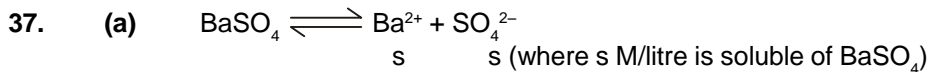
$$15 - 4.7 = \text{pK}_{a2} \quad \Rightarrow \quad \text{pK}_{a2} = 10.3 \quad \Rightarrow \quad \text{K}_{a2} = 5 \times 10^{-11}$$

36. $[\text{Sr}(\text{OH})_2] \longrightarrow \text{Sr}^{2+} + 2\text{OH}^-$

$$[\text{Sr}(\text{OH})_2] = \frac{19.23}{121.62 \times 1} = 0.158 \text{ M}$$

$$\therefore [\text{OH}^-] = 2 \times 0.158 \text{ M} = \mathbf{0.316 \text{ M}}$$

or $\text{pOH} = 0.5$ \therefore **pH = 13.5**
 $[\text{Sr}^{2+}] = \mathbf{0.158 \text{ M}}$.



(i) $K_{\text{SP}} = s \times s$

$\therefore s = \sqrt{K_{\text{SP}}} = \sqrt{1.6 \times 10^{-9}} = \mathbf{4 \times 10^{-5} \text{ mol litre}^{-1}}$

(ii) In presence of 0.10 M BaCl_2 , let s mol/litre BaSO_4 is dissolved

$K_{\text{SP}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
 $1.6 \times 10^{-9} = (0.1 + s)(s)$ $[(0.1 + s) = 0.1 \text{ as } s \lll 0.1]$
 $\therefore s = \mathbf{1.6 \times 10^{-8} \text{ M}}$

(b) For CaSO_4 , Let solubility be s mol/litre

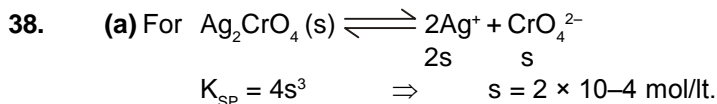
Then $s = \sqrt{K_{\text{SP}}} = \sqrt{9 \times 10^{-6}} = 3 \times 10^{-3} \text{ mol litre}^{-1}$

Thus, 3×10^{-3} mole of CaSO_4 is soluble in water = 1 litre

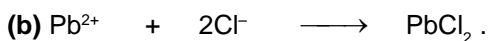
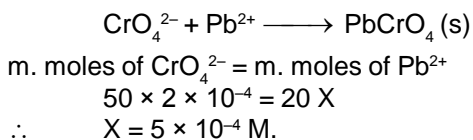
$\therefore \frac{1}{136}$ mole (1 g) of CaSO_4 is soluble in = $\frac{1}{136 \times 3 \times 10^{-3}} = \mathbf{2.45 \text{ litre water}}$

(c) Let solubility of Mg(OH)_2 be s mol litre⁻¹

$\text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$
 $\therefore [\text{Mg}^{2+}][\text{OH}^-]^2 = K_{\text{SP}}$
 $4s^3 = 8.9 \times 10^{-12}$
 $\therefore s = 1.305 \times 10^{-4} \text{ mol litre}^{-1}$
 $\therefore [\text{OH}^-] = 2 \times 1.305 \times 10^{-4} \text{ mol litre}^{-1}$
 $\therefore \text{pOH} = 3.58$
 $\therefore \text{pH} = \mathbf{10.42}$



Now,



$\frac{10}{101} - x \quad \frac{1}{101} - 2x \approx 0$.

$[\text{Pb}^{2+}] = \left(10 - \frac{1}{2}\right) \times \frac{1}{101} = \frac{9.5}{101} = \mathbf{9.4 \times 10^{-2} \text{ M}}$.

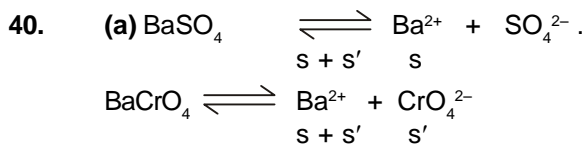
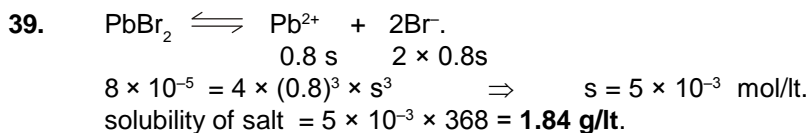
(c) Taking density of water to be 1 g/cc.

$[\text{CaSO}_4] = \frac{136}{10^6} \times \frac{1000}{136} = 10^{-10} \text{ M}$.

Concentration of CaSO_4 in saturated solution. = $\sqrt{K_{\text{SP}}} = 3 \times 10^{-3}$.

$M_1V_1 = M_2V_2$
 $10^{-10} \times V_1 = 3 \times 10^{-3} \times V_2$.

$\frac{V_2}{V_1} = \frac{1}{3} \Rightarrow \frac{V_1 - V_2}{V_1} = 0.67$.



$$[\text{Ba}^{2+}] = 1.4 \times 10^{-5} = \sqrt{K_{\text{sp1}} + K_{\text{sp2}}}$$

$$\therefore K_{\text{sp1}} + K_{\text{sp2}} = (1.4 \times 10^{-5})^2$$

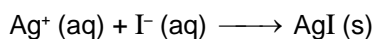
$$\& \frac{K_{\text{sp1}}}{K_{\text{sp2}}} = \frac{1}{2.5}$$

On solving, $K_{\text{sp1}} = 5.6 \times 10^{-11}$
 $K_{\text{sp2}} = 1.4 \times 10^{-10}$

Solubility of BaSO_4 in $0.01 \text{ M Na}_2\text{SO}_4 = \frac{5.6 \times 10^{-11}}{0.01} = 5.6 \times 10^{-9} \text{ M.}$

(b). milli moles of $\text{I}^- = 25 \times 2 \times \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}}$

milli moles of $\text{Ag}^+ = 13.3 \times \text{M.}$

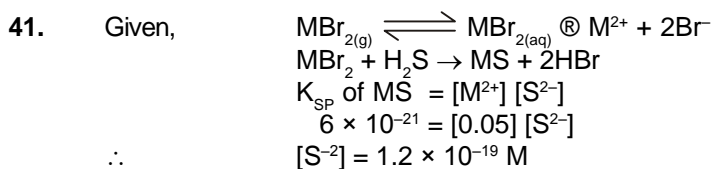


Equating both $\text{M} = 4.55 \times 10^{-3}$.

(c). $[\text{F}^-]$ concentration when $[\text{Sr}^{2+}]$ is $2.5 \times 10^{-3} = \sqrt{\frac{2.8 \times 10^{-9}}{2.5 \times 10^{-3}}} = 1.058 \times 10^{-3} \text{ M.}$

Total m. moles of F^- added = $100 \times [1.058 \times 10^{-3} + 2(0.016 - 0.0025)] = 2.8$

Mass of NaF added = $2.8 \times 10^{-3} \times 42 = 0.1776 \text{ g.}$



$\therefore [\text{S}^{2-}] = 1.2 \times 10^{-19} \text{ M}$

Thus, MS will be precipitated if H_2S provides $1.2 \times 10^{-19} \text{ M}$ ions of S^{2-}



$$K_1 \times K_2 = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[\text{H}^+]^2[1.2 \times 10^{-19}]}{[0.1]}$$

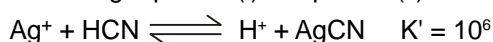
$\therefore [\text{H}^+] = 1.04 \times 10^{-1}$ and $\text{pH} = 0.983$

42. Volume of both AgNO_3 & HCN are equal so. Their concentration is half

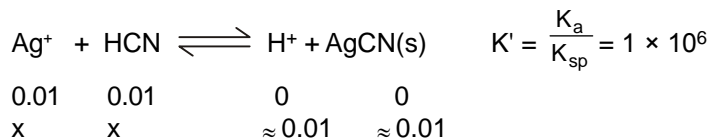
$[\text{AgNO}_3] = 0.01 \text{ M}$ $[\text{HCN}] = 0.01 \text{ M}$



on adding equation (i) & equation (ii)



As the value of K' is very high so almost all Ag^+ & HCN converted in product



$$K' = \frac{0.01}{(x)^2} = 10^6$$

$$x^2 = 10^{-8} \quad \Rightarrow \quad x = 10^{-4}$$

Conc. of $[\text{Ag}^+] = 10^{-4}$

43. For the precipitation of $\text{Mg}(\text{OH})_2$
 $[\text{Mg}^{2+}][\text{OH}^-]^2 = K_{sp}$
 $[\text{OH}^-] = 5 \times 10^{-5}$
 For $\text{NH}_3 - \text{NH}_4^+$ buffer solution,

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} \quad \Rightarrow \quad [\text{NH}_3] = \frac{(5 \times 10^{-6})(0.4)}{2 \times 10^{-5}} = 0.1 \text{ M.}$$

44. Let final concentration of SO_4^{2-} in solution = $[\text{SO}_4^{2-}]_{\text{left}} = x$
 Mole balance equation for SO_4^{2-}

$$[\text{SO}_4^{2-}]_{\text{initial}} = [\text{SO}_4^{2-}]_{\text{left}} + [\text{SO}_4^{2-}]_{\text{combined}}$$

$$\frac{0.3 \times 10}{30} = 0.1 = [\text{SO}_4^{2-}]_{\text{left}} + [\text{SO}_4^{2-}]_{\text{combined}}$$

$$0.1 = x + [\text{Ca}^{2+}]_{\text{combined}} + [\text{Sr}^{2+}]_{\text{combined}}$$

$$\Rightarrow 0.1 = x + ([\text{Ca}^{2+}]_{\text{initial}} - [\text{Ca}^{2+}]_{\text{left}}) + ([\text{Sr}^{2+}]_{\text{initial}} - [\text{Sr}^{2+}]_{\text{left}})$$

$$\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{K_{sp} \text{ of } \text{CaSO}_4}{[\text{SO}_4^{2-}]_{\text{left}}} \right) + \left(\frac{0.2}{3} - \frac{K_{sp} \text{ of } \text{SrSO}_4}{[\text{SO}_4^{2-}]_{\text{left}}} \right)$$

$$\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{2.4 \times 10^{-5}}{x} \right) + \left(\frac{0.2}{3} - \frac{7.6 \times 10^{-7}}{x} \right)$$

$$\Rightarrow 3x^2 + 0.1x + 7.428 \times 10^{-5} = 0$$

on solving, $x = [\text{SO}_4^{2-}]_{\text{left}} = 7.26 \times 10^{-4} \text{ M}$

$$[\text{Ca}^{2+}]_{\text{left}} = \frac{2.4 \times 10^{-5}}{7.26 \times 10^{-4}} = 0.033 \text{ M}$$

$$[\text{Sr}^{2+}]_{\text{left}} = \frac{7.6 \times 10^{-7}}{7.26 \times 10^{-4}} = 1.05 \times 10^{-3} \text{ M}$$

45. $[\text{Ag}^+]$ concentration = $\frac{100}{350} \times 2 \times \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}} = 8.68 \times 10^{-3}$.

$$[\text{SO}_4^{2-}] \text{ concentration} = \frac{100}{350} \times 3 \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}} = 4.34 \times 10^{-3}$$

$$[\text{Pb}^{2+}] = \frac{250}{350} \times \sqrt{2.8 \times 10^{-13}} = 3.78 \times 10^{-7}$$

$$[\text{CrO}_4^{2-}] = 3.78 \times 10^{-7}$$

$$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 2.85 \times 10^{-11} > K_{sp} \text{ of } \text{Ag}_2\text{CrO}_4$$

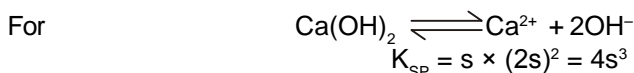
$$[\text{Pb}^{2+}] [\text{SO}_4^{2-}] = 1.64 \times 10^{-9} < K_{sp} \text{ of } \text{PbSO}_4$$

Only Ag_2CrO_4 will precipitate.

46. $[Ag^+][Cl^-] = 1.75 \times 10^{-10}$
 $[Ag^+][Br^-] = 5.25 \times 10^{-13}$

$$\Rightarrow [Br^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times [Cl^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times (0.075) = 2.25 \times 10^{-4} \text{ M.}$$

47. (a) 500 mL of 0.4 M NaOH are mixed with 500 mL of $Ca(OH)_2$ a saturated solution having $Ca(OH)_2$ solubility as s M.



Then, $4s^3 = 4.42 \times 10^{-5}$

$$\therefore s = \sqrt[3]{\left(\frac{4.42 \times 10^{-5}}{4}\right)} = 0.0223 \text{ M}$$

Now $Ca(OH)_2 + NaOH$ are mixed

\therefore Solution has Ca^{2+} and OH^- out of which some Ca^{2+} are precipitated

On mixing, $[Ca^{2+}] = \frac{0.0223 \times 500}{1000} = 0.01115 = 111.5 \times 10^{-4} \text{ M}$

$$[OH^-] = \frac{0.0223 \times 2 \times 500}{1000} + \frac{500 \times 0.4}{1000} = 0.2223 \text{ M}$$

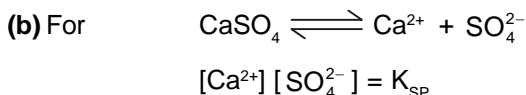
[from $Ca(OH)_2$] [from NaOH]

$\therefore [Ca^{2+}][OH^-]^2 = K_{SP}$
 $[Ca^{2+}]_{left} [0.2223]^2 = 4.42 \times 10^{-5}$

$$[Ca^{2+}]_{left} = \frac{4.42 \times 10^{-5}}{[0.2223]^2} = 8.94 \times 10^{-1} \text{ mol litre}^{-1}$$

\therefore Mole of $Ca(OH)_2$ precipitated = Mole of $[Ca^{2+}]$ precipitated
 $= 111.5 \times 10^{-4} - 8.94 \times 10^{-4} = 102.46 \times 10^{-4}$

\therefore Wt. of $Ca(OH)_2$ precipitated from $Ca(OH)_2$ solution
 $= 102.46 \times 10^{-4} \times 74 = 7582.04 \times 10^{-4} \text{ g} = \mathbf{759 \text{ mg}}$



Let $[SO_4^{2-}] = a$, just sufficient to precipitate $CaSO_4$ from a solution having $[Ca^{2+}] = 0.005 \text{ M}$

Then, $[0.005][a] = 2.4 \times 10^{-5} \quad \therefore a = \frac{2.4 \times 10^{-5}}{0.005}$

$$[SO_4^{2-}] = \mathbf{4.8 \times 10^{-3} \text{ mol litre}^{-1}}$$

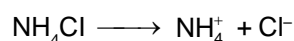
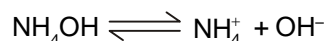
(c). The minimum $[OH^-]$ at which there will be no precipitation of $Mg(OH)_2$ obtained by

$$K_{SP} = [Mg^{2+}][OH^-]^2$$

$$6.0 \times 10^{-12} = [0.05][OH^-]^2$$

$\therefore [OH^-] = 1.34 \times 10^{-5} \text{ M}$

Thus, a solution having $[OH^-] = 1.34 \times 10^{-5} \text{ M}$ will not show precipitation of $Mg(OH)_2$ in 0.05 M Mg^{2+} solution. These hydroxyl ions are to be derived by a buffer of NH_4Cl and NH_4OH i.e.,



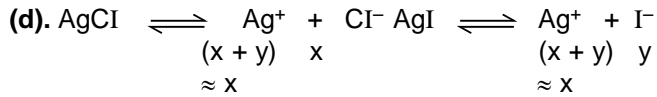
For NH_4OH $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

In presence of NH_4Cl ; all the $[NH_4^+]$ are provided by NH_4Cl since common ion effect decreases dissociation of NH_4OH .

$\therefore 1.8 \times 10^{-5} = \frac{[NH_4^+][1.34 \times 10^{-5}]}{[0.05]}$

$$\therefore [\text{NH}_4^+] = 0.067 \text{ M}$$

$$\text{or } [\text{NH}_4\text{Cl}] = 0.067 \text{ M}$$



$$\frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgI})} = \frac{x}{y} = \frac{1 \times 10^{-10}}{8.5 \times 10^{-17}} = \frac{10}{8.5} \times 10^{+6}$$

$$x = 1.8 \times 10^6 y$$



$$x^2 = 10^{-10}$$

$$x = 10^{-5}$$

$$xy = 8.5 \times 10^{-17}$$

$$y = 8.5 \times 10^{-12}$$

$$\text{(e). } K_{sp} = 4 \times (6.7 \times 10^{-6})^3 = 1.203 \times 10^{-15}$$

$$s \times (10^{-6})^2 = 1.203 \times 10^{-15}$$

$$s = 1.203 \times 10^{-3} \text{ M}$$

$$48. \text{ Concentration of CaCO}_3 = \left[\frac{7 \times 10^{-3}}{100} \right] \text{ mole/lit} = 7 \times 10^{-5} \text{ mole/lit}$$

$$K_{sp} \text{ of CaCO}_3 = 49 \times 10^{-5} \text{ mole/lit}$$

when only $[\text{Ba}^{+2}]$ is 90% precipitated then only CaCO_3 starts precipitation then if & solution contain a mole/lit of Ca^{+2} & Ba^{+2}

$$[\text{Ca}^{+2}][\text{CO}_3^{-2}] = 49 \times 10^{-10} \quad [\text{CO}_3^{-2}] = \left[\frac{49 \times 10^{-10}}{a} \right]$$

$$\text{Now for BaCO}_3 \quad K_{sp} = [\text{Ba}^{+2}][\text{CO}_3^{-2}] = \frac{a \times 10}{100} \times \frac{49 \times 10^{-10}}{a} = 4.9 \times 10^{-10}$$

$$49. \text{ Al(OH)}_3(\text{s}) \rightleftharpoons \text{Al}^{+3} + 3 \text{OH}^- \quad K_{sp} = 5 \times 10^{-33}$$

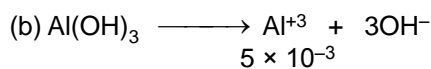
$$[\text{Al(OH)}_4]^- \rightleftharpoons \text{Al}^{+3} + 4 \text{OH}^- \quad K_d = 1 \times 10^{-34}$$

$$\text{Al(OH)}_3(\text{s}) + \text{OH}^- \rightleftharpoons [\text{Al(OH)}_4]^- \quad K_1 = \frac{K_{sp}}{K_d}$$

$$\begin{array}{ccc} 1 \times 10^{-3} & & 0 \\ 0 & & 1 \times 10^{-3} \end{array}$$

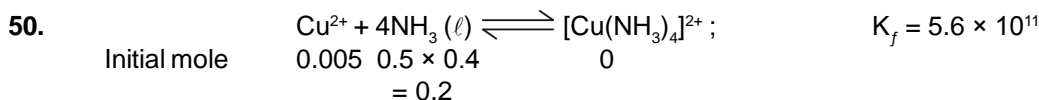
$$K_1 = \frac{[\text{Al(OH)}_4]^-}{[\text{OH}^-]} = \frac{5 \times 10^{-33}}{1 \times 10^{-34}} = 50 \Rightarrow [\text{OH}^-] = \frac{1 \times 10^{-3}}{50} = 2 \times 10^{-5}$$

$$\text{pOH} = 5 - \log 2 = 4.7 \Rightarrow \text{pH} = 14 - 4.7 = 9.3 \Rightarrow \text{pH} = 9.3$$



$$[\text{Al}^{+3}][\text{OH}^-]^3 = K_{sp} \Rightarrow [\text{OH}^-]^3 = \frac{5 \times 10^{-33}}{5 \times 10^{-3}}$$

$$[\text{OH}^-]^3 = 1 \times 10^{-30} \Rightarrow [\text{OH}^-] = 10^{-10} \Rightarrow \text{pOH} = 10 \Rightarrow \text{pH} = 4$$



K_f is large and thus all the Cu^{2+} will give $[\text{Cu(NH}_3)_4]^{2+}$

Let Cu^{2+} left is a, than

$$[\text{Cu(NH}_3)_4]^{2+} = 0.005 \text{ mole} = \frac{0.005}{0.5} \text{ M} \quad (0.005 \gg a)$$

$$[\text{Cu}^{2+}] = \frac{a}{0.5} \text{ M} \quad (\text{Let})$$

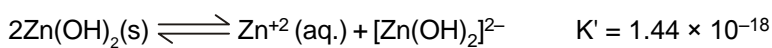
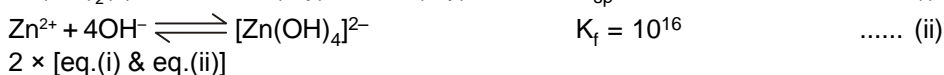
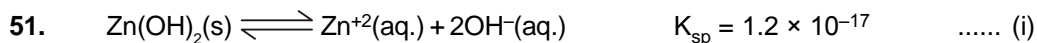
$$[\text{NH}_3] = 0.2 - 4 \times 0.005 + 2a$$

$$= 0.2 - 0.02 + 2a \quad (0.18 \gg 2a)$$

$$= 0.18 \text{ mole} = \frac{0.18}{0.5} \text{ M}$$

$$\therefore K_f = 5.6 \times 10^{11} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{\frac{0.005}{0.5}}{[\text{Cu}^{2+}] \times \left[\frac{0.18}{0.5}\right]^4}$$

$$\therefore [\text{Cu}^{2+}] = 1.06 \times 10^{-12} \text{ M}$$



$$\left(\frac{s}{2}\right) \quad \left(\frac{s}{2}\right)$$

$$\left(\frac{s^2}{4}\right) = 1.44 \times 10^{-18}$$

But $s^2 = 4 \times 144 \times 10^{-20} \Rightarrow s = 2.4 \times 10^{-9} \text{ M}$
 $K_{\text{sp}} [\text{Zn}(\text{OH})_2] = [\text{Zn}^{2+}] [\text{OH}^{-}]^2 = 1.2 \times 10^{-17}$

$\Rightarrow (1.2 \times 10^{-9}) [\text{OH}^{-}]^2 = 1.2 \times 10^{-17}$
 $[\text{OH}^{-}] = 10^{-4} \text{ M}$

EQUIVALENT CONCEPT & TITRATION

EXERCISE # 1

PART - I

- A-2.** In S_2Cl_2
 $2 \times 35.5 \text{ g Cl} \equiv 2 \times 32 \text{ g S}$
 $\therefore 35.5 \text{ g Cl} \equiv 32 \text{ g S}$
 \therefore Equivalent mass of S in S_2Cl_2 is 32.
- A-11.** Moles of pure NaOH required = $\frac{N \times V_L}{v.f} = \frac{0.5 \times 70}{1} = 35$
 Mass of pure NaOH required = $35 \times 40 = 1400 \text{ g} = 1.4 \text{ kg}$.
 Mass of wet NaOH required (containing 15% water) = $1.4 \times \frac{100}{85} = 1.65 \text{ kg}$.
- A-12.** eq. = $NV_L = 1/2 \times 1$
 eq. \times eq. mass = mass (g)
 $\frac{1}{2} \times 36.5 = 18.25 \text{ (g)}$
 mass remained = $18.25 - 2.675 = 15.575 \text{ g}$
 New normality = $\frac{15.575/36.5}{750/1000} = 0.569 \text{ N}$
- B-8.** $Na_2 \overset{+2}{S}_2 \overset{+3}{O}_3 \longrightarrow Na_2 \overset{+6}{S} \overset{+4}{O}_4$
 the total change in oxidation number = $4 \times 2 = 8$
 $\therefore E_{Na_2S_2O_3} = \frac{\text{mol. wt.}}{V.f} = \frac{M}{8}$
- C-3.** Eq. of $Na_2CO_3 = \text{Eq. of } H_2SO_4$
 $\frac{1.06}{106} \times 2 = \frac{25}{1000} \times N$
 $N = 0.8 \text{ N}$
- C-4.**

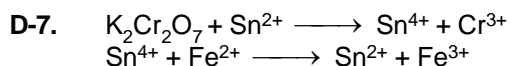
$H_2C_2O_4$	$NaOH$
$M = \frac{63 \times 1000}{126 \times 100}$	$M = \frac{40 \times 1000}{40 \times 100}$
$M = 5$	$M = 10$
$N = 10$	$N = 10$
$V = 125 \text{ mL}$	$V = 125 \text{ mL}$
$N_1V_1 = 1250 \text{ milli equivalent}$	$N_2V_2 = 1250 \text{ milli equivalent}$

 so, resulting solution will be neutral.
- C-9.** $eq_{HNO_3} = eq_{NaOH}$
 $\frac{18.9}{63} \times 1 \times V_1 = \frac{3.2}{40} \times 1 \times V_2$
 $\frac{V_1}{V_2} = \frac{4}{15}$
- C-10.** $eq_{acid} = eq_{base}$ (VF = 1 for both)
 $CHCl_2COOH + NH_3 \longrightarrow CHCl_2COONH_4$
 From reaction, m. moles of $NH_3 = \text{m. moles of dichloroacetic acid} = 100$

$$\therefore \text{Moles of NH}_3 = \frac{100}{1000} = 0.1$$

D-4. $1.68 \times 10^{-3} \times 6 = 3.36 \times 10^{-3} \times x$
 $x = 3$

So, oxidation number of A increases by 3.
 \therefore New oxidation number of A = $-n + 3 = 3 - n$.



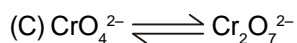
$$\text{Milli equivalent of K}_2\text{Cr}_2\text{O}_7 \text{ in 10 mL solution} = \frac{4.9}{(294/6) \times 0.1} \times 10 = 10$$

$$\text{so, milli mole of Fe}^{3+} = \frac{10}{1} = 10 \text{ (V.F. of Fe}^{3+} = 1)$$

D-10. (A) Formula of silver chromate (VI) will be Ag_2CrO_4

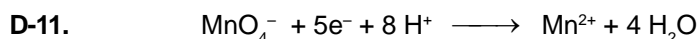
(B) Minimum mass of zinc required for reduction of 0.1 mole of Cr^{3+} to $\text{Cr}^{2+} = \frac{0.1}{2}$ moles of Zn

$$\begin{aligned} \text{(v.f. of Zn} = 2 \text{ \& v.f. of Cr}^{3+} = 1) & & = \frac{6.54}{2} \text{ g} = 3.27 \text{ g} \end{aligned}$$



in both ions, chromium is in +6 oxidation state.

(D) Given reaction is correct.

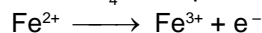


\Rightarrow 1 mole of MnO_4^- accepts 5 mole of e^-

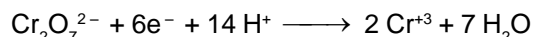
1/5 mole of MnO_4^- accepts 1 mole of e^-

\Rightarrow 0.2 mole of MnO_4^- accepts 1 mole of e^-

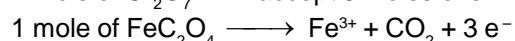
\Rightarrow 0.6 mole of MnO_4^- accepts 3 mole of e^-



\Rightarrow 1 mole of Fe^{2+} will liberate 1 mole of e^-



\Rightarrow 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ will accept 6 moles of e^-



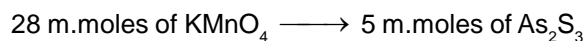
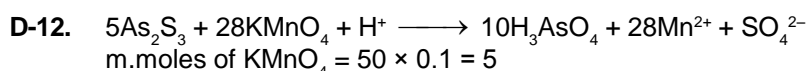
\Rightarrow 1 moles of ferrous oxalate gives 3 moles of e^-

\Rightarrow 0.2 moles of $\text{KMnO}_4 = 1/5$ moles of KMnO_4 oxidises 1 mole of Fe^{2+} ion. (Tallies with statement A)

0.6 moles of $\text{KMnO}_4 = 3/5$ moles of KMnO_4 will oxidise 1 mole of ferrous oxalate (Tallies with statement C)

1 mole of $\text{K}_2\text{Cr}_2\text{O}_7$ will oxidise 2 moles of ferrous oxalate. (Tallies with statement D)

Hence ,(A) , (C) , (D) are correct while (B) is incorrect.

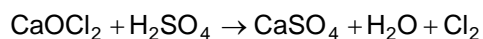


\therefore 1 m.mole of $\text{KMnO}_4 \longrightarrow 5/28$ m.moles of As_2S_3

\therefore 5 m.mole of $\text{KMnO}_4 \longrightarrow \frac{5 \times 5}{28}$ m.moles of As_2S_3

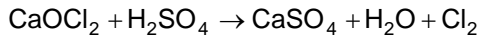
$$\text{Mass of As}_2\text{S}_3 = x = 246 \times \frac{5 \times 5}{28} \times 10^{-3} = 0.22 \text{ g}$$

E-2. The weight % of available Cl_2 from the given sample of bleaching powder on reaction with dil acids or CO_2 is called available chlorine.



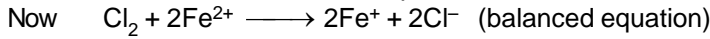
$$\text{Max. \% of available of Cl}_2 = \frac{71}{127} \times 100 = 55.9\%$$

- E-3.** The weight % of available Cl_2 from the given sample of bleaching powder on reaction with dil acids or CO_2 is called available chlorine.



$$\% \text{ of available } \text{Cl}_2 = \frac{3.55 \times 10 \times 0.125}{\frac{3.55}{100} \times 25} = 5\%$$

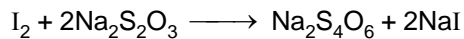
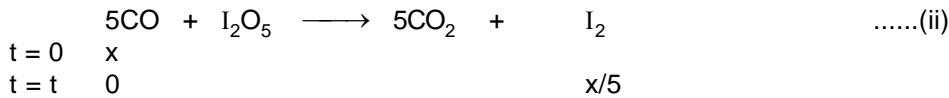
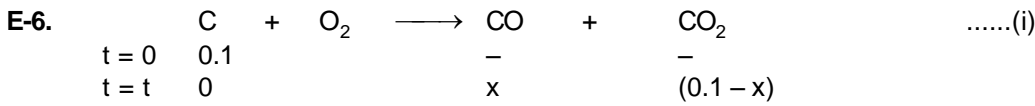
- E-5.** Excess of Mohr's salt = $30 \times 0.1 \times 5$ meq.
= 15 meq
Mohr's salt consumed = $[(35 \times 1.0 \times 1) - 15]$ meq
= 20 meq.



$$\text{So moles of } \text{Cl}_2 = \frac{1}{2} \times \text{moles of } \text{Fe}^{2+} = \frac{1}{2} \text{ eq. of } \text{Fe}^{2+} = \frac{1}{2} \times 20 \text{ m moles} = 10 \text{ mmoles}$$

$$= 10 \times 10^{-3} \times 71 \text{ gm} = 0.71 \text{ gm}$$

$$\text{So, required } \% = \frac{0.71}{10} \times 100 = 7.1\%$$



$$\therefore \text{moles of } \text{I}_2 \text{ liberated} = \frac{1}{2} \times \text{moles of hypo consumed} = \frac{1}{2} \times 120 \times 10^{-3} \times 0.1 = 60 \times 10^{-4}$$

So, $x = 5 \times 60 \times 10^{-4} = 0.03$ moles (from reaction (ii) : 5 × mole of I_2 = mole of CO)

$$\text{So, } \% \text{ of C forming CO} = \frac{0.03 \times 12}{1.2} \times 100 = 30\%$$

- E-7.** From given reactions :

m.moles of hypo = m.moles of iodine $\times 2$ = m.moles of Cu^{2+} ions = 24.5×0.1 m.moles
so, mass of copper = $24.5 \times 0.1 \times 10^{-3} \times 63.5$ g

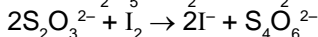
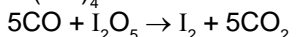
$$\text{so, } \% \text{ of copper} = \frac{24.5 \times 0.1 \times 10^{-3} \times 63.5}{0.305} \times 100 = 51\%$$

- E-8.** 2 moles of Cu^{2+} = 1 mole of I_2
= 2 moles of hypo.

so moles of hypo used = $20 \times 10^{-3} \times 0.1 = 2$ m moles = moles of copper hence

$$\% \text{ of copper} = \frac{2 \times 10^{-3} \times 63.5}{0.2} \times 100 = 63.5\%$$

- E-9.** $\text{Ni}(\text{CO})_4 \xrightarrow{\Delta} \text{Ni} + 4\text{CO}$



so moles of I_2 produced = 4 moles

so moles of hypo used = 8 moles = (4 M) (2 litres).

- F-3.** $\text{BrO}_3^- + 6\text{I}^- \longrightarrow 3\text{I}_2 + \text{Br}^-$

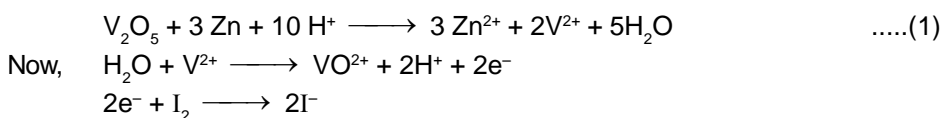
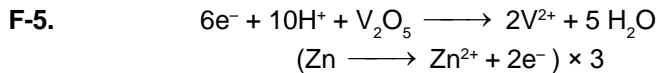
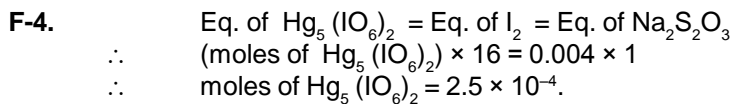
moles of $\text{I}_2 = 3 \times$ moles of KBrO_3

$$\therefore \text{moles of } \text{I}_2 = 0.02 \times 3 = 0.06$$

Eq of $\text{I}_2 = \text{Eq of Hypo}$

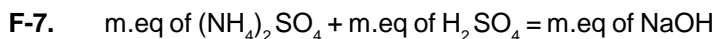
$$0.06 \times 2 = 0.1 \times V$$

$$V = 1.2 \text{ L} = 1200 \text{ mL.}$$



$\text{V}^{2+} + \text{I}_2 + \text{H}_2\text{O} \longrightarrow 2\text{I}^- + \text{VO}^{2+} + 2\text{H}^+$
so, we have overall 1 mole of V_2O_5 reducing 2 moles of iodine

so, $\left(\frac{10}{102 + 80}\right)$ moles of V_2O_5 will be reduce = $\frac{10}{182} \times 2 = 0.11$ moles of I_2

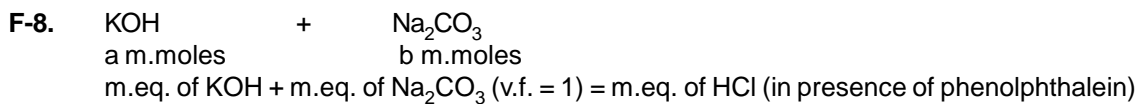


$(\text{m.moles} \times 2) + (0.1 \times 10 \times \frac{250}{25}) = 0.2 \times 100$

$\therefore \text{m.mole of } (\text{NH}_4)_2\text{SO}_4 = 5$

wt. of $(\text{NH}_4)_2\text{SO}_4 = \frac{5}{1000} \times 132 = 0.66 \text{ g}$

$\therefore \% \text{ of } (\text{NH}_4)_2\text{SO}_4 = \frac{0.66}{0.7} \times 100 = 94.28 \% \approx 94.3 \%$



$a \times 1 + b \times 1 = 15 \times \frac{1}{20}$

$\therefore a + b = 0.75 \quad \dots(i) \quad (\text{in presence of phenolphthalein})$

m.eq. of $\text{KOH} + \text{m.eq. of Na}_2\text{CO}_3$ (v.f. = 2) = m.eq. of HCl (in presence of methyl orange)

$1 \times a + 2 \times b = 25 \times \frac{1}{20}$

$\therefore a + 2 \times b = 1.25 \quad \dots(ii) \quad (\text{in presence of methyl orange})$

by solving (i) & (ii), $a = 0.25$ m.moles.

$\therefore \text{mass of KOH} = \frac{0.25}{1000} \times 56 = 0.014 \text{ g}$



$N \times 25 = 0.5 \times 50 + \frac{0.265}{106/2} \times 10^3 \quad \text{or} \quad N = 1.2$

In original H_2SO_4 solution

$N_1V_1 = N_2V_2 \quad \text{or} \quad N_1 \times 10 = 1.2 \times 100 \quad \text{or} \quad N_1 = 12 \text{ N}$

PART - II

2. (A) Eq of $\text{Sn}^{2+} = \text{Moles} \times \text{v.f.} = 3.5 \times 2 = 7.$
Eq of $\text{MnO}_4^- = \text{Moles} \times \text{v.f.} = 1.2 \times 5 = 6.$
Since MnO_4^- (O.A) is the LR, so the amount of oxidant available decides the number of electron transfer.
Also, electron involved per mole of OA (5) > electron involved per mole of RA (2).
(B) Eq of $\text{H}_2\text{C}_2\text{O}_4 = \text{Moles} \times \text{v.f.} = 8.4 \times 2 = 16.8.$
Eq of $\text{MnO}_4^- = \text{Moles} \times \text{v.f.} = 3.6 \times 5 = 18.$
Since $\text{H}_2\text{C}_2\text{O}_4$ (RA) is the LR, so the amount of reductant available decides the number of electron transfer.

Also, electron involved per mole of OA (5) > electron per mole of RA (2).

(C) Eq of $S_2O_3^{2-}$ = Moles \times v.f. = $7.2 \times 1 = 7.2$.

Eq of I_2 = Moles \times v.f. = $3.6 \times 2 = 7.2$.

Since $S_2O_3^{2-}$ (RA) and I_2 (OA) both completely get consumed, so both the amount of reductant and oxidant decides the number of electron transfer.

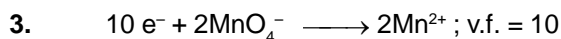
Also, electron involved per mole of OA (2) > electron involved per mole of RA (1).

(D) Eq of Fe^{2+} = Moles \times v.f. = $9.2 \times 1 = 9.2$.

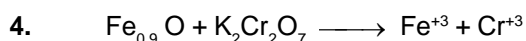
Eq of $Cr_2O_7^{2-}$ = Moles \times v.f. = $1.6 \times 6 = 9.6$.

Since Fe^{2+} (RA) is the LR, so the amount of reductant available decides the number of electron transfer.

Also, electron involved per mole of OA (6) > electron involved per mole RA (1).



$$\therefore \text{Eq. mass of } Ba(MnO_4)_2 = \frac{M}{10}$$



$$n \text{ factor of } Fe_{0.9}O = 0.9 \left(3 - \frac{2}{0.9} \right) = 0.7$$

$$\therefore \text{Eq mass} = \frac{M}{0.7} = \frac{10M}{7}$$

5. n factor is 2

$$\text{Eq. weight} = \frac{M}{2} = \frac{128}{2} = 64.$$

EXERCISE # 2

1. (a) $E = \frac{23}{1} = 23$ (b) $E = \frac{27}{3} = 9$ (c) $E = \frac{30}{1} = 30$

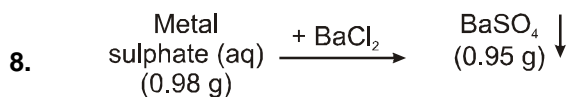
(d) $E = \frac{35.5}{1}$ (e) $E = \frac{60}{2} = 30$ (f) $E = \frac{96}{2} = 48$

(g) $E = \frac{95}{3} = 31.67$

6. v.f. of Cu_2S is $2 + 6 = 8$ \therefore Eq. wt. of $Cu_2S = \frac{M_2}{8}$

v.f. of CuS is 6 \therefore Eq. wt. of $CuS = \frac{M_1}{6}$

v.f. of $KMnO_4$ is 5 \therefore Eq. wt. of $KMnO_4 = \frac{M_3}{5}$



Now, $233.34 \text{ g } BaSO_4 \equiv 96 \text{ g } SO_4^{2-}$

$$\therefore 0.95 \text{ g } BaSO_4 \equiv \frac{96}{233.34} \times 0.95 \text{ or } 0.39 \text{ g } SO_4^{2-}$$

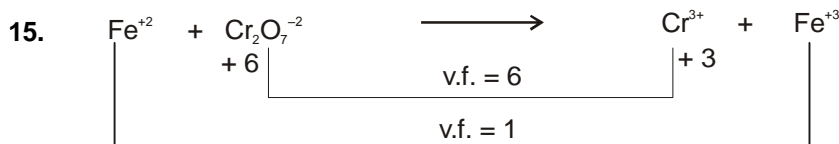
$$\therefore \text{Mass of metal in metal sulphate} = 0.98 - 0.39 = 0.59 \text{ g}$$

Now, $eq_{\text{metal}} = eq_{SO_4^{2-}}$

$$\frac{0.59}{E_{\text{metal}}} = \frac{0.39}{96/2}$$

$$E_{\text{metal}} = 72.61$$

$$\begin{aligned}
 10. \quad \text{Final No. of eq. of H}_2\text{SO}_4 &= 0.2 \times 30 \times 10^{-3} \\
 &= 6 \times 10^{-3} \\
 \text{Initial No. of eq. of H}_2\text{SO}_4 &= 1 \times 30 \times 10^{-3} \\
 &= 30 \times 10^{-3} \\
 \text{No. of reacted Eq. of H}_2\text{SO}_4 &= 24 \times 10^{-3} \\
 \text{So, No. of equivalent of NH}_3 &= 24 \times 10^{-3} \\
 \text{No. of Mole of NH}_3 &= 24 \times 10^{-3} \text{ (v.f. = 1)} \\
 \text{Volume at S.T.P} &= 24 \times 22400 \times 10^{-3} \\
 &= 24 \times 22.4 \text{ mL} \\
 &= 537.6 \text{ mL}
 \end{aligned}$$



$$\begin{aligned}
 \text{No. of m.eq. of Fe}^{+2} &= \text{No. of m.eq. of Cr}_2\text{O}_7^{-2} \\
 [M \times 25] \times 1 &= [0.01 \times 50] \times 6
 \end{aligned}$$

$$M = \frac{0.01 \times 50 \times 6}{25}$$

$$M = 0.02 \times 6 = 0.12$$

18. Lets mole of $\text{FeSO}_4 = x$
 Now, KMnO_4 oxidises only FeSO_4
 equivalent of $\text{FeSO}_4 =$ equivalent of KMnO_4

$$x \times 1 = \frac{100}{1000} \times 2 \times 5 \quad \Rightarrow \quad x = 1$$

$$\text{so, mole fraction of FeSO}_4 = \frac{n_{\text{FeSO}_4}}{n_{\text{mixture}}} = \frac{1}{3}$$

20. Excess of Mohr's salt = $30 \times 0.1 \times 5 \text{ meq.} = 15 \text{ meq}$
 Mohr's salt consumed = $[(35 \times 1 \times 1) - 15] \text{ meq} = 20 \text{ meq.}$
 Now $\text{Cl}_2 + 2\text{Fe}^{2+} \longrightarrow 2\text{Fe}^{3+} + 2\text{Cl}^-$ (balanced equation)

$$\text{So moles of Cl}_2 = \frac{1}{2} \times \text{moles of Fe}^{2+} = \frac{1}{2} \times 20 \times 10^{-3} \text{ moles} = 10 \times 10^{-3} \text{ moles}$$

$$\text{Mass of Cl}_2 = 10 \times 10^{-3} \times 71 = 0.71 \text{ g}$$

$$\text{So, required \% of available Cl}_2 = \frac{0.71}{10} \times 100 = 7.1\%$$

22. Let moles of As_2O_3 and As_2O_5 are x and y respectively. In first step, only As_2O_3 react with I_2 .

$$\begin{aligned}
 \text{So, eq. of As}_2\text{O}_3 &= \text{eq. of I}_2 \\
 x \times 4 &= 20 \times 0.05 \times 10^{-3} \\
 x &= 0.25 \times 10^{-3}
 \end{aligned}$$

$$\begin{aligned}
 \text{wt. of As}_2\text{O}_3 &= x \times \text{Mol. mass} \\
 &= 0.25 \times 10^{-3} \times 198
 \end{aligned}$$

$$\text{wt. of As}_2\text{O}_3 = 0.0495 \text{ g}$$

In second step, As_2O_5 react with I^-

So, total eq. of $\text{As}_2\text{O}_5 =$ eq. of I^- reacted = eq. of I_2 released = eq. of hypo used

$$\text{Total moles of As}_2\text{O}_5 \times \text{v.f.} = \frac{\text{wt. of Hypo} \times \text{v.f.}}{\text{Mol. Mass}}$$

(Total moles of $\text{As}_2\text{O}_5 =$ moles of As_2O_5 formed in 1st stage + moles of As_2O_5 initially present)

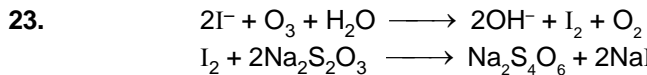
$$(25 \times 10^{-5} + y)4 = \frac{1.116}{248} \times 1$$

$$0.25 \times 10^{-3} + y = 1.125 \times 10^{-3}$$

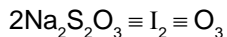
$$y = 0.875 \times 10^{-3}$$

$$\begin{aligned} \text{mass of As}_2\text{O}_5 &= y \times \text{Mol. mass} \\ &= 0.875 \times 10^{-3} \times 230 \\ &= 0.20125 \text{ g} \end{aligned}$$

Total mass of mixture = 0.20125 + 0.0495 = **0.25075 g Ans.**



From the above reaction :

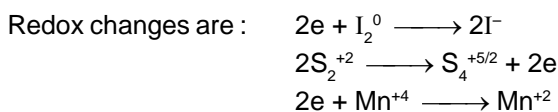
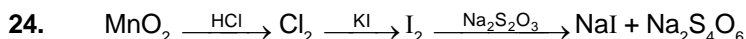


$$\text{moles of Na}_2\text{S}_2\text{O}_3 = \frac{40 \times 0.1}{1000} = 0.004$$

$$\text{moles of I}_2 = \text{moles of O}_3 = 0.002$$

$$\text{volume of O}_3 \text{ at STP} = 0.002 \times 22.4 = 0.0448 \text{ L (present in 1 L mixture)}$$

$$\text{Percentage of O}_3 = \frac{0.0448}{1} \times 100 = \mathbf{4.48\% \text{ (by volume)}}$$



The reactions suggest that :

m.eq. of MnO_2 = m.eq. of Cl_2 formed = m.eq. of I_2 liberated = m.eq. of $\text{Na}_2\text{S}_2\text{O}_3$ used

$$\therefore \frac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30 \quad [\text{v.f. : MnO}_2 = 2, \text{Na}_2\text{S}_2\text{O}_3 = 1]$$

$$\text{or } w = \frac{0.1 \times 1 \times 30 \times M}{2000} = \frac{0.1 \times 1 \times 30 \times 87}{2000} \quad (\because M_{\text{MnO}_2} = 87)$$

$$w_{\text{MnO}_2} = 0.1305 \text{ g} \quad \therefore \text{Purity of MnO}_2 \text{ sample} = \frac{0.1305}{0.5} \times 100 = \mathbf{26.1\%}$$

25. At phenolphthalein end point

eq. of Na_2CO_3 + eq. of NaOH = eq. of HCl used

Let x mole of Na_2CO_3 and y mole of NaOH present in 25 mL solution

$$x \times 1 + y \times 1 = 19.5 \times 0.995 \times 10^{-3}$$

$$x + y = 19.4 \times 10^{-3}$$

.... (i) (The v.f. of Na_2CO_3 is 1 when phenolphthalein is used)

At Methyl orange (MeOH) end point,

eq. of Na_2CO_3 + eq. of NaOH = eq. of HCl used

$$x \times 2 + y \times 1 = 25 \times 0.995 \times 10^{-3}$$

$$2x + y = 24.875 \times 10^{-3}$$

.... (ii) (The v.f. of Na_2CO_3 is 2 when methyl orange (MeOH) is used)

On solving eq. (1) and (2),

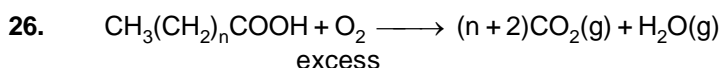
$$x = 5.475 \times 10^{-3} \text{ and } y = 13.925 \times 10^{-3}$$

or wt. of Na_2CO_3 in 25 mL = $5.475 \times 10^{-3} \times 106$

$$\text{wt. of Na}_2\text{CO}_3 \text{ in 1 litre} = \frac{5.475 \times 10^{-3} \times 106}{25} \times 1000 = \mathbf{23.2 \text{ g Ans.}}$$

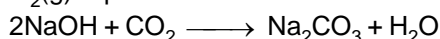
$$\text{wt. of NaOH in 25 mL solution} = 13.925 \times 10^{-3} \times 40$$

$$\text{wt. of NaOH in 1 litre} = \frac{13.925 \times 10^{-3} \times 40}{25} \times 1000 = \mathbf{22.28 \text{ g Ans.}}$$



$$\text{moles of CH}_3(\text{CH}_2)_n\text{COOH} = \frac{\text{moles of CO}_2}{(n+2)} \quad \text{..... (1)}$$

When $\text{CO}_2(\text{g})$ is passed into excess of NaOH solution, then Na_2CO_3 will form according to reaction :



$$\therefore \text{moles of NaOH reacted} = 2 \times \text{moles of Na}_2\text{CO}_3 \quad \text{..... (2)}$$

Now solution contain remaining NaOH and Na_2CO_3 formed.

Let moles of NaOH and Na_2CO_3 are x and y respectively and solution divided into two equal parts.

Part I : At Ph end point,
Eq. of NaOH + eq. of Na₂CO₃ = Eq. of HCl used

$$\frac{x}{2} \times 1 + \frac{y}{2} \times 1 = 50 \times 1 \times 10^{-3}$$

$$x + y = 0.1 \quad \dots\dots\dots (1)$$

Part II : At MeOH end point,
Eq. of NaOH + eq. of Na₂CO₃ = Eq. of HCl used

$$\frac{x}{2} \times 1 + \frac{y}{2} \times 2 = 80 \times 1 \times 10^{-3}$$

$$x + 2y = 0.16 \quad \dots\dots\dots (2)$$

On solving equation (1) and (2),
y = 0.06
x = 0.04

Since moles of CO₂ = moles of Na₂CO₃ = 0.06
∴ From equation (1),

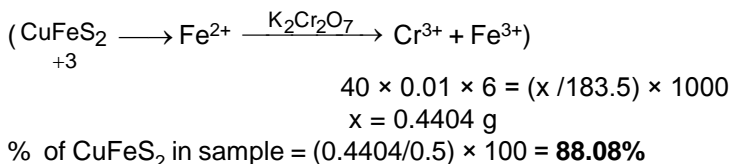
$$\frac{1.16}{48 + 14n} = \frac{0.06}{n + 2}$$

On solving, we get **n = 4 Ans.**
Amount of NaOH remaining = 0.04 mole
Amount of NaOH reacted = moles of Na₂CO₃ × 2
= 0.06 × 2 = 0.12
Total moles of NaOH taken = 0.04 + 0.12 = 0.16
wt. of NaOH taken = 0.16 × 40 = **6.4 g.**

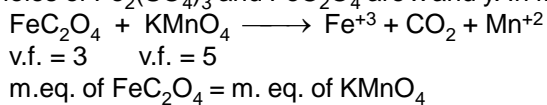
- 28.** millimoles of K₂Cr₂O₇ = 25 × 0.002 = 0.050
meq or millimoles of Fe²⁺ present in water sample = 25 × 0.002 × 6 – 7.5 × 0.01 = 0.225
∴ Mass of Fe²⁺ in water sample = 0.225 × 56 × 10⁻³ = 12.6 × 10⁻³ grams
assuming 100 mL water = 100 gram water

$$\text{ppm} = \frac{12.6 \times 10^{-3}}{100} \times 10^6 = \mathbf{126 \text{ ppm}}$$

- 29.** Each mole of K₂Cr₂O₇ releases 6 moles of electrons which is used by Fe for its reduction so assuming the sample contains x grams of CuFeS₂ originally.



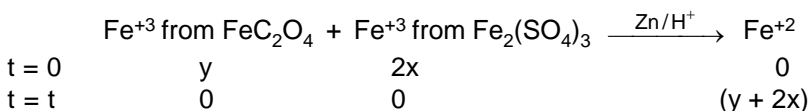
- 30.** Let m.moles of Fe₂(SO₄)₃ and FeC₂O₄ are x and y. In first reaction, only FeC₂O₄ react with KMnO₄ as :



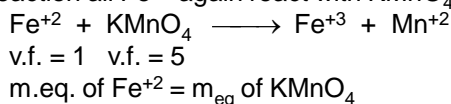
$$y \times 3 = 40 \times \frac{1}{16}$$

$$y = \frac{40}{48} \quad \dots\dots\dots (1)$$

In IInd reaction, all Fe⁺³ is convert into Fe⁺² :



In IIIrd reaction all Fe⁺² again react with KMnO₄ as :



$$y + 2x = 60 \times \frac{1}{16}$$

Putting the value of y from equation 1st,

$$2x = \frac{60}{16} - \frac{40}{48}$$

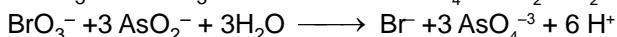
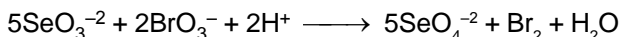
$$2x = \frac{140}{48}$$

$$x = \frac{70}{48} \quad \dots\dots\dots (2)$$

From eq. (1) and (2),

$$\frac{x}{y} = \frac{7}{4} \text{ Ans.}$$

31. Balanced reactions are :



total millimoles of $\text{BrO}_3^- = 20 \times 1/60 = 1/3$

millimoles of BrO_3^- backtitrated = $5 \times 1/25 \times 1/3 = 1/15$

millimoles of BrO_3^- consumed for $\text{SeO}_3^{-2} = 1/3 - 1/15 = 4/15$

5 millimoles of $\text{SeO}_3^{-2} = 2$ millimoles of BrO_3^- (from 1st reactions)

millimoles of SeO_3^{-2} for reaction = $4/15 \times 5/2 = 2/3$

mass of $\text{SeO}_3^{-2} = 2/3 \times 127 = 84.67 \text{ mg}$

EXERCISE # 2

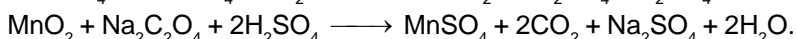
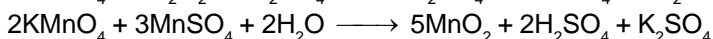
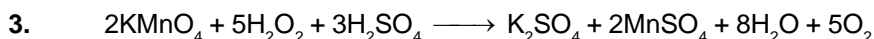
1. Eq. mass = $\frac{\text{Molecular weight}}{\text{Change in oxidation No. of Mn}} = \frac{\text{Mol. wt.}}{4-2} = \frac{\text{Mol. wt.}}{2}$

(O.N. of Mn in $\text{MnSO}_4 = +2$; O.N. of Mn in $\text{MnO}_2 = +4$).

2. (A) Equivalents of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 10 mL = Equivalents of NaOH

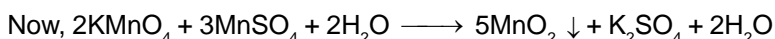
$$\left(\frac{6.3}{126/2} \times \frac{1000}{250} \right) \times \frac{10}{1000} = 0.1 \times V \text{ (in litre)}$$

$$\therefore V = 0.04 \text{ L} = 40 \text{ mL.}$$



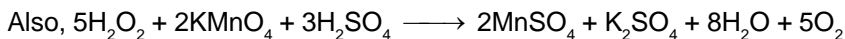
$$\therefore \text{meq. of MnO}_2 = \text{meq of Na}_2\text{C}_2\text{O}_4 = 10 \times 0.2 \times 2 = 4$$

$$\therefore \text{millimoles of MnO}_2 = \frac{4}{2} = 2 \quad \left[\begin{array}{l} \text{Mn}^{4+} + 2\text{e} \rightarrow \text{Mn}^{2+} \\ \therefore \text{Valency factor of MnO}_2 = 2 \end{array} \right]$$



Since MnO_2 is derived from KMnO_4 and MnSO_4 both, thus it is better to proceed by mole concept

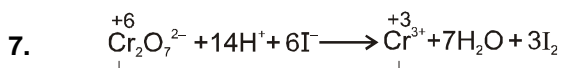
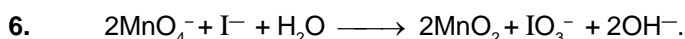
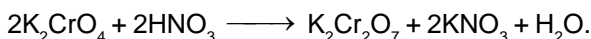
millimoles of $\text{KMnO}_4 = \text{millimoles of MnO}_2 \times (2/5) = 4/5$



$$\therefore \text{millimoles of H}_2\text{O}_2 = \text{millimoles of KMnO}_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$$

$$\therefore M_{\text{H}_2\text{O}_2} \times 20 = 2 \quad \text{or} \quad M_{\text{H}_2\text{O}_2} = 0.1 \text{ M}$$

5. Dilute nitric acid converts chromate into dichromate and H_2O .



8.
$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \longrightarrow 2\text{Cr}^{3+} + \text{Fe}^{3+} + 7\text{H}_2\text{O}$$

$$n = 6 \qquad n = 1$$

 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ will require six moles of Fe^{2+} ions.
9. HCl reduces MnO_4^- to Mn^{2+} and itself oxidises to Cl_2 .
10. Weight of organic compound = 29.5 mg
 $\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$
 HCl (remaining) + NaOH \longrightarrow NaCl + H_2O
 (1.5 m mole)
 Total millimole of HCl = 2
 milli mole of HCl used by $\text{NH}_3 = 2 - 1.5 = 0.5$
 milli mole of $\text{NH}_3 = 0.5$
 weight of $\text{NH}_3 = 0.5 \times 17 \text{ mg} = 8.5 \text{ mg}$
 weight of nitrogen = $\frac{14}{17} \times 8.5 \text{ mg} = 7 \text{ mg}$
 \therefore % of Nitrogen in compound = $\frac{7}{29.5} \times 100 = 23.7 \%$.
11. milli mole of Hypo = 0.25×48
 $= 2 \times$ milli mole of Cl_2
 milli mole of $\text{Cl}_2 = \frac{0.25 \times 48}{2} = 6$ milli mole
 $=$ milli mole of $\text{Cl}_2 =$ milli mole of CaOCl_2
 So, molarity = $\frac{6}{25} \text{ M} = 0.24 \text{ M}$
12. $\text{CaOCl}_2 = \text{Ca}(\text{OCl})\text{Cl}$
 OCl^- – Hypochlorite ion
 which is anion of HOCl
 Anhydride of HOCl = Cl_2O .

SOLUTION OF ADVANCED LEVEL PROBLEM

1. $85.5 = E_{\text{metal}} + E_{\text{OH}^-}$
 or $85.5 = E_{\text{metal}} + 17$
 or $E_{\text{metal}} = 68.5$
2. (a) $E_{\text{P}} = \frac{31}{3} = 10.33$ (b) $E_{\text{Al}} = \frac{27}{3} = 9$ (c) $E_{\text{Fe}} = \frac{56}{2} = 28$ (d) $E_{\text{S}} = \frac{32}{6} = 5.33$
3. 40 g, O \equiv 60 g metal
 \therefore 8 g, O \equiv 12 g metal (E)
4. v.f. of $\text{Na}_2\text{S}_2\text{O}_3 = 2(2.5 - 2) = 1$
 \therefore Eq. wt. = $M/1$
5. v.f. of $\text{KBrO}_3 = 1(5 - (-1)) = 6$
 \therefore Eq. wt. = $\frac{M}{6}$
6. v.f. of oxalic acid = $2(4 - 3) = 2$
 \therefore Eq. wt. = $\frac{M}{2}$
7. $\text{meq}_{\text{H}_2\text{SO}_4} = \text{meq}_{\text{NaOH}}$
 $0.2 \times V = 0.02 \times 20$
 $V = 2 \text{ mL}$

8. m eq. of HCl reacted with alkaline earth metal carbonate = $(25 \times 1) - (50 \times 0.1) = 20$

\therefore m eq. of alkaline earth metal carbonate = 20

$\therefore \frac{1}{\text{Eq. wt.}} \times 1000 = 20$

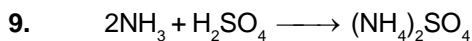
\therefore Eq. wt. of metal carbonate = $\frac{1000}{20} = 50$

Eq. wt. of Metal = Eq. wt. of metal carbonate – Eq. wt. of carbonate

$= 50 - \frac{60}{2} = 20$

At wt. of metal = (Eq. wt. of metal) \times Valency of metal

$= 20 \times 2 = 40$

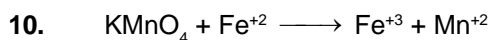


\therefore m.eq of H_2SO_4 neutralized by $\text{NH}_3 = (50 \times 1) - (24.5 \times 1) = 25.5$

\therefore m.moles of NH_3 present in double sulphate = 25.5

\therefore Mass of NH_3 present in double sulphate = $\left(\frac{25.5}{1000} \times 17\right) = 0.4335 \text{ g}$

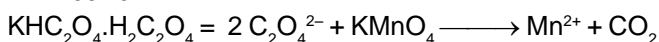
\therefore % of NH_3 in double sulphate = $\frac{0.4335}{5} \times 100 = 8.67\%$



milli equivalent of $\text{KMnO}_4 =$ milli equivalent of Fe^{2+}

$1 \times 5 \times M = 1 \times \frac{140}{56}$

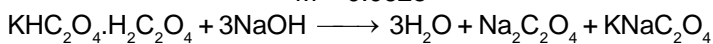
$M = \frac{140 \times 1}{56 \times 5} = 0.5$



milli eq. of $\text{KMnO}_4 =$ milli eq. of $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$

$100 \times 5 \times 0.5 = 1 \times 2 \times 2 \times M$

$M = 0.0625$



meq of $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 =$ meq of NaOH

$3 \times 1 \times 0.0625 = 0.20 \times V$

$V = \frac{3 \times 0.0625}{0.20} = 0.9375 \text{ mL} \quad \text{or} \quad \frac{15}{16} \text{ mL.}$

11. milli eq. of $\text{FeSO}_4 =$ milli eq. of KMnO_4

$N_1 V_1 = N_2 V_2$

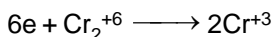
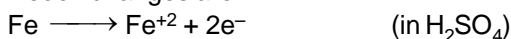
$N_1 \times 25 = \frac{1}{10} \times 20$

$N_1 = \frac{20}{10 \times 25} = M_1 \text{ (V.f. = 1)}$

Weight of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $W = \frac{20}{10 \times 25} \times 278 = 22.24 \text{ g}$

% of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{22.24}{25} \times 100 = 88.96 \%$

12. Redox changes are :



m.eq. of Fe^{+2} in 20 mL = m.eq. of $\text{K}_2\text{Cr}_2\text{O}_7 = 30 \times \frac{1}{30} = 1$

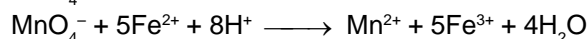
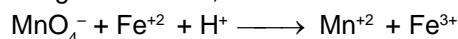
\therefore m.eq. of Fe^{+2} in 100 mL = $\frac{1 \times 100}{20} = 5$

$$\therefore \text{m.moles of Fe}^{+2} = \frac{\text{meq}}{\text{v.f.}} = \frac{5}{1} = 5 = \text{m.moles of Fe}$$

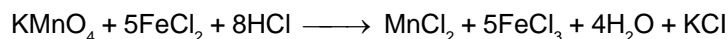
$$\therefore \text{Mass of pure Fe in wire} = 5 \times 10^{-3} \times 56 = 0.28 \text{ g}$$

$$\% \text{ of Fe in wire} = \frac{0.28}{0.2828} \times 100 = \mathbf{99\%}$$

13. On balancing the reaction,



or



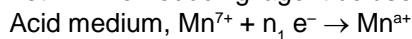
$$\text{moles } \frac{10}{158} \quad 1.07 \quad \frac{500}{1000} \times 3 = 1.5$$

So, KMnO_4 is limiting reagent.

$$\therefore \frac{\text{mole of KMnO}_4}{1} = \frac{\text{Mole of FeCl}_3}{5}$$

$$\text{mole of FeCl}_3 = \frac{10}{158} \times 5 = 0.316$$

14. Let V mL of reducing agent be used for KMnO_4 in different medium which act as oxidant



$$\therefore n_1 = 7 - a$$



$$\therefore n_2 = 7 - b$$



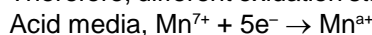
$$\therefore n_3 = 7 - c$$

$$\begin{aligned} \therefore \text{meq of reducing agent} &= \text{meq. of KMnO}_4 \text{ in acid} \\ &= \text{meq. of KMnO}_4 \text{ in neutral} \\ &= \text{meq. of KMnO}_4 \text{ in alkali} \\ &= 1 \times n_1 \times 20 = 1 \times n_2 \times 33.3 = 1 \times n_3 \times 100 \end{aligned}$$

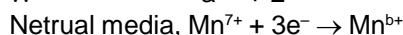
$$\therefore n_1, n_2, n_3 \text{ are integers and are } \leq 7,$$

$$\therefore n_1 = 5, n_2 = 3 \text{ and } n_3 = 1$$

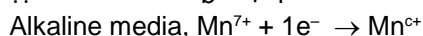
Therefore, different oxidation state of Mn are :



$$\therefore a = +2$$



$$\therefore b = +4$$



$$\therefore c = +6$$

Now, same volume of reducing agent is treated with $\text{K}_2\text{Cr}_2\text{O}_7$ and therefore,

$$\text{m.eq. of reducing agent} = \text{m.eq. of } \text{K}_2\text{Cr}_2\text{O}_7$$

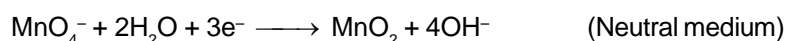
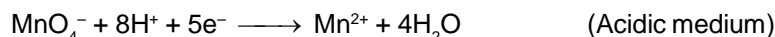
But, m.eq. of reducing agent = m.eq. of KMnO_4 in acid

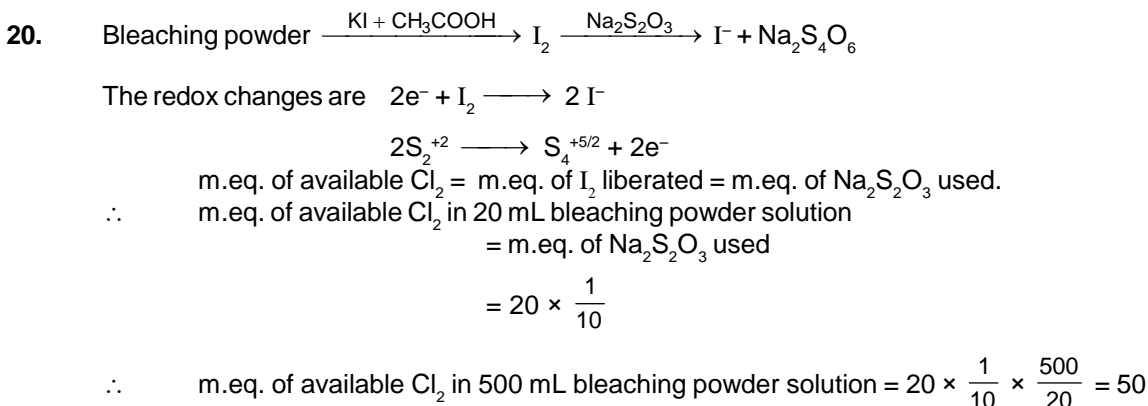
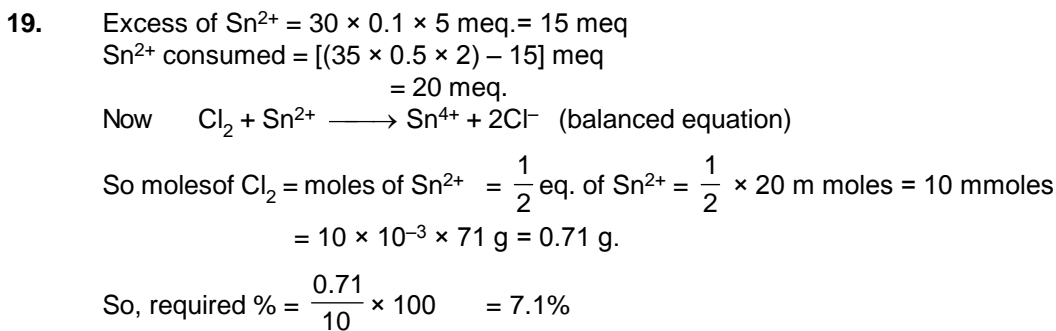
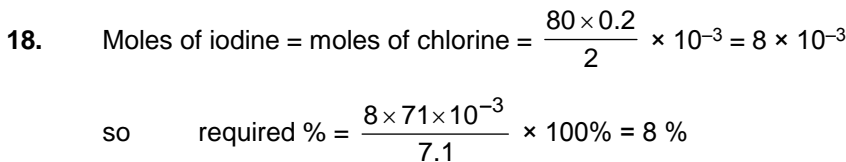
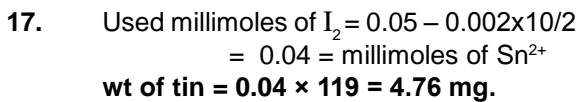
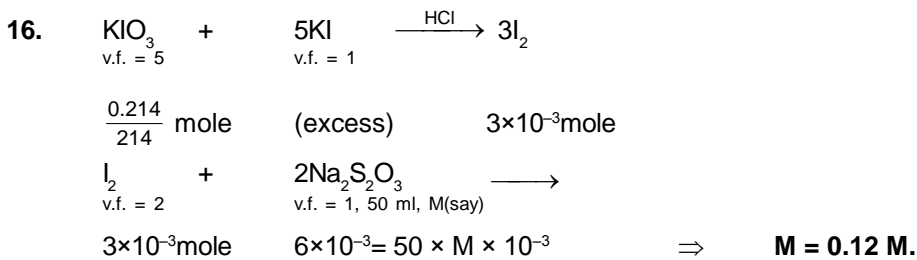
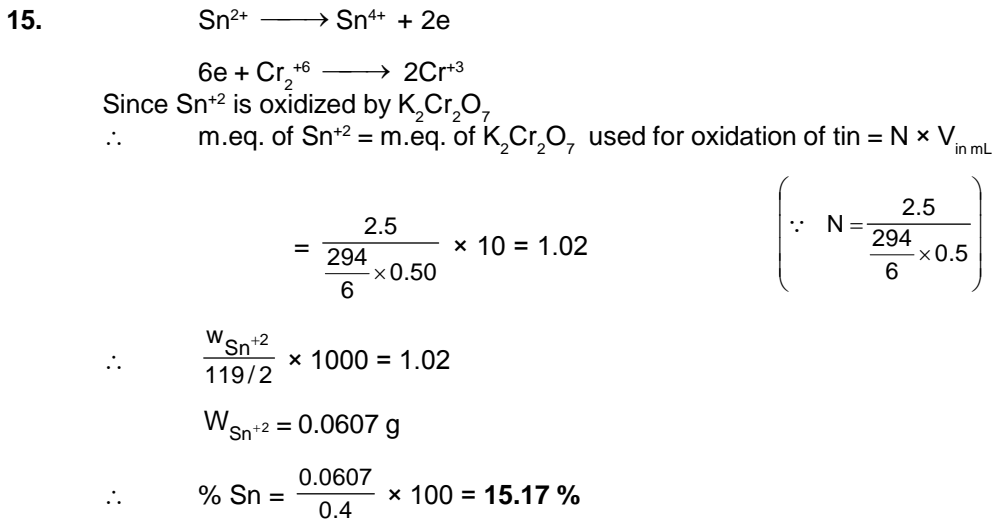
$$\therefore \text{m.eq. of KMnO}_4 \text{ in acid} = \text{m.eq. of } \text{K}_2\text{Cr}_2\text{O}_7 \quad (\text{v.f. for } \text{Cr}_2\text{O}_7^{2-} = 6)$$

$$V = \frac{100}{6} = \mathbf{16.67 \text{ mL}}$$

It is important to note that the conditions are valid only when Mn in each medium exist as monomeric atom, i.e. not as Mn_2 .

Balanced equations for three half reactions :

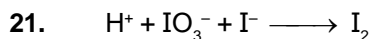




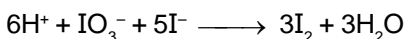
$$\therefore \frac{w}{71/2} \times 1000 = 50 \quad (w = \text{weight of available Cl}_2)$$

$$\therefore w = \frac{50}{1000} \times \frac{71}{2} = 1.775 \text{ g}$$

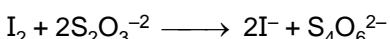
$$\therefore \% \text{ of available Cl}_2 \text{ in bleaching powder} = \frac{1.775}{5} \times 100 = 35.5\%$$



On balancing the reaction,



Let normality of HCl is X.



m.eq. of I_2 = m.eq. of $\text{Na}_2\text{S}_2\text{O}_3$

$$\therefore (\text{millimoles of I}_2) \times 2 = M \times \text{v.f.} \times V$$

$$\text{milli moles of I}_2 = \frac{0.021 \times 24 \times 1}{2} = 0.252$$

$$\text{Now, } \frac{\text{m.mole of HCl}}{6} = \frac{\text{m.mole of I}_2}{3}$$

$$\frac{25 \times X/1}{6} = \frac{0.252}{3} \quad (\text{v.f. for HCl} = 1)$$

$$\therefore X = 0.02 \text{ N}$$

$$\frac{\text{m.mole of IO}_3^-}{1} = \frac{\text{m.mole of I}_2}{3}$$

$$0.2 \times V = \frac{0.252}{3}$$

$$V = 0.42 \text{ mL}$$

22. Mole of $\text{KMnO}_4 = 20 \times 10^{-3} \times \frac{1}{50} = \frac{2}{5} \times 10^{-3}$

$$\text{so, mole of Fe}^{2+} = 5 \times \frac{2}{5} \times 10^{-3} = 2 \times 10^{-3}$$

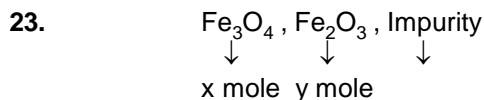
$$\text{so, mole of N}_2\text{H}_4 = \frac{1}{4} \times 2 \times 10^{-3} = \frac{1}{2} \times 10^{-3}$$

Now mole of $\text{N}_2\text{H}_6\text{SO}_4$ = mole of N_2H_4

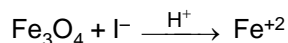
$$\text{so, mass of N}_2\text{H}_6\text{SO}_4 = \frac{1}{2} \times 10^{-3} \times 130 = 65 \times 10^{-3} \text{ g}$$

$$\text{so, in 10 mL solution, quantity of N}_2\text{H}_6\text{SO}_4 = 65 \times 10^{-3} \text{ g}$$

$$\therefore \text{in 1 liter solution, quantity of N}_2\text{H}_6\text{SO}_4 = \frac{65 \times 10^{-3}}{10} \times 1000 \text{ g} = 6.5 \text{ g}$$

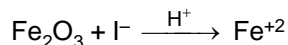


In first reaction,



v.f. = 2

x mole 3x mole



v.f. = 2

y mole 2y mole

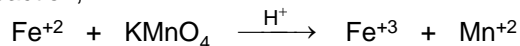
(Eq. of Fe_3O_4 + Eq. of Fe_2O_3) in 10 mL solution = Eq. of Hypo

$$2(x + y) \times \frac{10}{50} = 4.8 \times 1 \times 10^{-3}$$

$$2x + 2y = 4.8 \times 10^{-3} \times 5$$

$$x + y = 12 \times 10^{-3} \quad \dots(1)$$

In IInd reaction,



$$\text{v.f.} = 1 \quad \text{v.f.} = 5$$

$$\text{moles } 3x + 2y \quad 3.2 \times 10^{-3} \times 1$$

eq. of Fe^{+2} in 25 mL solution = eq. of KMnO_4

$$(3x + 2y) \times \frac{10}{20} = 3.2 \times 1 \times 5 \times 10^{-3}$$

$$3x + 2y = 32 \times 10^{-3} \quad \dots(2)$$

On solving eq. (1) and (2),

$$x = 8 \times 10^{-3}$$

$$y = 4 \times 10^{-3}$$

$$\text{wt. of } \text{Fe}_3\text{O}_4 = 8 \times 10^{-3} \times 232 = 1.856 \text{ g}$$

$$\text{wt. of } \text{Fe}_2\text{O}_3 = 160 \times 4 \times 10^{-3} = 0.64 \text{ g}$$

$$\% \text{Fe}_3\text{O}_4 = \frac{1.856}{6} \times 100 = \mathbf{30.93 \% \text{ Ans.}} ; \quad \% \text{Fe}_2\text{O}_3 = \frac{0.64}{6} \times 100 = \mathbf{10.67 \% \text{ Ans.}}$$

24. Let, weight of $\text{H}_2\text{C}_2\text{O}_4$ = 'a' g and weight of NaHC_2O_4 = 'b' g for acid base reaction

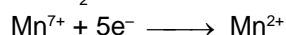
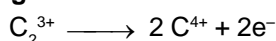
$$(\text{meq. of } \text{H}_2\text{C}_2\text{O}_4 + \text{meq. of } \text{NaHC}_2\text{O}_4) \text{ in } 10 \text{ mL} = 3 \times 0.1$$

$$\therefore \text{meq. of } \text{H}_2\text{C}_2\text{O}_4 + \text{meq. of } \text{NaHC}_2\text{O}_4 \text{ in one litre} = 3 \times 0.1 \times 100 = 30$$

$$\therefore \frac{a}{90/2} \times 1000 + \frac{b}{112/1} \times 1000 = 30$$

$$\therefore \frac{1000a}{45} + \frac{1000b}{112} = 30 \quad \dots(1)$$

For redox change :



$$(\text{meq. of } \text{H}_2\text{C}_2\text{O}_4 + \text{meq. of } \text{NaHC}_2\text{O}_4) \text{ in } 10 \text{ mL} = 4 \times 0.1$$

$$\therefore \text{meq. of } \text{H}_2\text{C}_2\text{O}_4 + \text{meq. of } \text{NaHC}_2\text{O}_4 \text{ in } 1 \text{ litre} = 4 \times 0.1 \times 100 = 40$$

$$\therefore \frac{a}{90/2} \times 1000 + \frac{b}{112/2} \times 1000 = 40$$

$$(\therefore \text{eq. wt. of } \text{H}_2\text{C}_2\text{O}_4 = \frac{M}{2} \text{ and eq. wt. of } \text{NaHC}_2\text{O}_4 = \frac{M}{2} \text{ as reductant})$$

$$\therefore \frac{1000a}{45} + \frac{2000b}{112} = 40 \quad \dots(2)$$

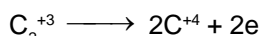
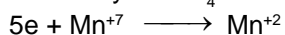
Solving equation (1) and (2), we get :

$$a = 0.9 \text{ g and } b = 1.12 \text{ g}$$

(Also given : $a + b = 2.02$ and thus equation (1) or (2) can be used to find a and b by using $a + b = 2.02$)

25. Let 'a' mole of Cu^{+2} and 'b' mole of $\text{C}_2\text{O}_4^{2-}$ be present in solution.

Case I : The solution is oxidized by KMnO_4 which reacts with only $\text{C}_2\text{O}_4^{2-}$.

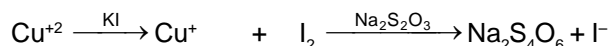


$$\therefore \text{m. eq. of } \text{C}_2\text{O}_4^{2-} = \text{m. eq. of } \text{KMnO}_4$$

$$\therefore b \times 2 \times 1000 = 0.02 \times 5 \times 22.6$$

$$\therefore b = 1.13 \times 10^{-3}$$

Case II : After oxidation of $\text{C}_2\text{O}_4^{2-}$, the resulting solution is neutralized by Na_2CO_3 , acidified with dilute CH_3COOH and then treated with excess of KI . The liberated I_2 required $\text{Na}_2\text{S}_2\text{O}_3$ for its titration :



$$\begin{aligned} \therefore \text{m. eq. of Cu}^{+2} &= \text{m. eq. of I}_2 \text{ liberated} = \text{m. eq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \\ \therefore \text{m. eq. of Cu}^{+2} &= \text{m. eq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \\ a \times 1 \times 1000 &= 11.3 \times 0.05 \times 1 \\ \therefore a &= 5.65 \times 10^{-4} \\ \therefore \text{Molar ratio} &= \frac{\text{Cu}^{+2}}{\text{C}_2\text{O}_4^{2-}} = \frac{a}{b} = \frac{5.65 \times 10^{-4}}{1.13 \times 10^{-3}} = \frac{1}{2} \end{aligned}$$

26. Number of millimoles of KIO_3 in 30 mL of solution = Molarity \times Volume in mL

$$= \frac{1}{10} \times 30 = 3$$

Given equation : $\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \longrightarrow 3\text{ICl} + 3\text{KCl} + 3\text{H}_2\text{O}$

According to the equation of the reaction given, 1 mole of KIO_3 is equivalent to 2 moles of KI

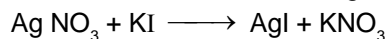
\therefore No. of millimoles of KI in 20 mL of stock solution = $2 \times 3 = 6$

\therefore No. of millimoles of KI in 50 mL of the same solution = $6 \times \frac{50}{20} = 15$

No. of millimoles of KIO_3 in 50 mL of solution = $\frac{1}{10} \times 50 = 5$

\therefore No. of millimoles of KI used with 50 mL of KIO_3 solution = $2 \times 5 = 10$ (from reaction)

\therefore No. of millimoles of KI used with $\text{AgNO}_3 = 15 - 10 = 5$



1 mole of AgNO_3 reacts with 1 mole of KI. Therefore,

\therefore No. of millimoles of AgNO_3 is equal to 5.

\therefore Weight of $\text{AgNO}_3 = 5 \times 10^{-3} \times 170 \text{ g} = 0.85 \text{ g}$

\therefore % of $\text{AgNO}_3 = \frac{0.85 \times 100}{1} = 85 \%$

27. Assume 10 mL of titrant, so there is $0.1 \times 10 = 1$ m.mole NaOH or KMnO_4 . The acidity is due of $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 (\text{KH}_3\text{A}_2)$

m.eq. of $\text{KH}_3\text{A}_2 = \text{m.eq. of NaOH}$

$3 \times \text{m.mole of KH}_3\text{A}_2 = \text{m.mole of NaOH} \times 1$

\therefore m.moles of $\text{KH}_3\text{A}_2 = 1 \times \frac{1}{3} = 0.33$ (1)

m.eq. of $\text{KMnO}_4 = \text{m.eq. of Na}_2\text{A} + \text{m.eq. of KH}_3\text{A}_2$

$5 \times \text{m.mole of KMnO}_4 = \text{m.mole of Na}_2\text{A} \times 2 + \text{m.mole of KH}_3\text{A}_2 \times 4$ ($\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2$, v.f. = 2)

$\therefore 5 \times 1 = \text{m.mole of Na}_2\text{A} \times 2 + 0.33 \times 4$ (from (1))

\therefore m.mole of $\text{Na}_2\text{A} = 1.83$ (2)

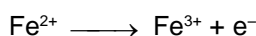
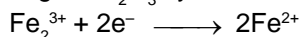
From (1) and (2),

$$\frac{m_{\text{Na}_2\text{A}}}{m_{\text{KH}_3\text{A}_2}} = \frac{1.83 \times 10^{-3} \times 134}{0.33 \times 10^{-3} \times 218} = 3.38$$

\therefore Mixing proportion by mass = 3.38 : 1.

28. The redox changes are :

for reducing of Fe_2O_3 by zinc dust



oxidant + $n\text{e}^- \longrightarrow$ product

meq. of Fe_2O_3 in 25 mL

= meq. of Fe^{3+} in Fe_2O_3

= meq. of Fe^{2+} formed

= meq. of oxidant used to oxidize Fe^{2+} again

\therefore meq. of Fe_2O_3 in 25 mL = meq of oxidant

$$= 17 \times 0.0167 \times n$$

Where, n is the number of electron gained by 1 mole of oxidant

\therefore meq. of Fe_2O_3 in 100 mL = $17 \times 0.0167 \times n \times \frac{100}{25}$

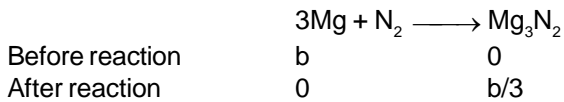
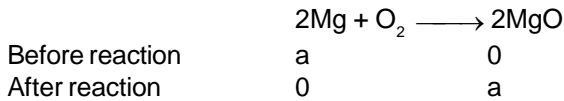
$$\therefore \frac{1 \times 55.2 \times 1000}{100 \times \frac{M}{2}} = 17 \times 0.0167 \times n \times 4$$

$$\therefore \text{molecular wt. of Fe}_2\text{O}_3 = 160$$

$$\therefore n = \frac{1 \times 55.2 \times 1000 \times 2}{100 \times 160 \times 17 \times 0.0167 \times 4} = 6$$

Hence, number of moles of electrons gained by one mole of oxidant = 6 .

29. Let total mole of Mg used for MgO and Mg_3N_2 be 'a' and 'b' respectively.



Now $(a + b/3)$ mole of MgO and Mg_3N_2 are present in the mixture.



or the solution contains 'a' mole of MgCl_2 from MgO and 'b' mole of MgCl_2 from Mg_3N_2 and $\frac{2b}{3}$ mole of NH_4Cl .

$$\text{Also mole of HCl used for this purpose} = 2a \quad + \quad \frac{8b}{3}$$

(for MgO) (for Mg_3N_2)

$$\text{Now mole of HCl reacted with MgO and } \text{Mg}_3\text{N}_2 = \frac{60-12}{1000} = 0.048$$

$$2a + \frac{8b}{3} = 0.048 \quad \dots (1)$$

$$\begin{aligned} \text{Further, mole of } \text{NH}_4\text{Cl} \text{ formed} &= \text{mole of } \text{NH}_3 \text{ liberated} \\ &= \text{mole of HCl used for absorbing } \text{NH}_3 \\ &= \text{Total equivalent of acid} - \text{equivalent of base used for back titration} \\ &= \frac{10-6}{1000} = 4 \times 10^{-3} \end{aligned}$$

$$\therefore \frac{2b}{3} = 4 \times 10^{-3} \quad \text{or} \quad b = 6 \times 10^{-3} \quad \dots (2)$$

$$\text{From (1)} \quad 2a + \frac{8 \times 6 \times 10^{-3}}{3} = 0.048 \quad \text{or} \quad a = 16 \times 10^{-3}$$

$$\text{Thus, \% of Mg burnt to } \text{Mg}_3\text{N}_2 = \frac{6}{(6+16)} \times 100 = \mathbf{27.27\%}$$

30. In presence of Hph indicator

$$\text{m. eq. of HCl} = \text{m. eq. of Na}_2\text{CO}_3 + \text{m. eq. of NaOH}$$

$$30 \times 0.1 = (a \times 1) + (a \times 1)$$

$$\therefore a = 1.5$$

In presence of MeOH indicator

$$\text{m. eq. of } \text{H}_2\text{SO}_4 = \text{m. eq. of Na}_2\text{CO}_3 + \text{m. eq. of NaOH}$$

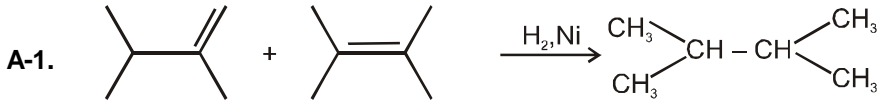
$$0.15 \times 2 \times V = (a \times 2) + (a \times 1)$$

$$V = 15 \text{ ml}$$

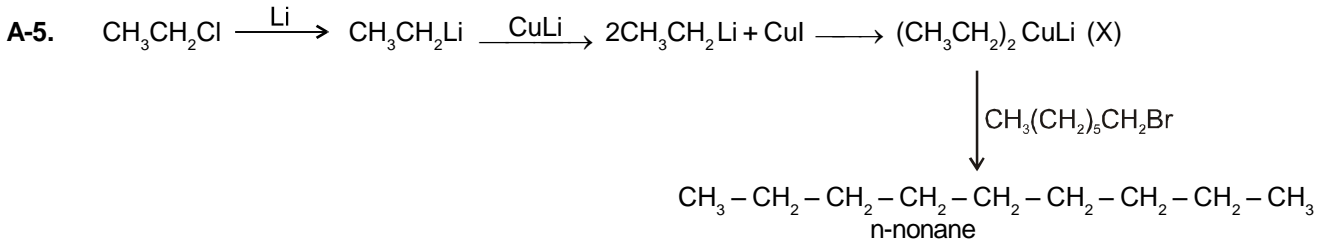
HYDROCARBONS

EXERCISE # 1

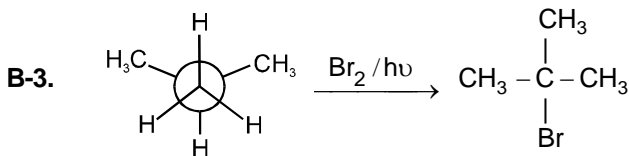
PART - I



A-2. Symmetrical alkane with even no. of carbon atoms can be prepared by Wurtz reaction.

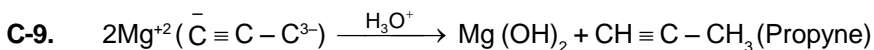
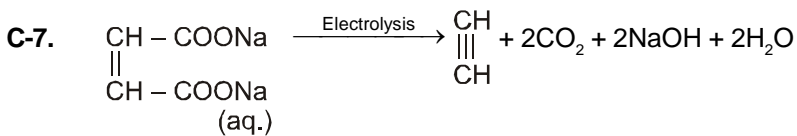
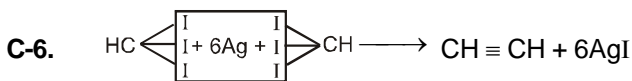
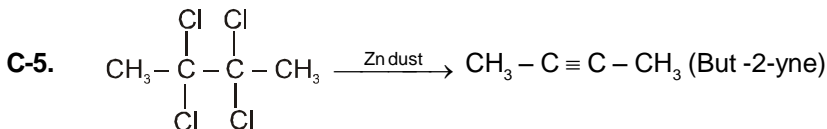
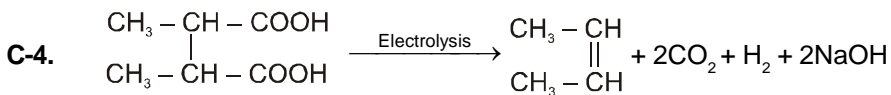


A-6. β -keto acid decarboxylate readily.



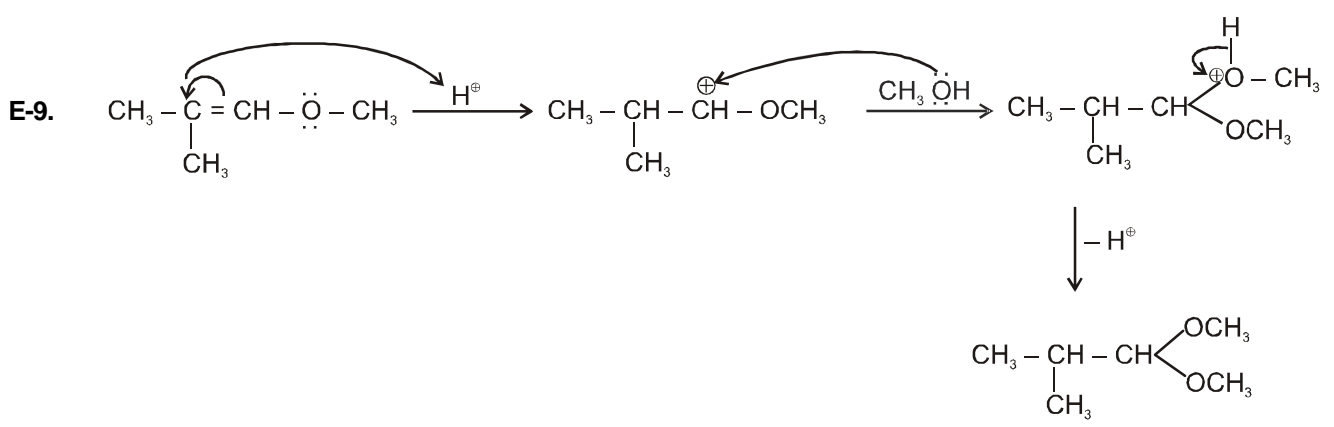
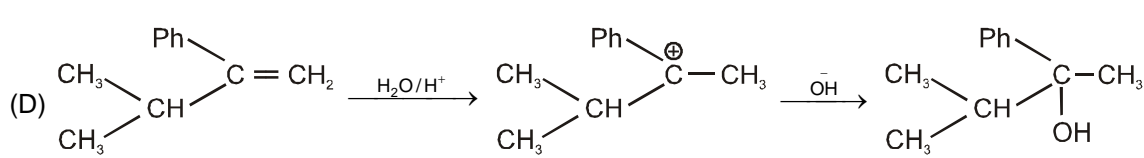
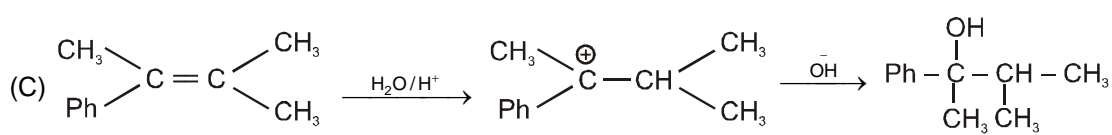
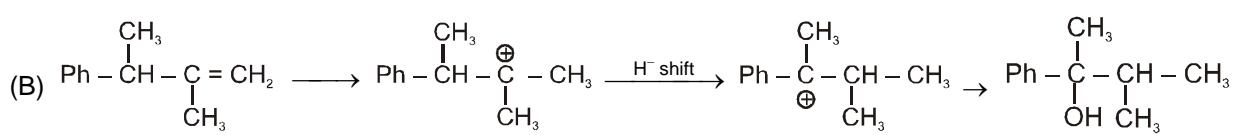
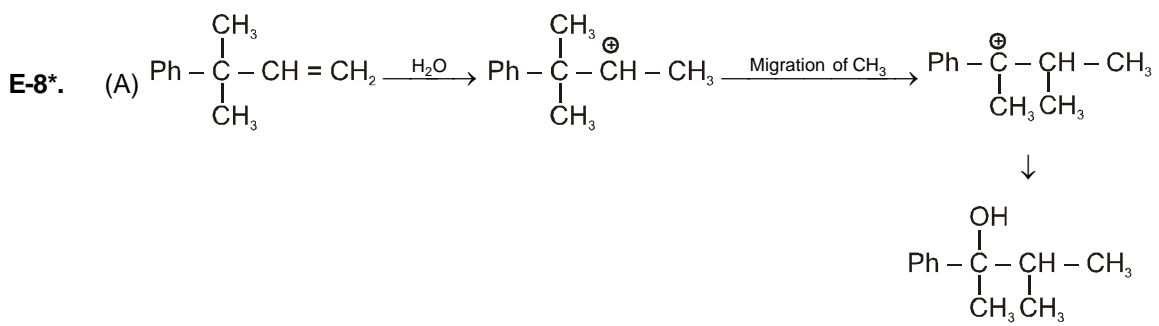
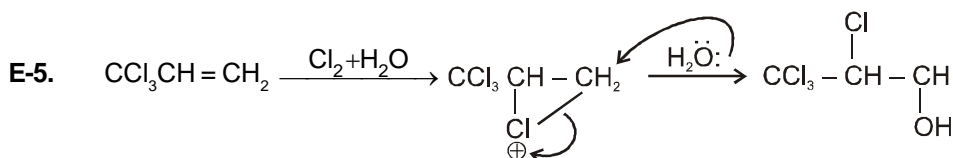
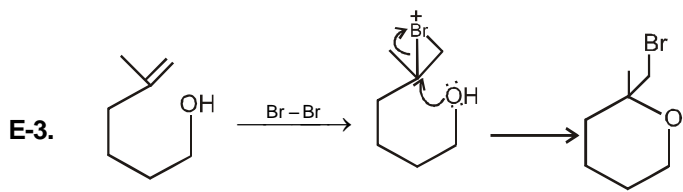
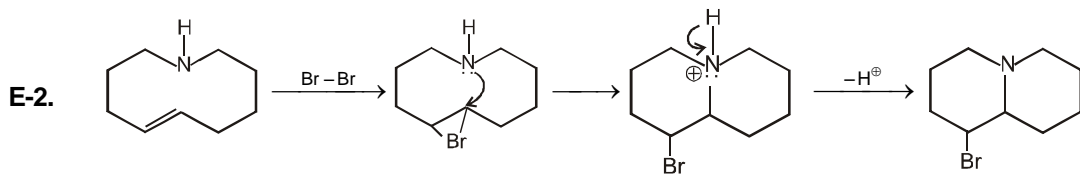
B-5. Bromine atom has a much higher regioselectivity than chlorine atom in abstracting 3° hydrogen.

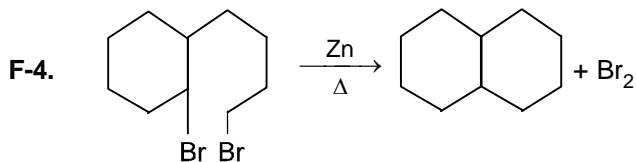
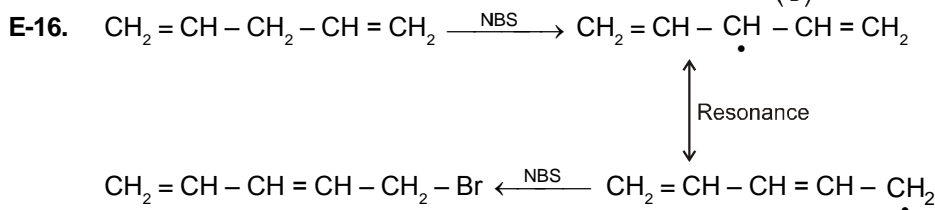
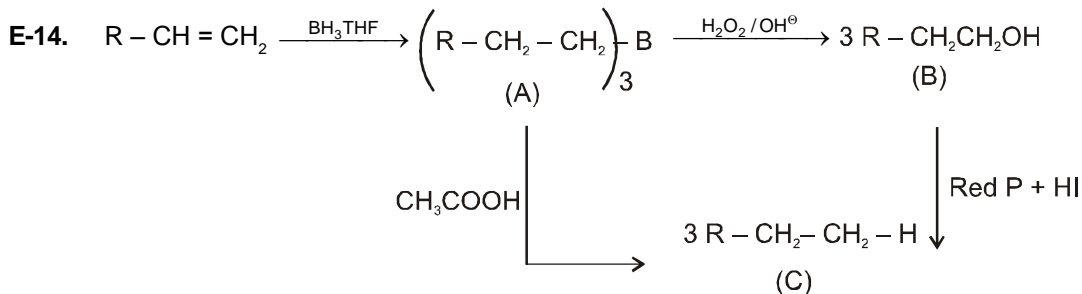
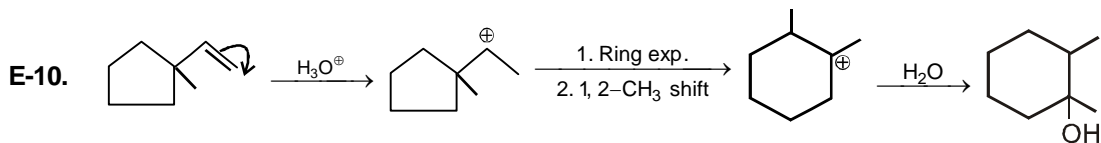
B-7. Initial and final energy difference will be -134 kJ/mol .



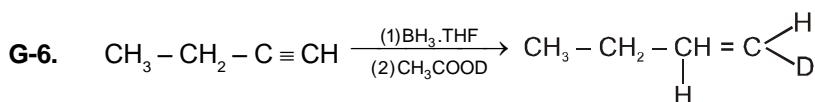
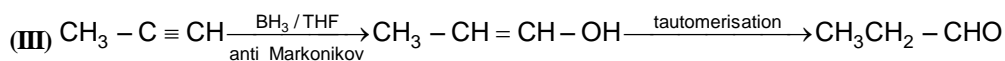
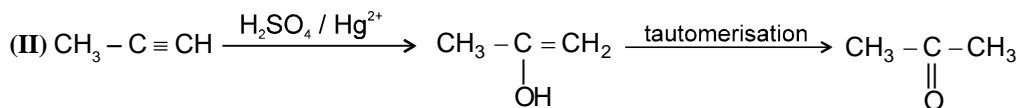
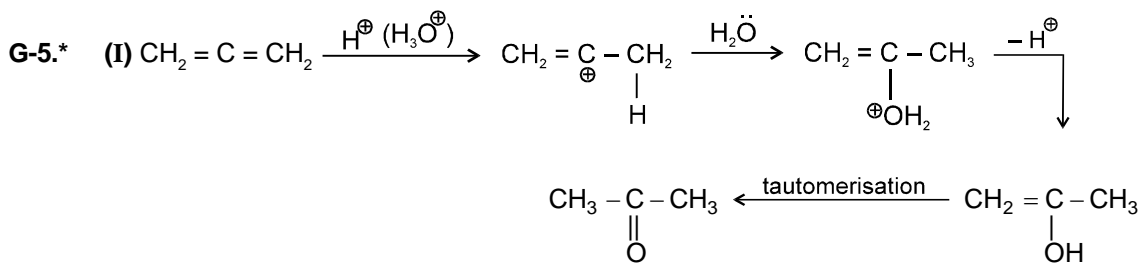
D-1. Electron releasing group and stability of carbocation will decide rate of reaction in electrophilic addition reaction.

D-3. $\text{C}=\text{C}$ at position 1 is more reactive towards electrophile Br^\oplus as this is adjacent to O atom to provide +m effect. $\text{C}=\text{C}$ at position 3 is more substituted as compared to $\text{C}=\text{C}$ at position 2. Alkyne is less reactive towards Br^\oplus as compared to alkene.

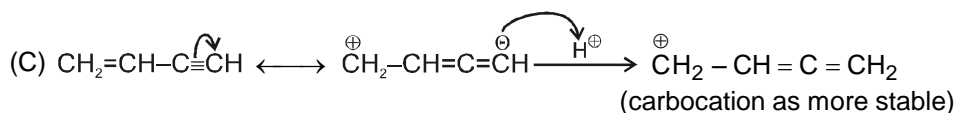


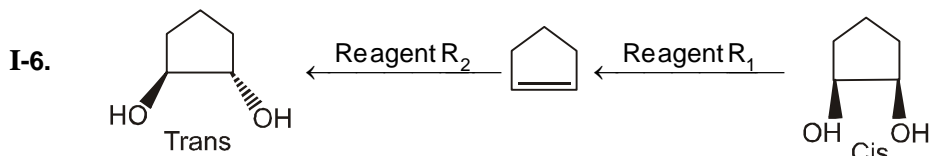
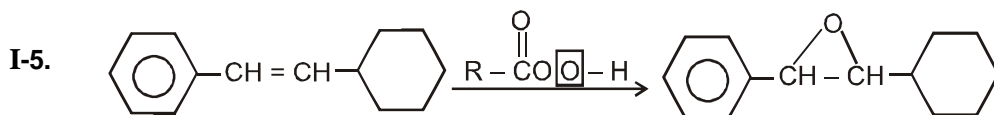


Note : Addition of HBr by free radical mechanism.

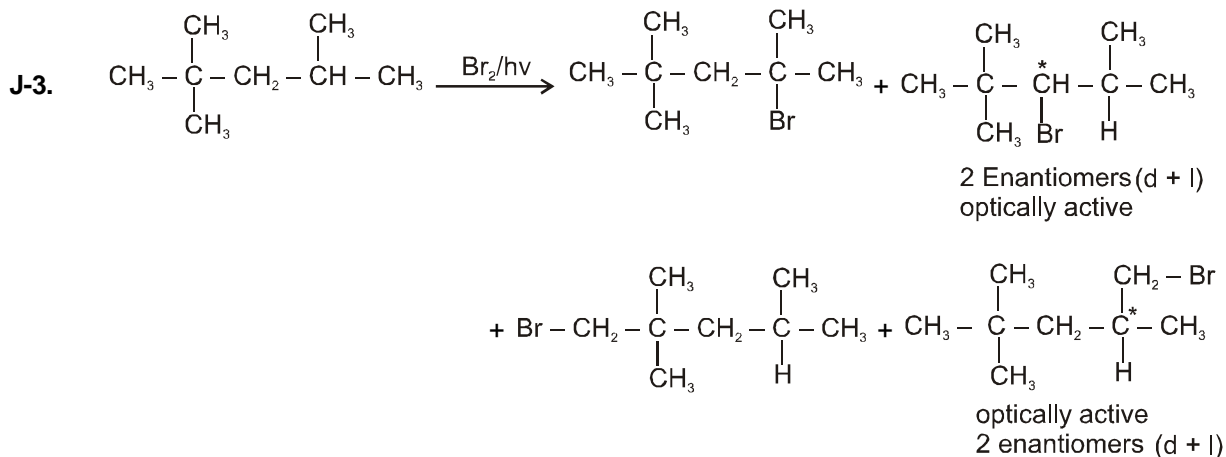
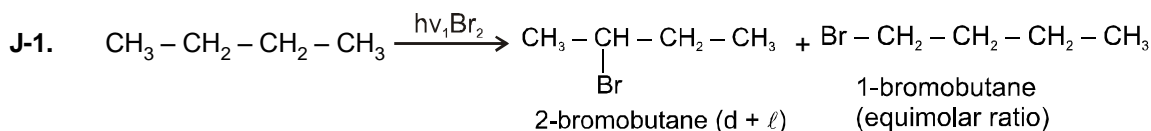
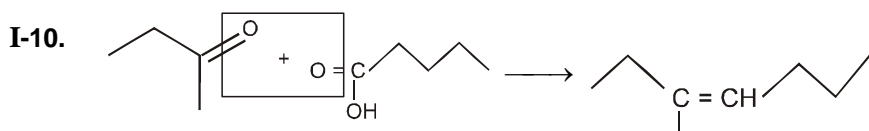
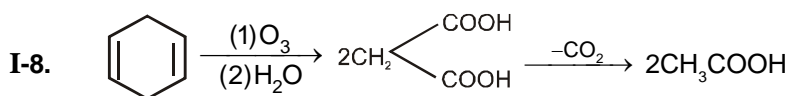
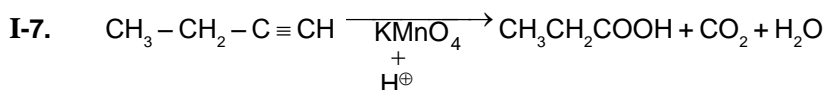


H-2.* (A) when H^\oplus add to the Buta-1, 3-diene in the r.d.s., an allylic carbocation is formed, however from But-1-ene, an 2° carbocation will form which will be less stable.
(B) At room temperature, product will be TCP.

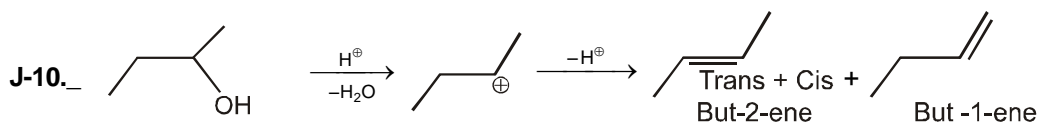
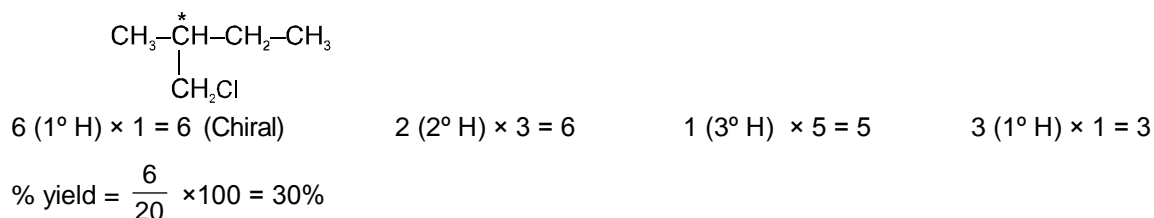


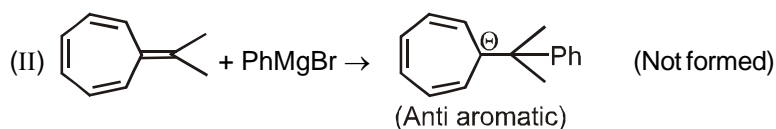
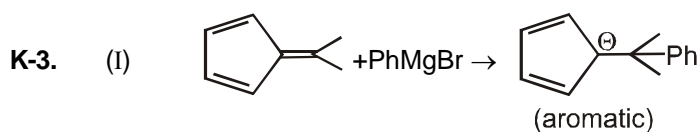
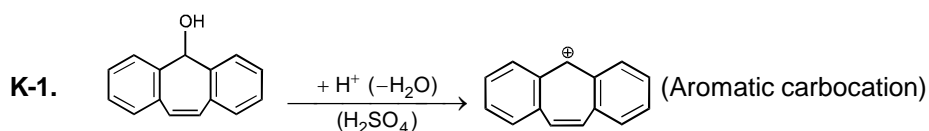
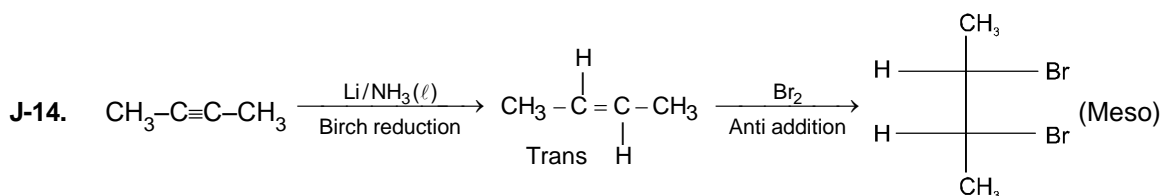
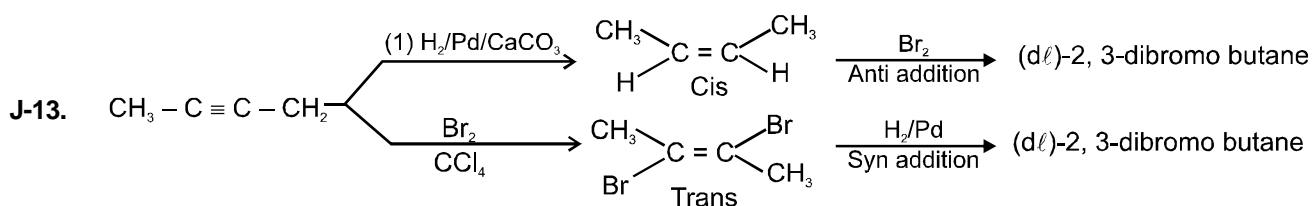
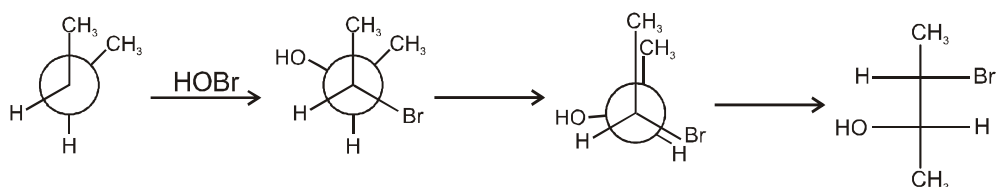
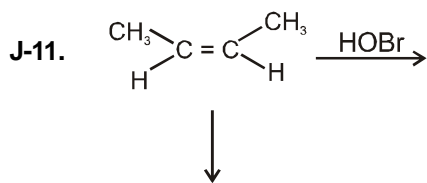
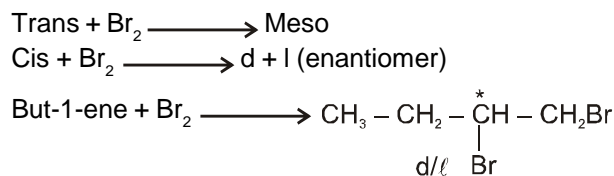


Syn addition with Baeyer's Reagent, So cis will form meso compound however peroxy acid in anti addition gives enantiomer.

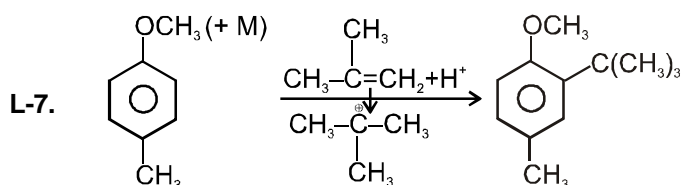
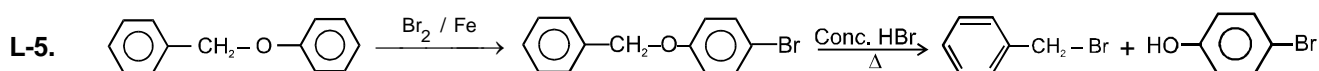


J-8. Primary monochloride can be which is chiral

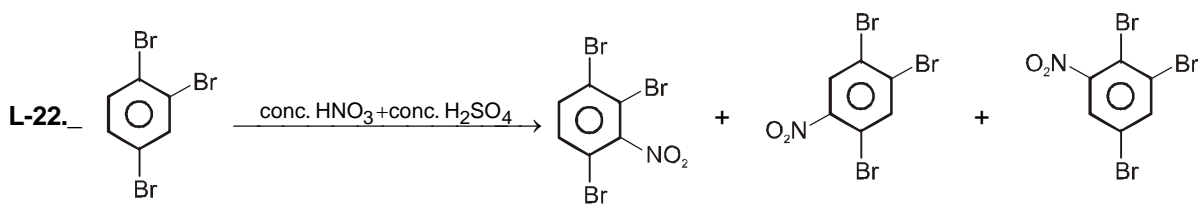
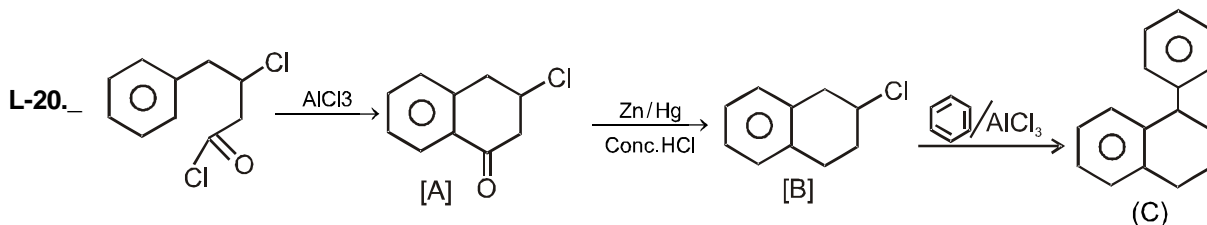
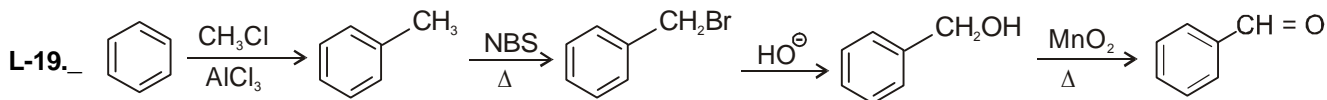
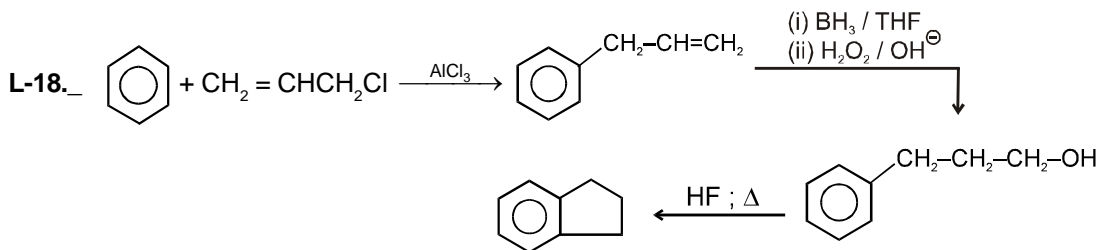
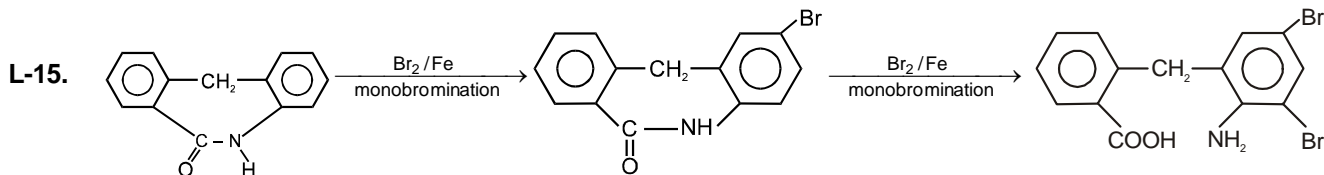
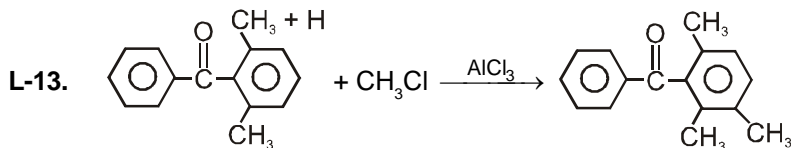




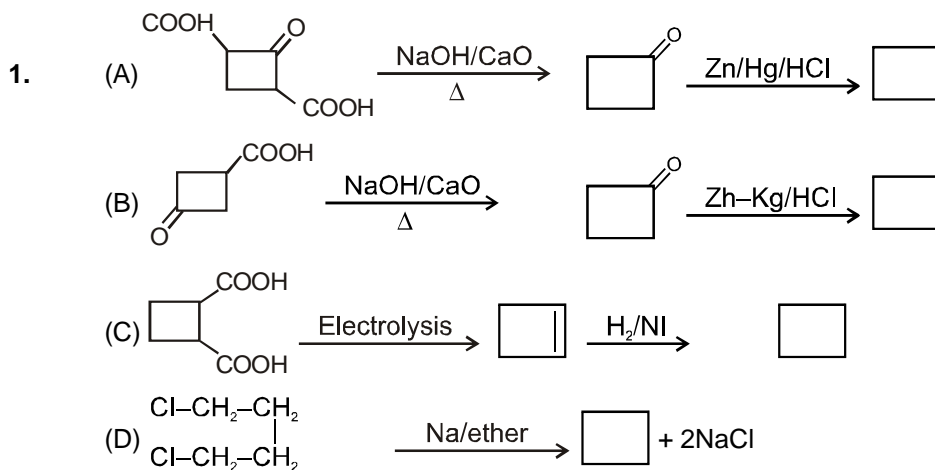
L-4. Rate of electrophilic substitution \propto Stability of arenium ion.



- L-11. (1) Strong activity group ($-\text{NH}_2$ and $-\text{OH}$) and $-\text{M}$ groups do not show Friedel-Crafts reaction.
 (2) Vinyl halide and aryl halide do not give Friedel-Crafts reaction.



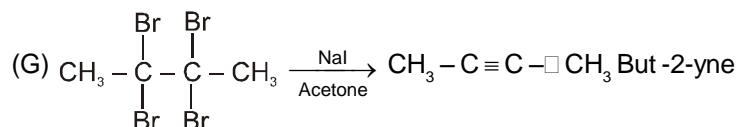
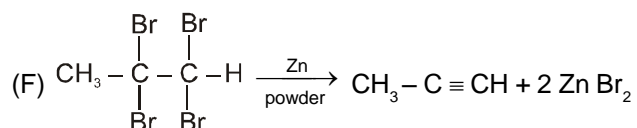
PART - II



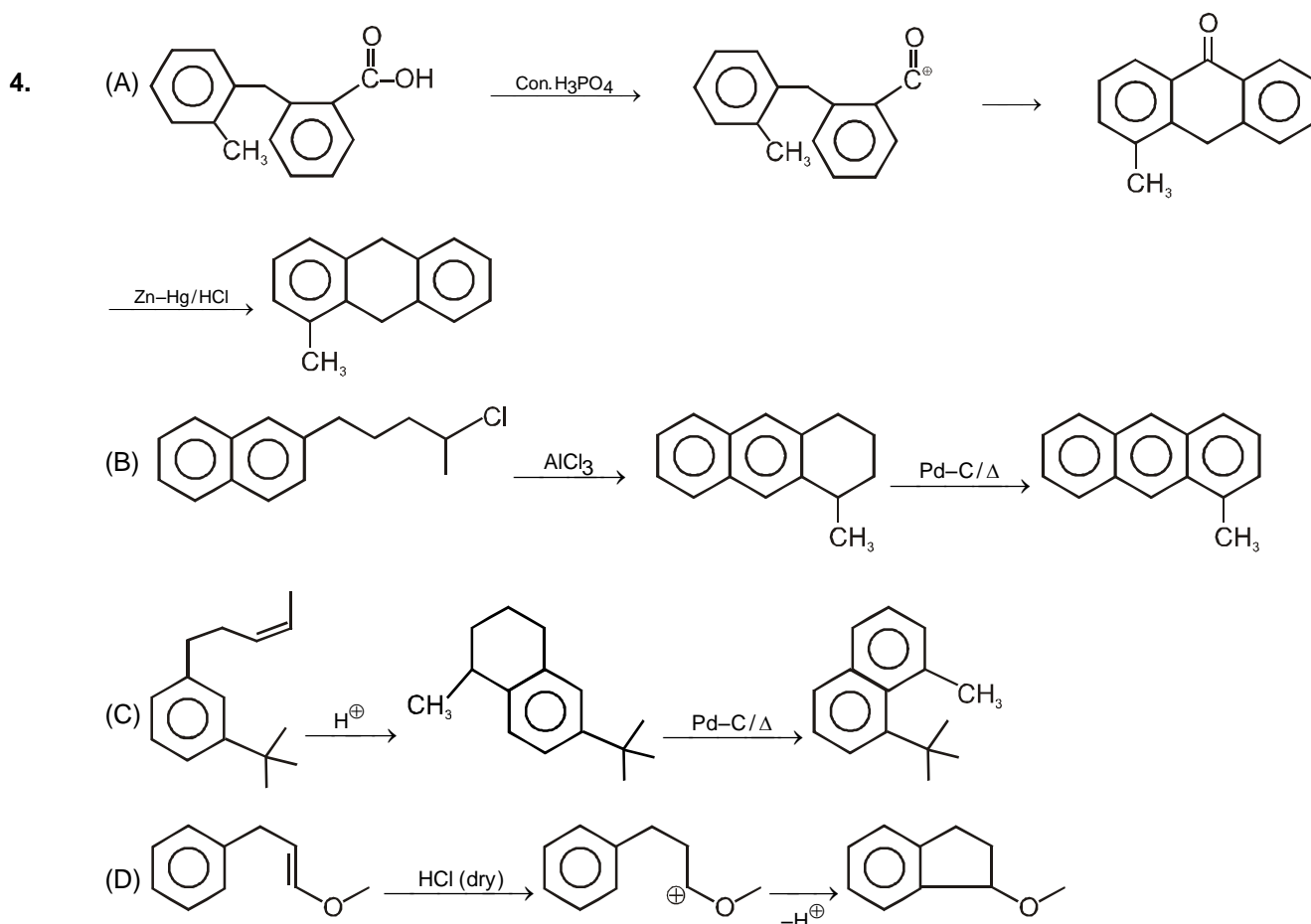
2. (A) $\text{CaC}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{CH} \equiv \text{CH}$
 (B) $\text{Mg}_2\text{C}_3 + \text{H}_2\text{O} \longrightarrow \text{Mg(OH)}_2 + \text{CH}_3 - \text{C} \equiv \text{CH}$
 (C)
$$\begin{array}{ccc} \text{HC} - \text{COOK} & \xrightarrow[\text{Electrolysis}]{\text{Kolbe's}} & \text{HC} \\ || & & || \\ \text{HC} - \text{COOK} & & \text{HC} \end{array}$$

 (D)
$$\begin{array}{ccc} \text{HC} - \text{COOK} & \xrightarrow[\text{Electrolysis}]{\text{Kolbe's}} & \text{HC} \\ || & & || \\ \text{KOO} - \text{C} - \text{H} & & \text{HC} \end{array}$$

 (E) $2\text{HCl}_3 + 6\text{Ag} \longrightarrow \text{CH} \equiv \text{CH} + 6\text{AgI}$



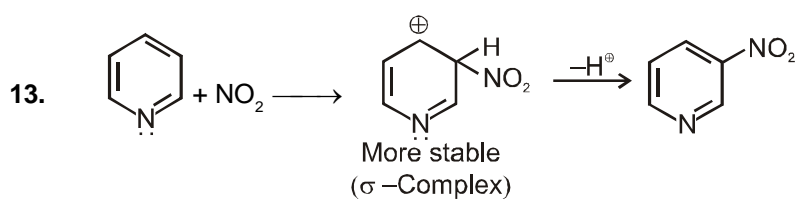
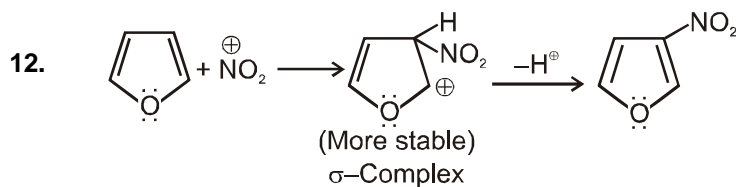
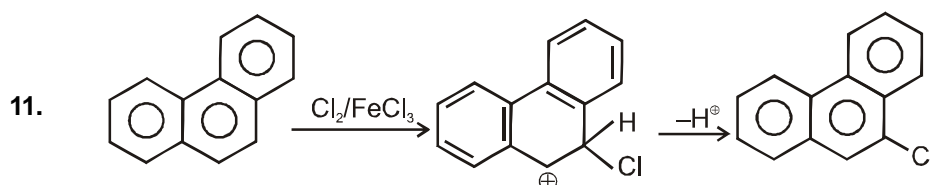
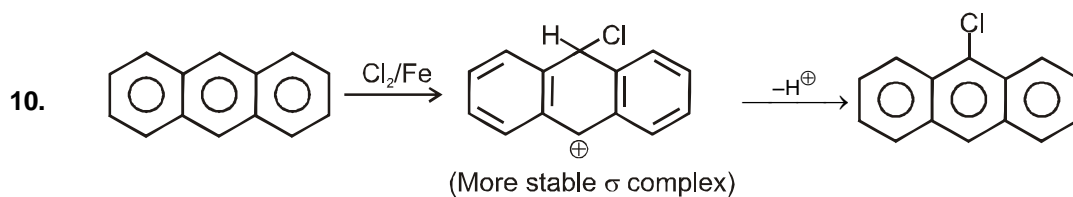
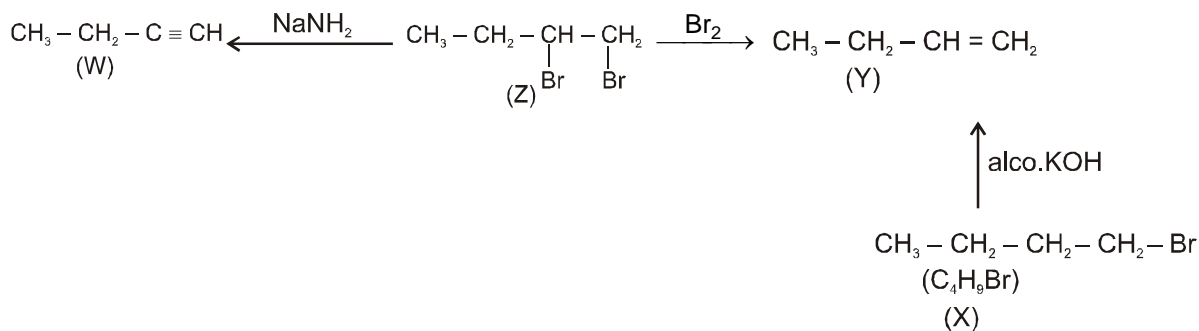
3. (A) $-\text{CH}=\text{CHCOOH}$ is deactivating due to $-I$ of $-\text{COOH}$ group, but o,p -directing due to stability of carbocation.
 (B) $-\text{CCl}_3$ is electron withdrawing group due to $-I$ nature.
 (C) $-\text{OH}$ is electron donating due to $+m$.
 $-\text{NO}_2$ is electron withdrawing due to $-m$.



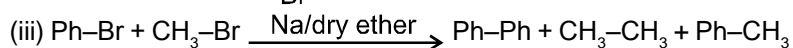
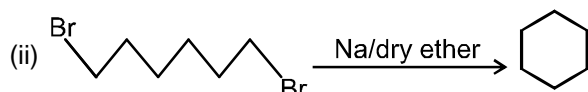
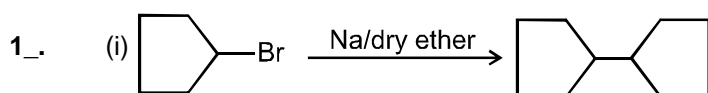
(5 to 6)

$$\text{Heat of hydrogenation} \propto \frac{1}{\text{stability of alkene}}$$

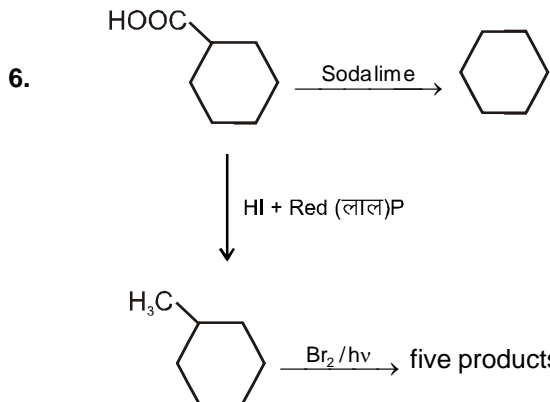
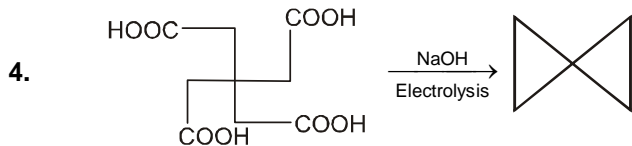
7. Solution by reverse synthesis: W must be terminal alkyne, since it gives white Precipitate with Tollen's Reagent



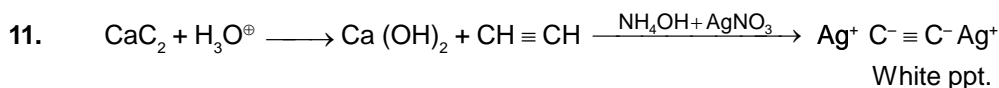
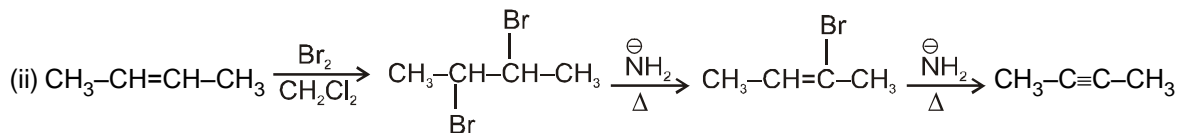
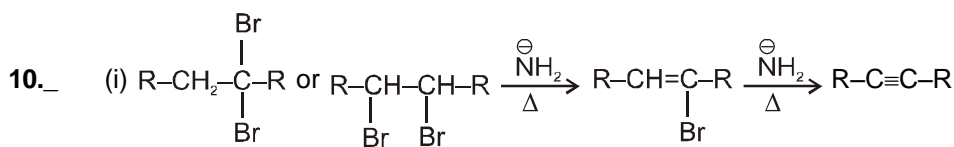
EXERCISE # 2



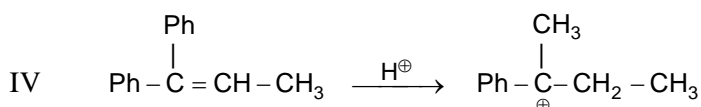
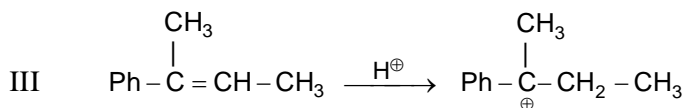
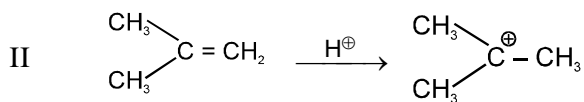
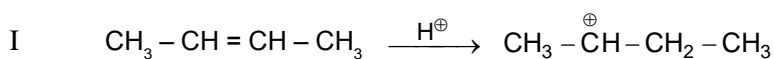
These are wurtz reaction.



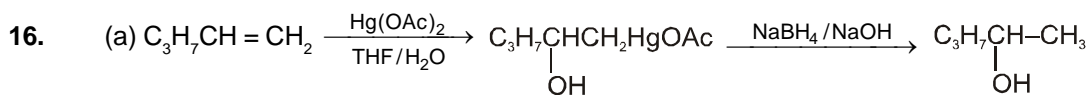
8. Stability of alkene $\propto \frac{1}{\text{heat of hydrogenation}}$



13. Since the reactivity towards ionic addition \propto stability of carbocation intermediate formed.



Stability of carbocation intermediate : IV > III > II > I. reactivity of alkene : IV > III > II > I.

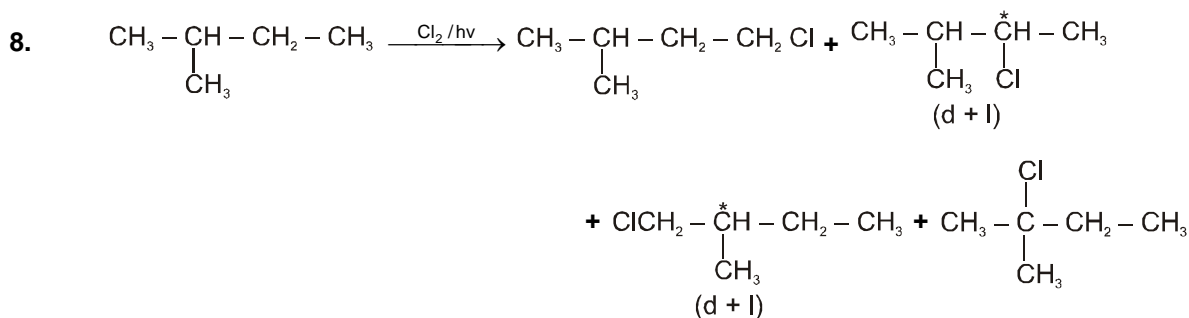
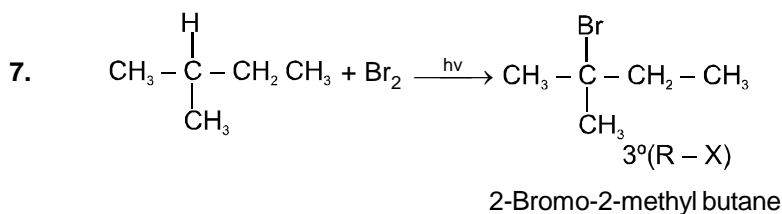
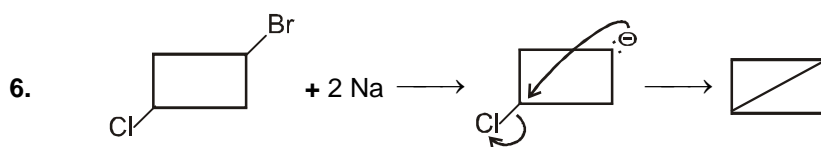
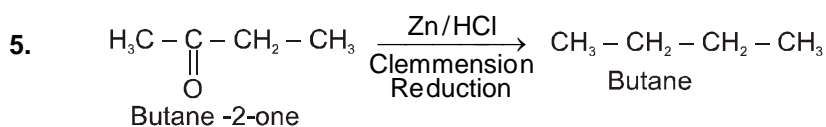
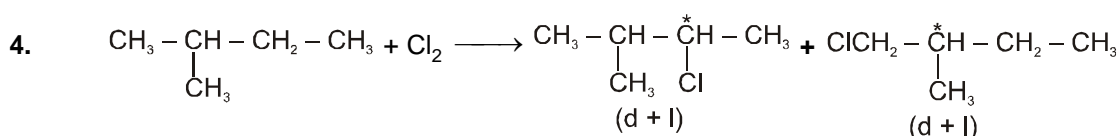
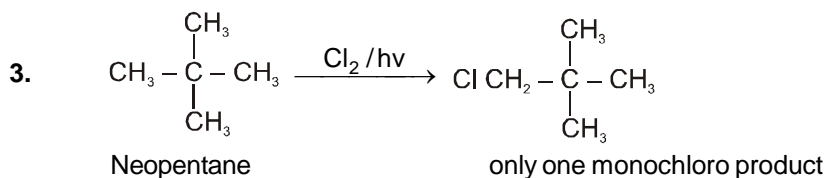
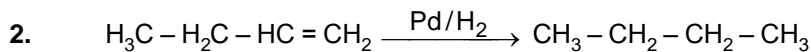


- (b) Self explanatory.
(c) Self explanatory.
(d) Self explanatory.

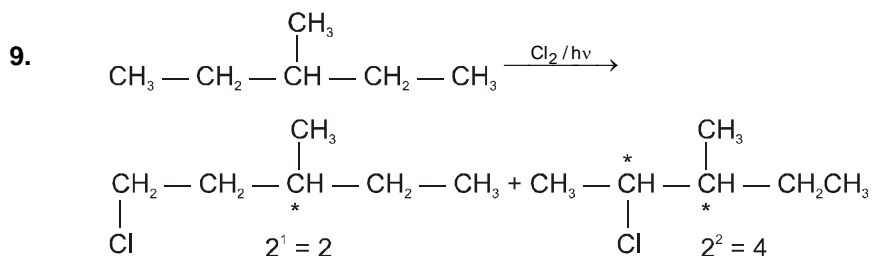
EXERCISE # 3

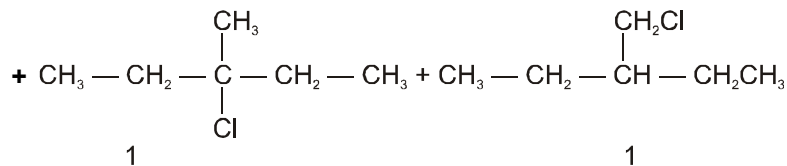
ALKANE

1. Clemmensen's reagent or Wolf kishner reagent are preferred for reduction of $>C=O$ group into $-CH_2$. With $Zn(Hg)/HCl$ OH group will also undergo S_N reaction.

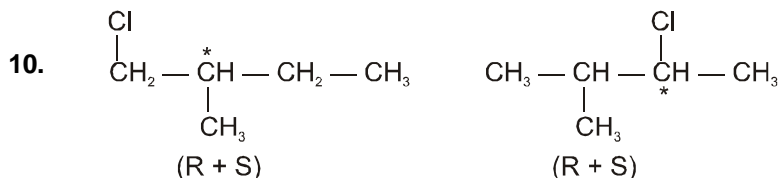


$N = 6, P = 4$

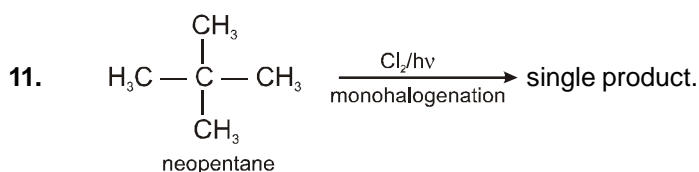




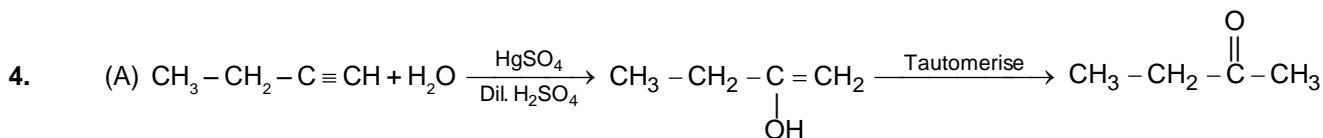
Total = 8



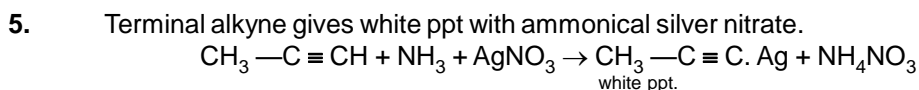
Four monochloro derivatives are chiral.



ALKENE & ALKYNE

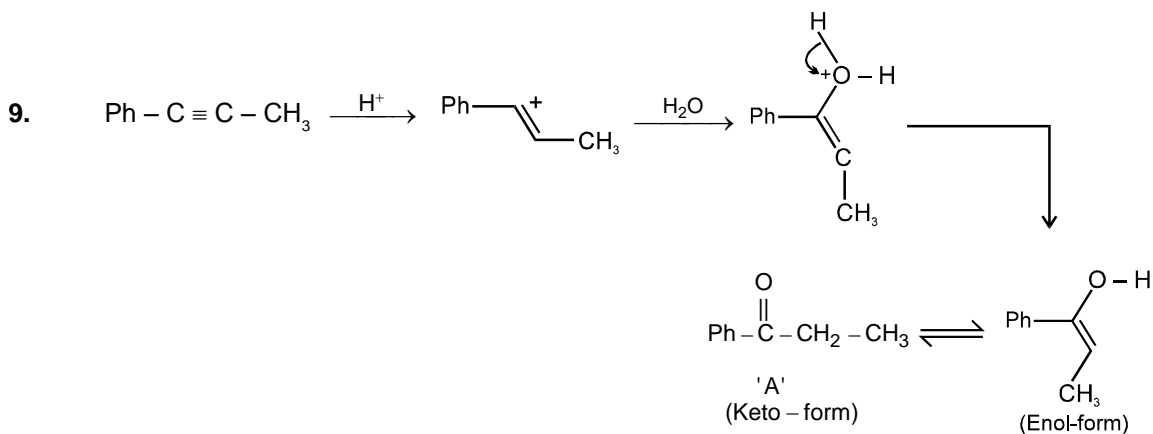
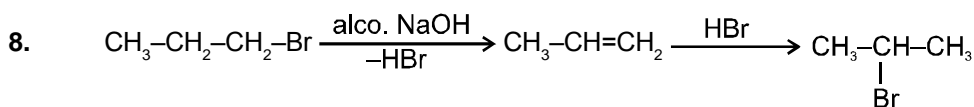
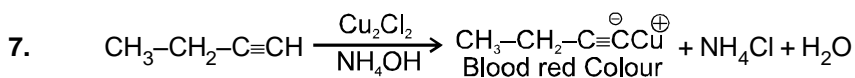


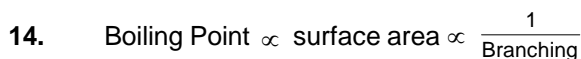
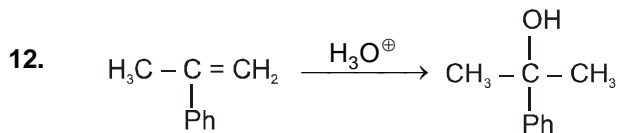
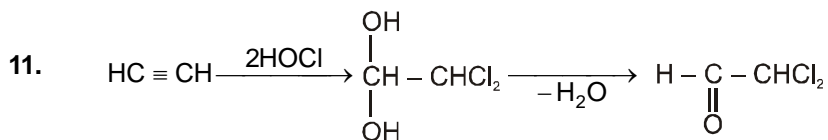
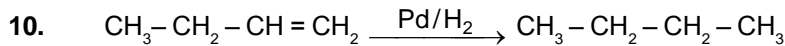
(Because keto form is more stable than enol)



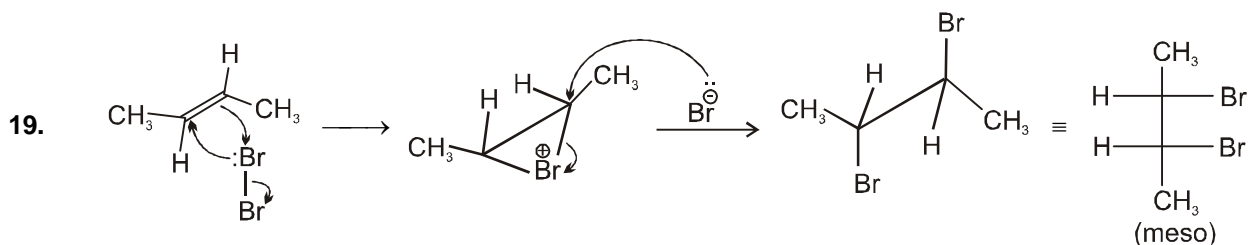
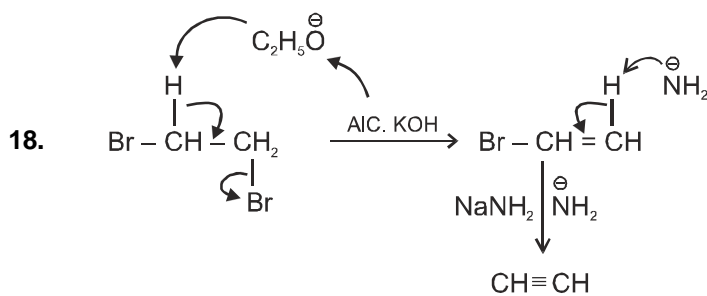
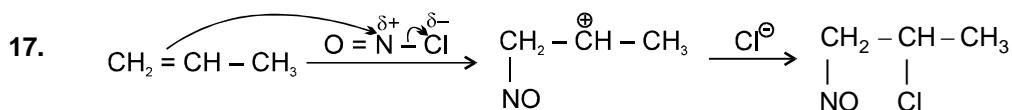
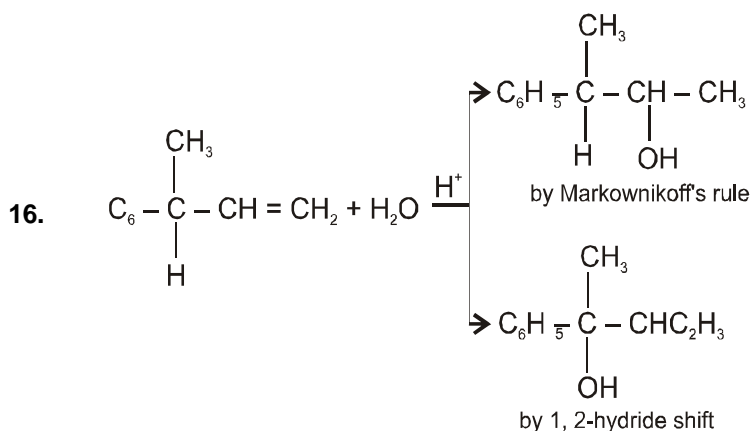
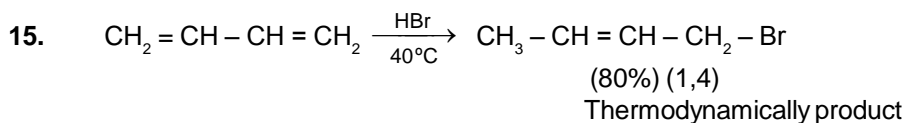
while propene does not give any reaction with ammonical AgNO_3 due to absence of acidic hydrogen.

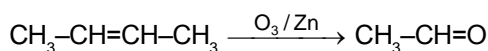
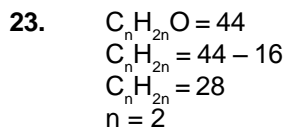
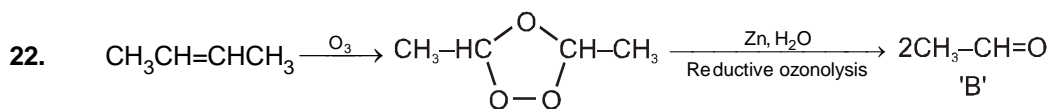
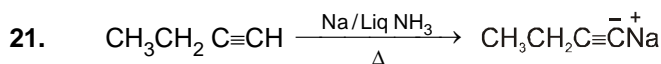
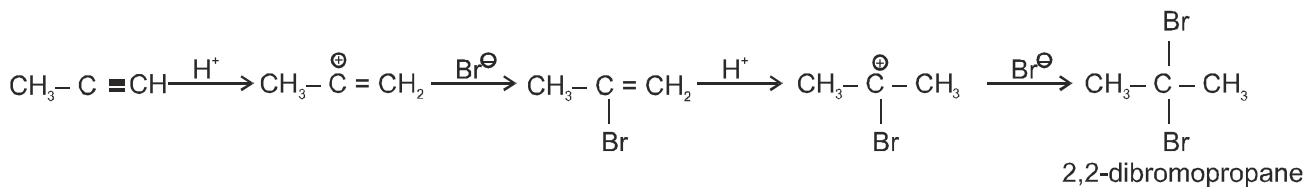
6. Addition of bromine to an alkene is an anti addition a symmetrical trans alkene on anti addition forms a meso compound. Also in addition of alkene first of all Br^\ominus attacks therefore it is an electrophilic addition.



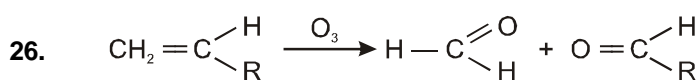
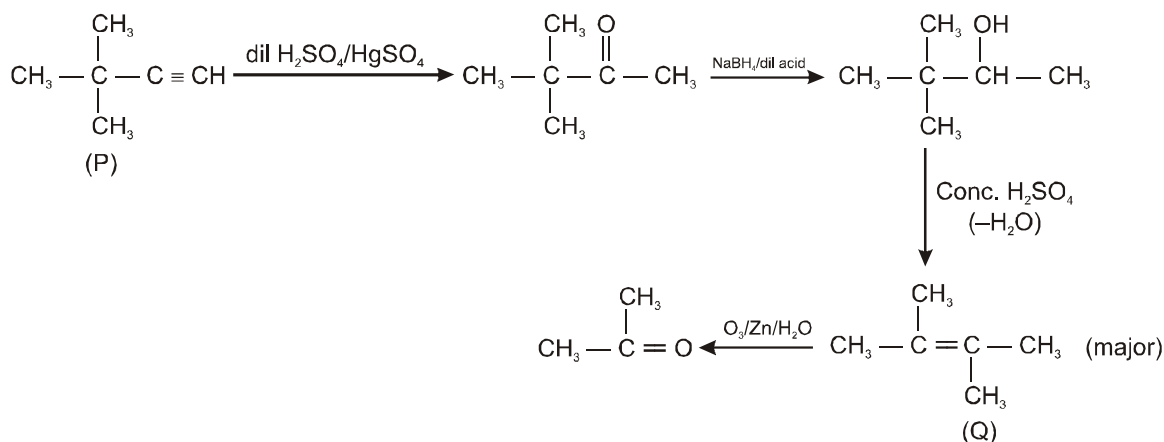


Iso butene has smallest vander wall surface area of contact so its boiling point least.





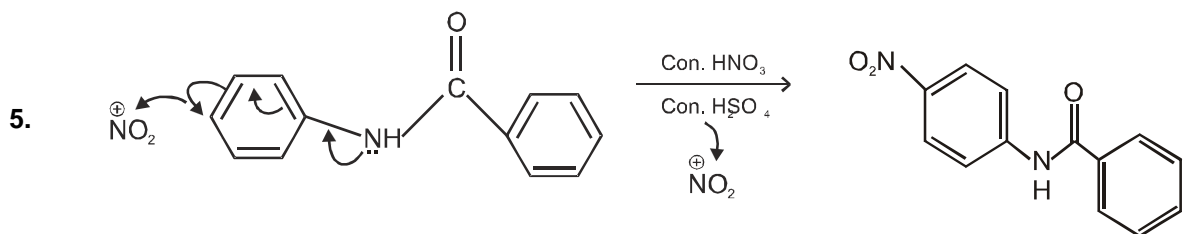
Sol. (24 & 25)



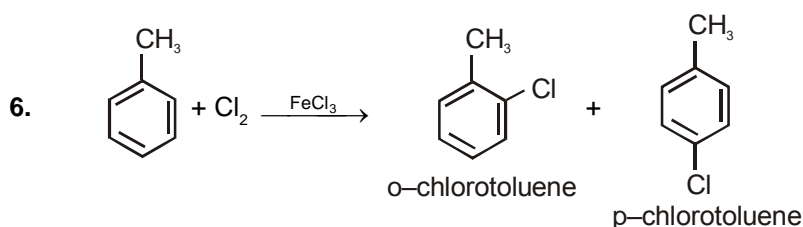
Presence of one vinyl group gives formaldehyde as one of the product in ozonolysis.

BENZENE

- 'N' has lone pair, so it is activating and o/p directing % p > % O.
- It is ArS_E^2 reaction, N has lone pair so it is activating and substitutions occurs at most activated position.
- Reaction involved are
 (1) $\text{A} \longrightarrow \text{B}$
 $3\text{H}_2\text{SO}_4 + 2\text{NaBr} + \text{MnO}_2 \longrightarrow \text{Br}_2 + \text{MnSO}_4 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O}$
 (A) (B)
 (2) $\text{A} \longrightarrow \text{C}$
 $2\text{H}_2\text{SO}_4 + \text{H}-\text{O}-\text{N}=\text{O} \longrightarrow (\text{H}-\overset{\oplus}{\text{O}}-\text{N}=\text{O} + \text{HSO}_4^- + \text{H}_2\text{SO}_4) \longrightarrow \text{H}_3\text{O}^{\oplus} + \text{NO}_2^{\oplus} + 2\text{HSO}_4^{\ominus}$
 $\downarrow \quad \quad \quad \downarrow$
 $\text{O} \quad \quad \quad \text{H} \quad \quad \quad \text{O}$



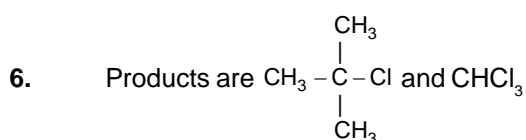
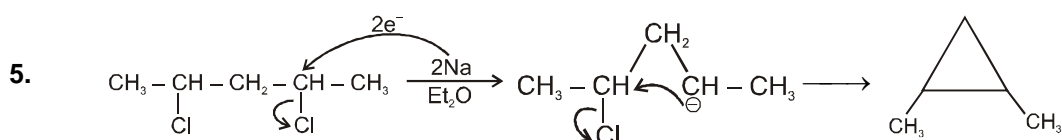
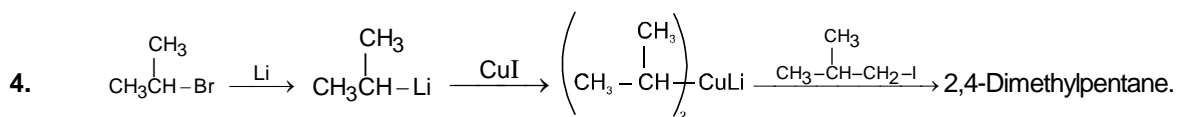
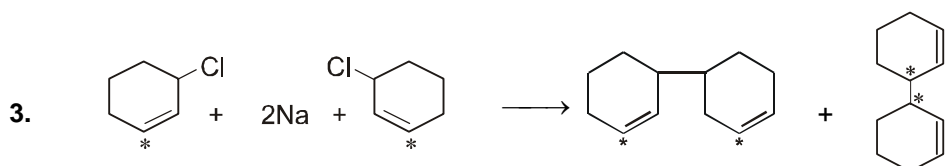
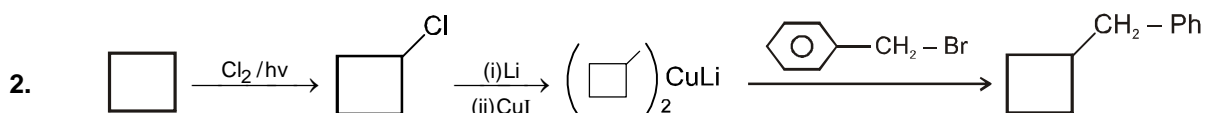
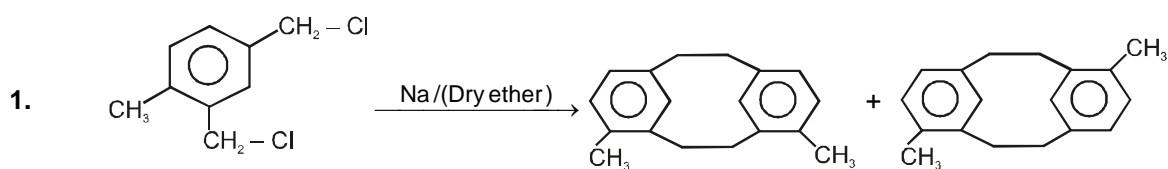
Note : (-NH- part is p-directing).



The reaction proceeds by electrophilic substitution mechanism. The CH_3 group is o/p directing.

7. $-\text{NO}_2$ group in benzene ring shows -I and -R effect, which deactivates the ring towards electrophilic substitution but activates it towards nucleophilic substitution.

SOLUTION OF ADVANCED LEVEL PROBLEM



9. $1^\circ \text{C} - \text{H} = 12 \times 1 = 12$
 $2^\circ \text{C} - \text{H} = 2 \times 3 = 6$
 $3^\circ \text{C} - \text{H} = 2 \times 6 = 12$

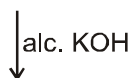
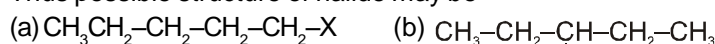
$$\text{Minimum yield} = \frac{6}{30} \times 100 = 20\%$$

Ans. 20 %

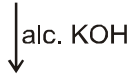
10. 1° halides : $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_3$
 $\text{BrCH}_2\text{CH}(\text{CH}_3)_2 \rightarrow \text{CH}_2=\text{C}(\text{CH}_3)_2$
 3° halides : $(\text{CH}_3)_3\text{CBr} \rightarrow \text{CH}_2=\text{C}(\text{CH}_3)_2$

11. $\text{C}_5\text{H}_{11}\text{X} \xrightarrow[\text{-HX}]{\text{alc.KOH}} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2 / \text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$
pent-1-ene pent-2-ene

Thus possible structure of halide may be

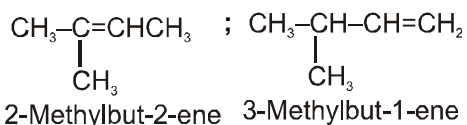
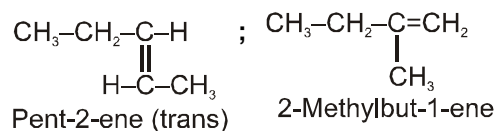
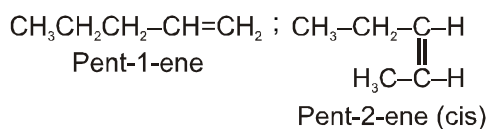


Pent -1-ene only



Pent-2-ene only

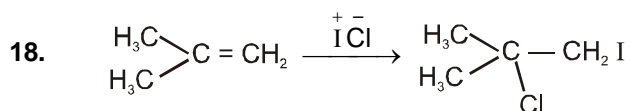
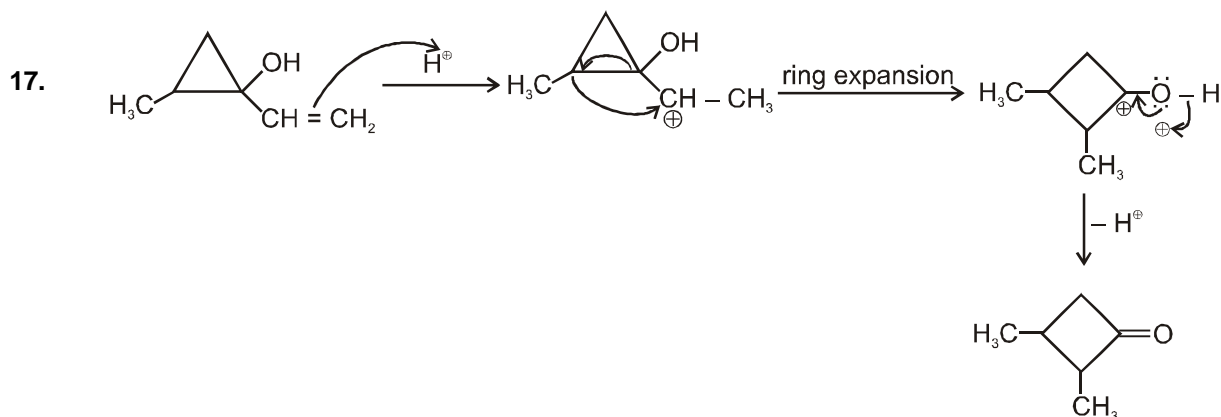
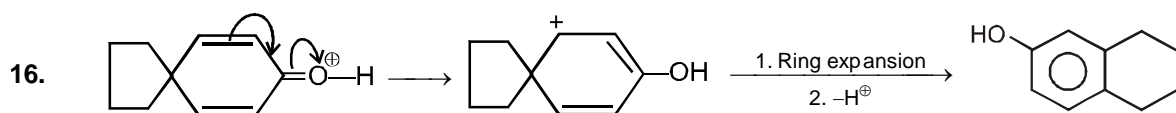
13. Pentene exist in the following isomeric forms :

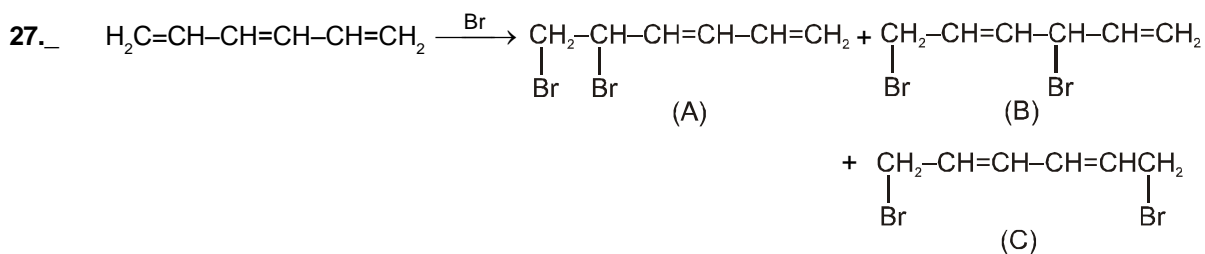
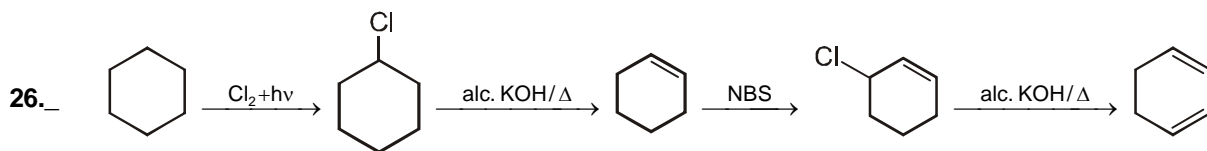
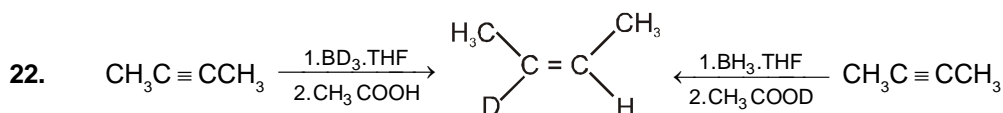
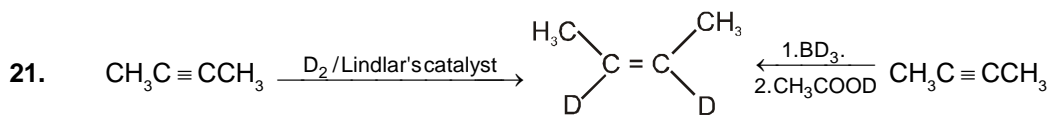
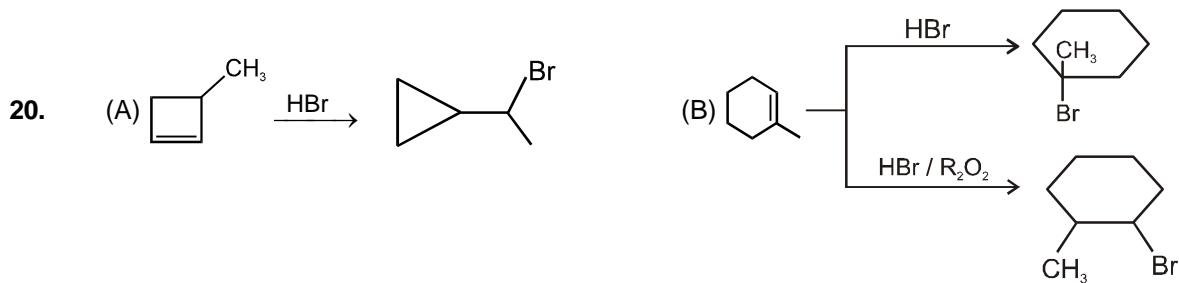


and the stability order is :

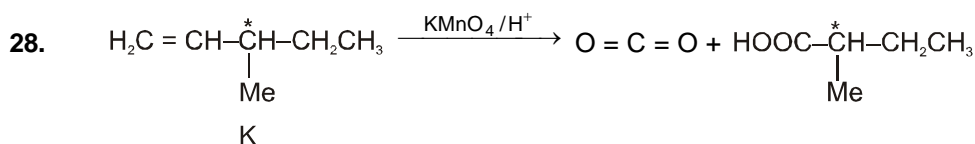
Pent-1-ene < pent-2-ene (cis) < pent-2-ene (trans) < 2-methylbut-2-ene

(Since stability increase with increasing number of electron releasing alkyl group).





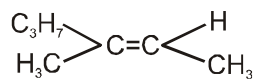
(C) will be thermodynamically controlled.



29. The products of ozonolysis are 2-pentanone and acetaldehyde. Writing the structure of both the carbonyl compounds.

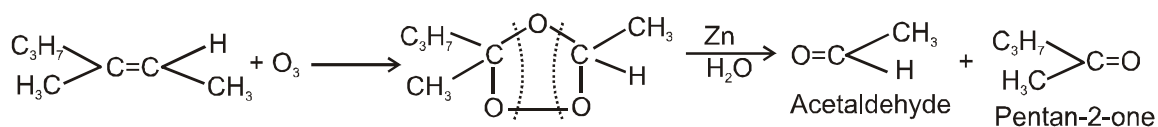


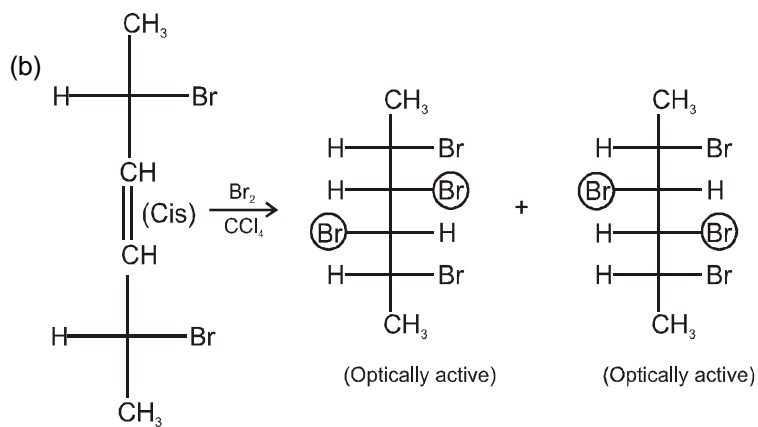
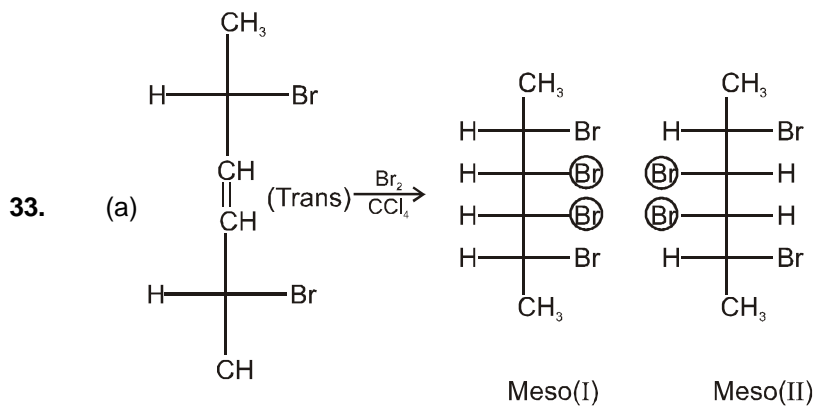
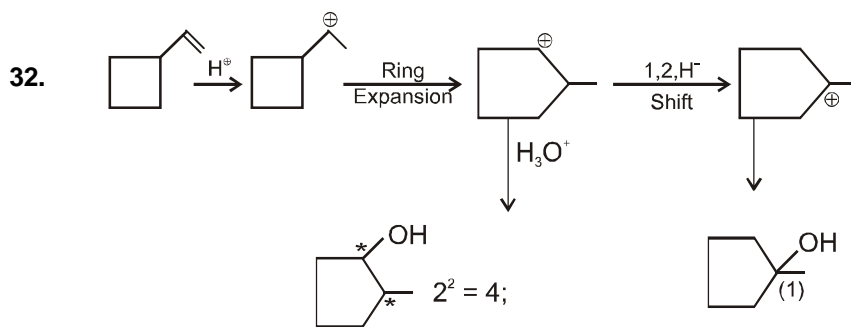
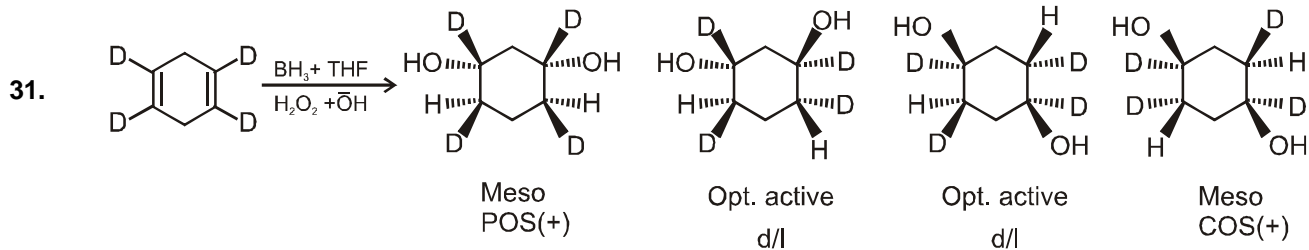
Removing =O of the compounds and linking both through double bond, we get the alkene.

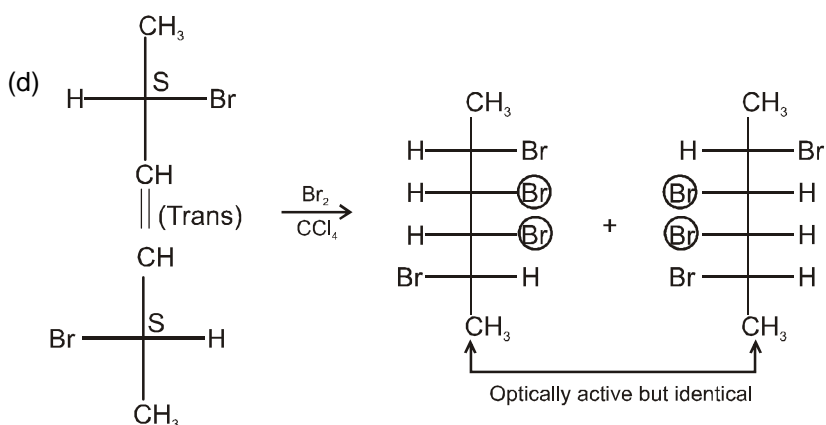
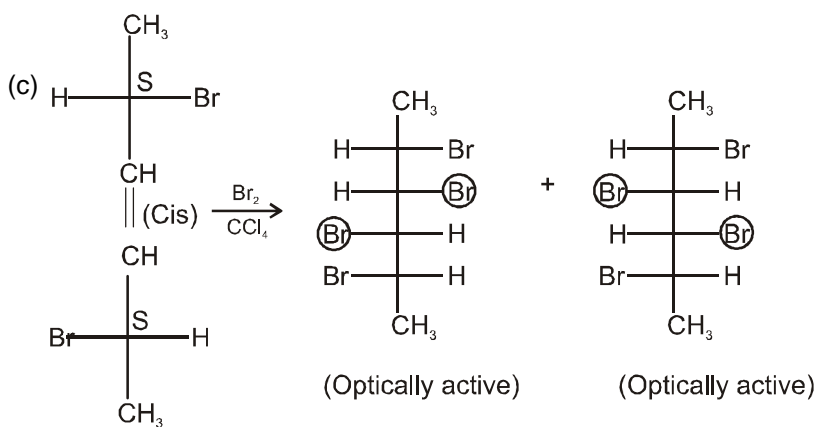


Thus, the alkene is 3-methylhex-2-ene.

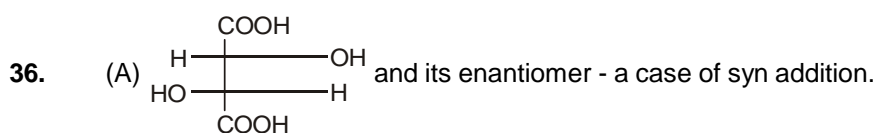
Reaction :



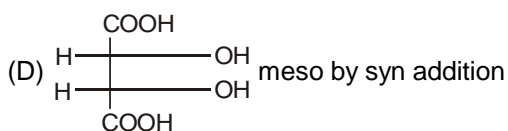
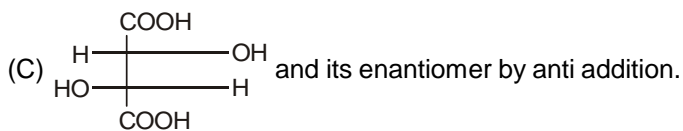
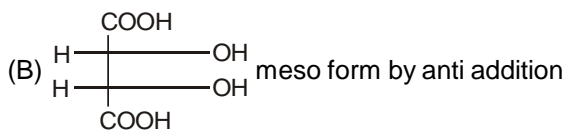




34. (A) But-2-yne + Na / liq. $\text{NH}_3 \longrightarrow$ trans But-2-ene + $\text{Br}_2 \longrightarrow$ Meso-2,3-dibromobutane
 (B) But-2-yne + Lindlar \longrightarrow cis But-2-ene + $\text{HOCl}/\text{H}^+ \longrightarrow$ Racemic -3-chloro-2-butanol
 (C) But-2-yne + Lindlar \longrightarrow cis But-2-ene + Beyer's reagent \longrightarrow Meso - 2,3-butanediol
 (D) But-2-yne + Birch \longrightarrow trans But-2-ene + (i) HCOOOH / (ii) $\text{H}_3\text{O}^+ \longrightarrow$ Racemic-2,3-butanediol



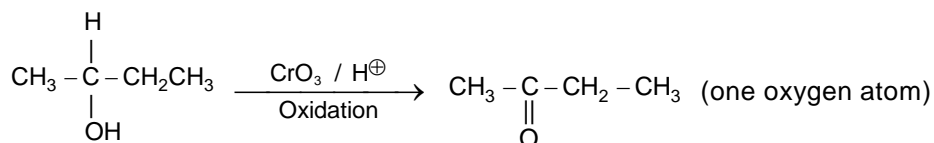
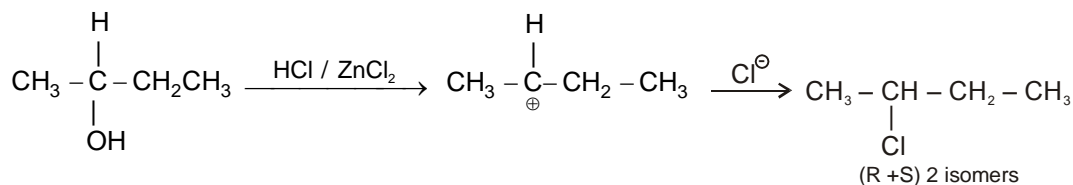
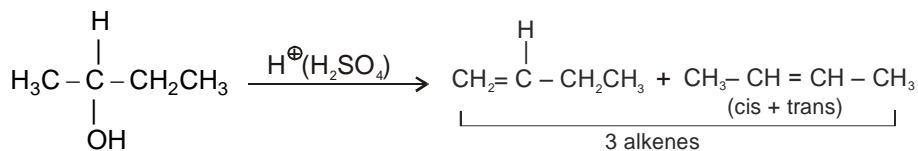
Mixture is optically inactive (racemic mix).



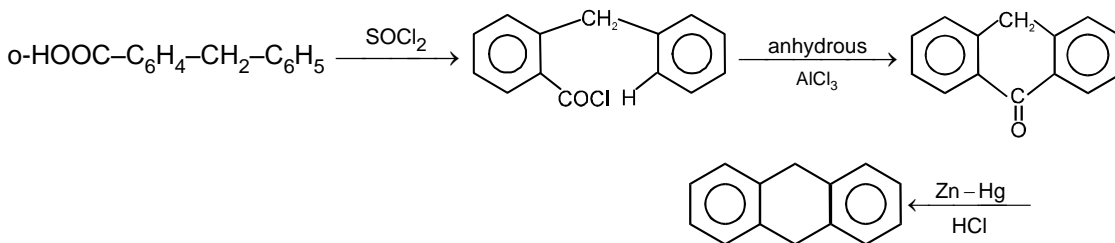
38.

3	2	1
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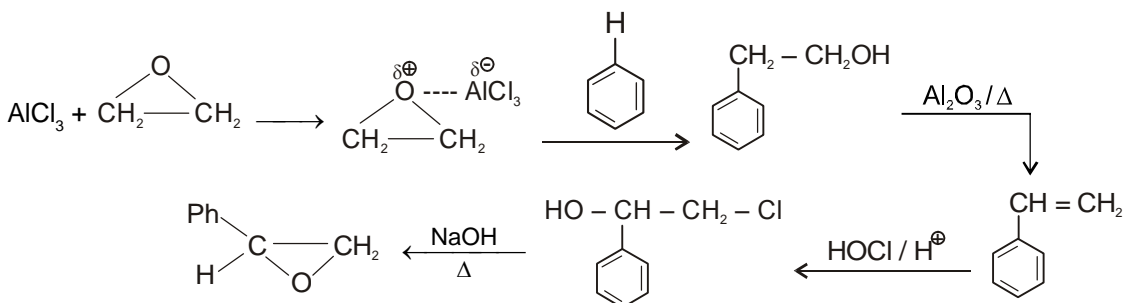
'X' will be :



42.



43.



44.

