CHEMISTRY
CLASS : XI

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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 shows 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]$^{3d^{10}}$ $4s^2$ $4p^3$. 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 4$^{th}$ period element.

B-3. $\Delta$ $Z_{n} = 1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$, $3d^{10}$, $4s^2$
$\sigma = 0.35 \times 1 + 18 \times 0.85 + 10 \times 1 = 25.65$
$\Rightarrow Z_{eff} = 30 - 25.65 = 4.35$

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 $_{13}Al^{3+} < _{12}Mg^{2+} < _{11}Na^+ < _{9}F^-$. Al belongs to third period and has no charge so it is largest. $Na^+ = 102$ pm; $Mg^{2+} = 72$ pm; $Al = 143$ pm; $F^- = 133$ pm.
(B) Isoelectronic series of ions; all have the xenon electron configuration.

C-8. $D_2 = T_2 = P_2$
(The ionisation potential of isotopes of an elements will be same)

C-9. $D_2 = T_2 = P_2$

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 mor electrons are ionized off. $Cr^{6+} = 44$ pm, $Cr^{3+} = 61.5$ pm.

D-8. All are isoelectronic species so with increasing effective nuclear charge.
(i) size decreases (as $r \propto 1/$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 $P_2O_5$ 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 alkalies forming salts.
(C) the NaO 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.

SnO + H$_2$SO$_4$ $\rightarrow$ SnSO$_4$ + H$_2$O ; SnO + 2NaOH $\rightarrow$ Na$_2$SnO$_2$ + H$_2$O.
ZnO + H$_2$SO$_4$ $\rightarrow$ ZnSO$_4$ + H$_2$O ; ZnO + 2NaOH $\rightarrow$ Na$_2$ZnO$_2$ + H$_2$O.

E-6. As $\Delta E_n$ (difference in electronegativities between element and oxygen) decreases, the acidic character increases. So, SiO$_2$ < CO$_2$ < N$_2$O$_5$ < SO$_3$.

**PART - II**

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

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

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

(D) 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^6$ 4s$^2$
   \[ \sigma \text{ for 2p electron} = 0.35 \times 7 + 0.85 \times 2 = 4.15 \]
   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.

2. Fe = 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^6$ 4s$^2$
   \[ S = 0.3 \]
   \[ Z^* = 26 - 0.3 = 25.7 \]

3. Na = 1s$^2$ 2s$^2$ 2p$^6$

6. 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.

7. Z = 19 = K ; Z = 17 = Cl ; Z = 30 = Zn ; Z = 20 = Ca ; Z = 51 = 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) 30Zn = [Ar]$^{18}$ 3d$^{10}$ 4s$^2$ ; 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) 20Ca = [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$^{5-}$ (as nonmetals form).

**EXERCISE # 2**

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

**EXERCISE # 3**

1. 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. SiO$_2$ + 2NaOH $\rightarrow$ Na$_2$SiO$_3$ + H$_2$O.

2. $\text{IE}_2$ 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$.

3. 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 $\propto \frac{1}{\text{Nuclear charge}}$.

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$_2$O is neutral and CO$_2$ is acidic.

11. $^6\text{Li}^-$ - $1s^2$ $2s^2$ 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 $\text{Be}^-$ has less nuclear charge than $\text{B}^-$, so it will have lower ionisation energy than $\text{B}^-$. 

12. According to their positions in the periods, these values are in the order.

\[
\begin{align*}
\text{Yb}^{3+} & < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+} \\
\text{At. Nos.} & \quad 70 \quad 61 \quad 58 \quad 57 \\
\text{Ionic radii (pm)} & \quad 86 \quad 98 \quad 103 \quad 106
\end{align*}
\]

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.

\[
\begin{align*}
\text{ZnO} + \text{H}_2\text{SO}_4 & \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O} & \text{zinc sulphate} \\
\text{ZnO} + 2\text{NaOH} & \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} & \text{sodium zincate}
\end{align*}
\]

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.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} \rightarrow \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} \rightarrow \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} \rightarrow \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{N} \rightarrow \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]
17. The basic nature of oxides can be predicted on the basis of the factors given below.
   (i) 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.
   (ii) The basic character increases with increasing metallic character down the groups and decreases across the period.
   (iii) For the same element the basic character of their oxides increases with decreasing oxidation state.

Hence the correct of increasing Bronsted basicity order is $\text{Cl}_2\text{O}_7 < \text{SO}_3 < \text{CO}_2 < \text{B}_2\text{O}_3 < \text{BaO}$

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

   $^{19}\text{K}^+ = 19 - 1 = 18; ^{20}\text{Ca}^{2+} = 20 - 2 = 18$
   $^{23}\text{Sc}^{3+} = 21 - 3 = 18; ^{17}\text{Cl}^- = 17 + 1 = 18$

Thus all these ions have 18 electrons in them.

19. $\text{O}_2^-$ has the highest value of ionic radii as this can be explained on the basis of $z/e$ ratio. 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.

   $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_3 < \text{SO}_2$

Al$_2$O$_3$ is amphoteric. SiO$_2$ is slightly acidic whereas P$_2$O$_3$ and SO$_2$ are the anhydrides of the acids H$_3$PO$_3$ and H$_2$SO$_3$.

21. CaO - basic, CO$_2$ and SiO$_2$ - acidic, SnO$_2$ - amphoteric, as it reacts with both acids and bases.

   $\text{SnO}_2 + 4\text{HCl} \rightarrow \text{SnCl}_4 + 2\text{H}_2\text{O}$
   $\text{SnO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O}$

22. Nitrogen has half filled stable configuration, ns$^2$np$^3$. 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 B < P < C < O < N. (Ionisation energy in kJ mol$^{-1}$ B = 801 ; P = 1011 ; C = 1086 ; O = 1314 ; N = 1402).

23. Number of electrons in SO$_2^2-$ = 16 + 8 x 3 + 2 = 42
   Number of electrons in CO$_3^{2-}$ = 6 + 8 x 3 + 1 = 32
   Number of electrons in NO$_3^-$ = 7 + 8 x 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. $K^+ = 19 - 1 = 18$ 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.

   $\text{NO}^+ = 7 + 8 - 1 = 14$ ; $C_2^-= 2 \times 6 + 2 = 14$
   $\text{CN}^- = 6 + 7 + 1 = 14$ ; $\text{N}_2 = 7 + 7 = 14$.

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 Na$^+ > \text{Li}^+ > \text{Mg}^{2+} > \text{Be}^{2+}$.

   $\text{Be}^{2+} = 0.31$ Å
   $\text{Mg}^{2+} = 0.72$ Å
   $\text{Li}^+ = 0.76$ Å
   $\text{Na}^+ = 1.02$ Å
In hydrides of 15\textsuperscript{th} group elements the basic strength decreases down the group and the correct order is, 
\[ \text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3 \]

O\textsuperscript{2-}, F\textsuperscript{-}, Na\textsuperscript{+}, Mg and Al\textsuperscript{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 \( \text{O}^{2-} > \text{F}^{-} > \text{Na}^{+} > \text{Mg}^{2+} > \text{Al}^{3+} \).

Order of ionic radii Ca\textsuperscript{2+} < K\textsuperscript{+} < Cl\textsuperscript{-} < S\textsuperscript{2-} in isoelectronic species as \( \frac{Z}{e} \) increases size decreases.

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**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 \( [\text{Ar}]^{18} 3d^{10} 4s^{1} \).
   
   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. \( M = 2.1 \quad F = 4 \)
   \( x_{A} - x_{B} = (4 - 2.1) = 1.9 \)

   \% ionic character = 16(1.9) + 3.5 (1.9)\(^2\) = 43.03\%

   So, \% covalent character = 100 – 43.03 \( \equiv \) 57%.
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.

A-16*. (A) 
\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{Cl} \\
\end{array}
\]
(B) $K^+ C = N^-$

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

B-12. N atom in NO$^+$ is sp hybridised while in NO$_2^-$ and NO$_3^–$, it is sp$^2$ hybridised.

Bond order $= \frac{2\text{e}^-}{2} = 1$

Bond order $= \frac{2\text{e}^-}{2} = 1.5$

Bond order $= \frac{2\text{e}^-}{3} = 1.33$

So, bond length order is NO$_3^– >$ NO$_2^– >$ NO$^+$.

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

Bond order of CO $= 3$ (as isoelectronic with N$_2$)

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

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

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

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

B-14. (i) Negative charge should be at more electronegative atom.
(ii) Less formal charge provides more stability.
B-15. \[ P : CH_3 - C = N \]
\[ Q : H - N = C = O \]
\[ R : CH_3 - C \equiv N \]
\[ \text{NH}_2 \].

B-16. Bond energy \( \propto \) Bond order

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<th>Bond order</th>
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<tr>
<td>CO</td>
<td>3</td>
</tr>
<tr>
<td>CO_2</td>
<td>2</td>
</tr>
<tr>
<td>CO_3^-</td>
<td>1.33</td>
</tr>
</tbody>
</table>

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

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

C-1.

\[ \text{H} - \text{O} - \text{C} - \text{O} \rightarrow \text{H} - \text{O} - \text{C} = \text{O} \]
\[ \therefore x > y = z \]

C-2.

D-1. (A) \[ \rightarrow Z \]
(B) \[ \rightarrow Z \]

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

D-6. Since \( \pi \) bond is weaker than \( \sigma \) bond the stated value of bond energies are wrong.

D-7. Structure of \( C_3^{4-} \) is \( (C = C = C) \)

D-8. \( \text{CaC}_2 \) exists as \( \text{Ca}^{2+} \) and \( \text{C}_2^{2-} \left[ \text{\overset{\circ}{C}} \equiv \overset{\circ}{C} \right] \).
19σ and 4π.

D-13*. C* → 1s² 2s¹ 2p³  4 unpaired electron  :  4 bonds
B* → 1s² 2s¹ 2p²  3 unpaired electron  :  3 bonds
I* → 5s² 5p⁴ 5d¹  3 unpaired electron  :  3 bonds
P* → 3s² 3p³  3 unpaired electron  :  3 bonds
* represent excited state

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

<table>
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<th>Species</th>
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<td>CO₃²⁻</td>
<td>sp²</td>
</tr>
<tr>
<td>XeF₄</td>
<td>sp³d²</td>
</tr>
<tr>
<td>I₃⁻</td>
<td>sp³d</td>
</tr>
<tr>
<td>NCl₅</td>
<td>sp³</td>
</tr>
<tr>
<td>BeCl₂</td>
<td>sp</td>
</tr>
</tbody>
</table>

E-9. SnCl₂ – sp²
XeF₄ – sp³d²
I₃⁻ – sp³d
NCl₅ – sp³
HgCl₂ – sp

E-11. (a) Electronic configuration of boron in ground state is 1s²2s²2p¹.

\[ \text{BCl}_3 \]

(b) Electronic configuration of nitrogen in ground state is 1s²2s²2p³.

\[ \text{NH}_3 \]

(c) Electronic configuration of phosphorus in ground state is 1s²2s²2p⁶3s²3p³.

\[ \text{PCl}_3 \]

(d) Electronic configuration of boron in ground state is 1s²2s².

\[ \text{BeF}_2 \]

E-12. CH₄ = 4

sterc No. = 2

∴ Hybridisation sp.
E-15. \( \text{Cl}^+ \text{Cl}^- \) \( \text{sp}^3 \) \( \text{Cl}^+ \text{Cl}^- \) \( \text{sp}^3 \text{d}^2 \) E-17. \( \text{F}\text{B}^-\text{F} \) \( \text{sp}^2 \) \( \text{F}\text{B}^-\text{F} \) \( \text{sp}^3 \)

F-5. (i) \( \text{Xe} \quad \text{sp}^3 \) (ii) \( [\text{N}^+ = \text{N} = \text{N}]^{2-} \) sp

(iii) \( \text{PCl}_5 (s) \) exists as \( [\text{PCl}_4]^+ \) and \( [\text{PCl}_6]^- \),

\[
\begin{align*}
\text{PCl}_5 (s) & \rightarrow [\text{PCl}_4]^+ + [\text{PCl}_6]^- \\
\text{sp}^3 & \quad \text{sp}^3 \\
\end{align*}
\]

(iv) \( \text{ICl}_4 (\text{sp}^3) \) \( \xrightarrow{\text{self ionisation}} \) \( [\text{ICl}_3]^+ + [\text{ICl}_5]^+ \)

F-6. \( \text{sp}^3 \text{d} \) but see-saw shape \( \text{F} \quad \text{S} \quad \text{see-saw} \)

F-7. (A) \( \text{BF}_3 (\text{sp}^3) + \text{F}^- \rightarrow \text{BF}_4^- (\text{sp}^3) \)
(B) \( \text{NH}_3 (\text{sp}^3) + \text{H}^+ \rightarrow \text{NH}_4^+ (\text{sp}^3) \)
(C) \( 2 \text{SO}_2 (\text{sp}^3) + \text{O}_2 \rightarrow 2 \text{SO}_3 (\text{sp}^3) \)
(D) \( \text{H}_2\text{O} (\text{sp}^3) + \text{H}^+ \rightarrow \text{H}_3\text{O}^+ (\text{sp}^3) \)

F-9. \( \text{ClO}_3^\text{O} \) is \( \text{sp}^3 \) & pyramidal but hybridization & shape of \( \text{NO}_3^\text{O} \) is \( \text{sp}^2 \) & trigonal planar.

F-11.* (A) \( \text{XeO}_4 \) (one l.p.) (B) \( \text{XeF}_2 \) (Linear)
(C) \( \text{XeOF}_4 \) (one l.p.) (D) \( \text{XeOF}_5 \) (two l.p.)
F-14. The cation should be
\[\text{[H – C} = \text{N – Xe – F]}^+\]
Hybridisations sp sp sp'd

F-19. \[\text{:N=C=C=N,} \quad \text{[F–Xe–F]}^+\] sp but bent structure due to LP-BP repulsion.

G-2. (A) Bond angle is 180° because of sp hybridisation of nitrogen.

G-4. Generally lone pair causes more distortion than a double bond so
equitorial /FSF in SOF₄ > equitorial /FSF in SF₄

OCF₂ :

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

SF₄:

axial FSF < 180° due to lone pair.

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.

(B) \(\text{H}_3\text{C}^-\text{B}^-\text{CH}_3\) sp² hyb.

(C) \(\text{NH}_4\text{Cl}\) is an ionic compound and ‘N’ is in sp³ hybridisation.

(D) \(\text{S}_8\) molecule has 16 electron parirs 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. \[ \text{H}_2\text{S} - \text{No hybridisation bond angle} \approx 93^\circ \]
\[ \text{NH}_3 - \text{Pyramidal 104.5}^\circ \]
\[ \text{CH}_4 - \text{Tetrahedral 109^\circ 28'} \]
\[ \text{BF}_3 - \text{Triangularplaner 120}^\circ \]

G-11. \[ \text{P}_2\text{ bond angle} = 60^\circ \]
\[ \text{PH}_3\text{ bond angle} = 90^\circ \text{ (Drago's rule)} \]
\[ \text{H}_2\text{O bond angle} = 104.5^\circ \]

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
\[ \text{sp} > \text{sp}^2 > \text{sp}^3 \]
(c) \( \text{SF}_6 < \text{NH}_3 < \text{H}_2\text{O} < \text{OF}_2 \) in this case bond angle of \( \text{NH}_3 \) is highest because lp - lp repulsion is absent in it.
(d) \( \text{ClO}_2 > \text{H}_2\text{O} > \text{H}_2\text{S} > \text{SF}_6 \)
\( \text{ClO}_2\) bond angle is highest due to its sp\(^2\) hybridisation, rest all are sp\(^3\) or sp\(^3\)d\(^2\) hybridised more repulsion in double bond electrons.

\[
\begin{align*}
\text{ClO}_2 & > \text{H}_2\text{O} > \text{H}_2\text{S} > \text{SF}_6 (\text{Octahedral})
\end{align*}
\]

G-14. \[
\begin{align*}
\alpha &= 120^\circ \\
\beta &= 90^\circ \\
\gamma &= 180^\circ \\
\gamma > \alpha > \beta
\end{align*}
\]

G-15. \( \text{SnCl}_2 \); bonding takes place in ground state.
\[ \text{sp}^3 \text{ hybridisation} \]
\[ \text{Due to lp-bp repulsion bond angle slightly decrease from 120}^\circ. \]

\[ \text{SnCl}_2 \]

\[ \text{Due to bp-lp repulsions} \]
G-16.

Hydrogen atoms are in a vertical plane with axial fluorine atoms, \(\pi\)-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.

\[
\begin{array}{c}
\text{H} \quad \text{C} = \text{S} \\
\text{H} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{F} \quad \text{F}
\end{array}
\]

G-18*. B and C \(\Rightarrow\) Drago's rule, \(\text{ICl}_3\)

\(\text{sp}^3\text{d}.\) T. shaped

G-24.
\[
\begin{align*}
\text{XeF}_5 & \quad +6 \\
\text{XeF}_4 & \quad +4 \\
\text{XeF}_2 & \quad +2
\end{align*}
\]

As the oxidation no. increases, size of central atom decreases

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 \(\text{N}_2\text{O}_5\) is +5

Anhydride of \(\text{HOCl}\) is \(\text{Cl}_2\text{O}\).

The bond length decreases with increase in difference of electronegativity.

PART - II

1.

Cl-atom is in \(\text{sp}^3\text{d}\) hybridisation state. Hence geometry is trigonal bi-pyramidal which is similar to \(\text{I}_3^-\)

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.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]

3. \(\text{sp}^3\text{d}^2\)

\[
\begin{align*}
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]

(A) \(\text{Cl} \quad \text{P} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{sp}^3\text{d}\)

(B) \(\text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{sp}^3\text{d}^2\)

(C) \(\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{sp}^3\)
4. Valence shell electron configuration of Cl, 3s² 3p⁵

\[
\begin{array}{c|c|c|c}
3s & 3p & 3d \\
\hline
1 & 1 & 1 \\
\end{array}
\]

sp³ hybridisation

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 sp³d² 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 Fe³⁺ to Fe²⁺.

7. (A) linear
(B) sp³d²: bent (trigonal pyramid)
(C) sp³d²: square pyramidal
(D) XeF₁⁺: T-shaped

<table>
<thead>
<tr>
<th>Exercise #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. XeF₄</td>
</tr>
<tr>
<td>F₂SeO₂</td>
</tr>
<tr>
<td>XeOF₄</td>
</tr>
<tr>
<td>ClOF₃</td>
</tr>
<tr>
<td>XeF₅⁻</td>
</tr>
<tr>
<td>XeF₃⁺</td>
</tr>
</tbody>
</table>

Chemical Bonding # 13
8. \[
\left[ \begin{array}{c}
\text{O} \\
\text{C} \quad \text{O} \\
\text{O} \\
\text{O} \\
\end{array} \right]^{2-} = 4 \quad \text{(i)} \quad \left[ \begin{array}{c}
\text{Cl} \\
\text{I} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]^{4-} = 4 \quad \text{(ii)} \quad \text{F}^+ - \text{N} - \text{F}^- = 3 \quad \text{(iii)} \quad \text{O}^2- = \text{N} - \text{O} - \text{H} = 5
\]

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

**EXERCISE # 3**

1. \(\text{NO}_2^+\)
   - Number of electron pairs = 2
   - Number of bond pairs = 2
   - Number of lone pair = 0
   - So, the species is linear with sp hybridisation.

   \[\text{O} = \text{N} = \text{O}_{\text{sp}}\]

\(\text{NO}_3^-\)
   - 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.

   \[\text{O} - \text{N} - \text{O} \rightarrow \text{sp}^2\]

\(\text{NH}_4^+\)
   - Number of electron pairs = 4
   - Number of bond pairs = 4
   - Number of lone pair = 0
   - So, the species is tetrahedral with sp\(^3\) hybridisation.

   \[\begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \end{array} \rightarrow \text{sp}^3\]

2. According to VSEPR theory:
   - \(\text{sp}^3\text{d}\)-hybridisation: see-saw shape
   - \(\text{sp}^3\)-hybridisation: tetrahedral shape
   - \(\text{sp}^3\text{d}^2\)-hybridisation: square planar shape
3. According to VSEPR theory

\( \text{XeF}_2 \)

Number of electron pairs = 5,
Number of bond pairs = 2,
So, Number of lone pairs = 3
Thus \( \text{XeF}_2 \) is linear with 3 lone pairs occupying 3 equatorial positions of trigonal bipyramidal so as to minimize the repulsions.

\( \text{XeF}_4 \)

Number of electron pairs = 6,
Number of bond pairs = 4,
So, Number of lone pairs = 2
Thus \( \text{XeF}_4 \) is linear with 2 lone pairs occupying 2 axial positions of octahedral pyramidal so as to minimize the repulsions.

\( \text{XeO}_2\text{F}_2 \)

Number of electron pairs (including super electron pairs) = 5,
Number of bond pairs = 4,
So, Number of lone pairs = 1
Thus \( \text{XeO}_2\text{F}_2 \) is see-saw with 1 lone pairs occupying one equatorial position and two double bonds occupying other two equatorial positions of trigonal bipyramidal so as to minimize the repulsions.

4. \( \text{Cl}_2\text{Cl} \)

Steric number = 5, so sp\(^3\)d hybridisation;

\( \text{BCl}_3 \)

Steric number = 3, so sp\(^2\) hybridisation;

\( \text{NH}_3 \)

Steric number = 4, so sp\(^3\) hybridisation;

\([\text{PtCl}_4]^-\)

Is 5d\(^8\) configuration so square planar i.e. dsp\(^2\).

5. \( \text{XeF}_2 \)

\( \text{XeF}_4 \)

\( \text{XeO}_2\text{F}_2 \)

6. \( \text{AlH}_3 \) → \( \text{AlH}_3^+ \)

7. \( \text{NH}_3 \)
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.
$\text{NO}_3^-$ steric number = 3 ; $\text{CO}_3^{2-}$ steric number = 3.

\[
\begin{array}{c}
\text{NO}_3^- \quad \text{sp}^3 \\
\text{trigonal planar}
\end{array}
\quad \begin{array}{c}
\text{CO}_3^{2-} \quad \text{sp}^3 \\
\text{trigonal planar}
\end{array}
\]

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

9. In

\[
\text{H}_2\text{C} \rightarrow \text{CH} \quad \text{C} = \text{N}
\]

From left to right.

**Note:** Hybrid orbitals always form $\sigma$-bonds due to overlapping on their axis.

10. There are 5 electron pairs and all are bond pairs in $\text{PCl}_5$. So to have the minimum repulsions between bond pairs it acquires trigonal bipyramidal shape. In $\text{BrF}_5$, 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.

$$\text{PCl}_5 \quad \text{(trigonal bipyramidal)}, \quad \text{BrF}_5 \quad \text{(square pyramidal)}$$

11. $\text{H} \rightarrow \text{O} \rightarrow \text{C} \rightarrow \text{H} \quad \text{O} \rightarrow \text{C} \rightarrow \text{O}^{-} \quad \text{O}^{-} \rightarrow \text{C} \rightarrow \text{O}^{-}$

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

<table>
<thead>
<tr>
<th>Bond angle</th>
<th>$\text{SO}_2$</th>
<th>$\text{OH}_2$</th>
<th>$\text{SH}_2$</th>
<th>$\text{NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$119.5^\circ$</td>
<td>$104.5^\circ$</td>
<td>$92.5^\circ$</td>
<td>$107^\circ$</td>
<td></td>
</tr>
</tbody>
</table>

13. (A) $\text{CF}_4$ is tetrahedral where as $\text{SF}_4$ is see-saw shaped.

(B) $\text{XeOF}_2$, O = C = O both linear according to VSEPR.

(C) $\text{BF}_3$ is trigonal planar and $\text{PCl}_3$ is pyramidal.
(D) $\text{PF}_3$ is trigonal bipyramidal and $\text{IF}_5$ 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 $\pi$-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$^3$d$^2$ 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 singles 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 90º.

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

\[
\begin{align*}
H_2S &< NH_3 < SiH_4 < BF_3 \\
92.6º &< 107º < 109^o28' < 120º
\end{align*}
\]

18. (A) square planar  \hspace{1cm} (B) see-saw shaped  \hspace{1cm} (C) regular tetrahedral  \hspace{1cm} (D) square planar

19. (A) $sp^3 - sp^2$ \hspace{1cm} (B) $sp^3 - sp^2$ \hspace{1cm} (C) $sp^3 - sp$ \hspace{1cm} (D) $sp^3 - sp^2$

- Acetone
- Acetic acid
- Acetamine
- 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

\[ \begin{align*}
\text{sp}^3d\text{-hybridisation} & : \text{see-saw shape} \\
\text{sp}^3\text{-hybridisation} & : \text{tetrahedral shape} \\
\text{sp}^3d^2\text{-hybridisation} & : \text{square planar shape}
\end{align*} \]

22. Calcium carbide is ionic carbide having [: C = C :]$_2^-$. Ca$^{2+}$ [\(\text{C} = \text{C}^+:\) ]$^{2-}$

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.

\[ \begin{align*}
\text{Br} – F(b) & \quad \text{distance} = 1.79 \, \text{Å} \\
\text{Br} – F(a) & \quad \text{distance} = 1.68 \, \text{Å} \\
F(b) – \text{Br} – F(b) & \quad \text{angle} = 89^{\circ} 48' \\
F(b) – \text{Br} – F(a) & \quad \text{angle} = 86^{\circ} 30' \\
F(b) – \text{Br} – e & \quad \text{angle} = 93^{\circ} 30'
\end{align*} \]

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.

\[ \text{NO}_3^- \]
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.

\[ \text{NH}_4^+ \]
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:

\[
\begin{align*}
F_b - I - F_b &= 72^\circ \text{ (5 number)} ; \\
F_b - I - F_a &= 90^\circ \text{ (10 number)} ; \\
F_b - \text{I bond length} &= 1.858 \pm 0.004 \text{ Å} ; \\
F_a - \text{I bond length} &= 1.786 \pm 0.007 \text{ Å}.
\end{align*}
\]

27. Calcium carbide exists as \( \text{Ca}^{2+} \) and \( \text{C}_2^{2-} \). According to the molecular orbital model, \( \text{C}_2^{2-} \) should have a bond order of 3 (configuration \( \pi_u^2 \pi_u^2 \sigma_g^2 \)). MOT configuration suggests that it contains one \( \sigma \) and two \( \pi \)-bonds \( [\text{C} \equiv \text{C}]^2^- \).

28. \( \text{XeF}_2 \); \( \text{XeF}_4 \); \( \text{XeF}_6 \); \( \text{XeO}_3 \)

29. \( \text{XeOF}_2 \) 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 cental atom are same in all options)

31. \( \text{PF}_5 \) trigonal bipyramidal
    \( \text{BrF}_5 \) 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, \( AB = 2AP \)

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

\[
= \sin \left( \frac{109^\circ 28'}{2} \right) \\
\therefore \quad \text{in tetrahedral structure } \theta = 109^\circ 28'
\]

\[
= \sin (54^\circ 44') \\
\therefore \quad AP = AO \sin (54^\circ 44') = 1.54 \times 0.82 = 1.26 \text{ Å} \\
\therefore \quad AB = 2AP = 2.52 \text{ Å}
\]

Ans. 2.52 Å
8. \[ d_1 = 2 \times 134 \times \sin 60^\circ \text{ pm} = 227.8 \text{ pm} = 228 \text{ pm} \]
\[ d_2 = 134 \times 3 + 2 \times 134 \cos 60^\circ \text{ pm} = 536 \text{ pm} \]

---

**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 \( [(\text{CH}_3)_3\text{N}] \). \( \text{Me}_3\text{N} \) as donor (capacity). \( \text{BBR}_3 > \text{BCl}_3 > \text{BF}_3 \sim \text{BH}_3 > \text{BMe}_3 \).

**A-6.**

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} & \rightarrow \text{BH}_3 \\
\text{C}_2\text{H}_5 & \rightarrow \text{BH}_3
\end{align*}
\]

**A-12*.** Cl$_2$O > F$_2$O and F$_2$O < H$_2$O
\[
\begin{align*}
111^\circ & \text{ and } 102^\circ \\
102^\circ & \text{ and } 104^\circ
\end{align*}
\]

NO$_2^+$ > NO$_2^-$

sp$^2$ > sp$^3$

AsI$_3$ > AsBr$_3$ > AsCl$_3$ (due to size of halogen)

---

**B-3.** (A) F - N = \( N^+ \)

sp$^2$

(B) \( N = N = N \)

(C)

---

**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° (approximate) and OCl$_2$ = 112° (approximate).

(D) Exist in polymeric structure as

---

**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 \( P_\pi \) orbital and does not participate in sp$^3$ hybridisation.
B-9. In BF₃, the B - F bond length is shorter than normal bond character on account of pₓ – pₓ back bonding (1.30 Å). In 1 : 1 complex there is no pₓ – pₓ back bonding and hence the B – F bond length is longer (1.35 Å).

\[ \text{CH}_3 \quad \text{F} \]
\[ \text{CH}_3 \quad \text{N} \longrightarrow \text{B} \quad \text{F} \]
\[ \text{CH}_3 \quad \text{F} \]

Steric number 4

B-12*. (A) Steric repulsions of bulkier groups and pₓ – dₓ dative bonding favor for a linear Si–O–Si group.

(B) Due to stabilization of the conjugate base anion by O(pₓ) → Si(dₓ) bonding motion.

(C) It is pyramidal because pₓ – dₓ bonding is not effective on account of bigger phosphorus atom.

(D) It has most effective pₓ – dₓ overlapping due to small size of Cl and O.

C-7. \( S_{2-} : \text{ClF}_3 \)

\[ S_{2-} : \text{Cl} \quad \text{F} \]

\[ \text{F} \]

S₂⁻: In B₂, mixing of the \( \sigma_2 \) (2s) orbital with the \( \sigma_2 \) (2p) orbital lowers the energy of the \( \sigma_2 \) (2s) orbital and increases the energy of the \( \sigma_2 \) (2p) orbital to a higher level than the \( \pi \) orbitals. As a result, the last two electrons are unpaired in the degenerate (having the same energy) \( \pi \) orbitals, and the molecule is paramagnetic. In \( N_2 \), the \( \sigma_2 \) (2s) and \( \sigma_2 \) (2p) levels of \( N_2 \) interact (mix) less than the \( B_2 \) and \( C_2 \) levels, and the \( \sigma_2 \) (2p) and \( \pi_2 \) (2p) are very close in energy.

C-9. \( N_2^{2-} : \sigma_1 s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_x \pi 2p_y \pi^* 2p_x \pi^* 2p_y \).

B.O. \( N_2^{2-} = \frac{10 - 6}{2} = 2 \).

B.O. \( \text{O}_2 = \frac{10 - 6}{2} = 2 \).

NO⁻: isoelectronic with \( O_2 \), so B.O. = \( \frac{10 - 6}{2} = 2 \).

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

D-1. M.O for \( C_2 = \sigma_1 s^2 < \sigma_2 s^2 \sigma_1 \pi^2 < \sigma_2 \pi^2 < \pi_2 \pi^2 \).

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 \( C_2^{2-}[C \equiv C] \).

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

The bond order of \( N_2^+ \) is 1/2(10 – 4) = 3.

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

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

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

The bond order of \( O_2^- \) is 1/2(10 – 6) = 2.

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

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

NO⁺ derivative of \( O_2 \), and isoelectronic with \( O_2^- \); so \( \sigma (1s)^2 \sigma^* (1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) \).

The bond order of \( NO^+ \) is 1/2(10 – 4) = 3.

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

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

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

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

(B) \( O_2 \) B.O. = 2

(C) \( O_2^- = 2 \frac{1}{2} \)

(D) \( O_2^{2-} = 1 \)
D-11. (A) $\text{H}_2\text{O}_2 = 1.48 \, \text{Å}$ due to repulsions between non-bonded pairs of electron on O-atoms and $\text{O}_2\text{F}_2 = 1.217 \, \text{Å}$. (B) In $\text{O}_2^-$ very slightly increases due to charge (–ve) on two O atoms.

<table>
<thead>
<tr>
<th></th>
<th>Bond Order</th>
<th>Internuclear Distance (pm)</th>
<th>Number of unpaired(s) Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2^-$ (dioxygenyl)</td>
<td>2.5</td>
<td>112.3</td>
<td>1</td>
</tr>
<tr>
<td>$\text{O}_2$ (dioxygen)</td>
<td>2.0</td>
<td>120.07</td>
<td>2</td>
</tr>
<tr>
<td>$\text{O}_2^-$ (superoxide)</td>
<td>1.5</td>
<td>128</td>
<td>1</td>
</tr>
<tr>
<td>$\text{O}_2^-$ (peroxide)</td>
<td>1.0</td>
<td>149</td>
<td>0</td>
</tr>
</tbody>
</table>

D-15. NO$^-$ > NO > NO$^+$ (bond length)  
Bond order  

\[
\begin{array}{ccc}
\text{H}_2 & \text{H}_2^+ & \text{He}_2^+ \\
1 & 0.5 & 0.5 \\
\end{array}
\]

(In He$_2^+$ more electron in antibonding MO’s)  
NO$_2^+$ > NO$_2$ > NO$_2^-$ (bond angle)  
Bond angle  

\[
\begin{array}{ccc}
180^\circ & 133^\circ & 115^\circ \\
\end{array}
\]

No. of unpaired e$^-$  

D-19. NO$_2^+$ 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 trimethyphosphine.

(B) $\text{H}_3\text{Si} \rightarrow \text{O} \rightarrow \text{SiH}_3 \rightarrow \text{H}_3\text{Si} = \text{O} \rightarrow \text{SiH}_3$

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 $\pi$-bonds whereas, there is one $\sigma$ and one $\pi$-bond in O$_2$ molecule

\[
\begin{array}{c}
\text{C}_2 = 131 \, \text{pm} \\
\text{O}_2 = 121 \, \text{pm} \\
\end{array}
\]

(D) B$_2$ : $\sigma^1s^2 \sigma^1s^2 \sigma^2s^2 \sigma^2s^2 \sigma^3p^2 \sigma^3p^2$...

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$_2^-$ : $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p)^2 \sigma^*(2p)^2 \sigma(2p)^2 \sigma^*(2p)^2 \sigma(2p)^2 = \pi^*(2p)^2 \pi^*(2p)^2 \pi^*(2p)^2$

(B) NO is derivative of O$_2$ : NO(O$_2^-$) $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p)^2 \sigma^*(2p)^2 \sigma(2p)^2 = \pi^*(2p)^2 \pi^*(2p)^2 \pi^*(2p)^2$

(C) O$_2$ : $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p)^2 \sigma^*(2p)^2 \sigma(2p)^2 = \pi^*(2p)^2 \pi^*(2p)^2 \pi^*(2p)^2$

(D) B$_2$ : $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p)^2 \sigma^*(2p)^2 \sigma(2p)^2 \sigma^*(2p)^2 \sigma(2p)^2$...
D-28*. NO– > NO > NO– (bond length)
Bond order 2.0 2.5 3
H2 > H2+ > He2+ (bond energy)
Bond order 1 1 0.5
NO2– > NO2 > NO2– (more antibonding electron in He2+)
Bond angle 180° 133° 115°
O22– = O22+ > O22– (paramagnetic moment)
No. of unpaired e– 0 0 2

E-3. (A) N2O3  Dinitrogen trioxide
(B) N2O22– Hyponitrite ion
(C) N2O5  Dinitrogen pentoxide
(D) N2O4  Dinitrogen tetroxide

E-4. The correct formula of borax is Na2[B4O5(OH)4]. 8H2O. The structure of anion is:

E-8.*  P4O10
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 $\pi$–p$^\pi$ back bonding. A full p-orbital on the oxygen atom overlaps sideway 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) $[\text{PCl}_4]^+ \rightarrow \text{sp}^3$

(II) $\text{PF}_4^-$ has $\approx 102^\circ$ bond angle due to $\text{lp} - \text{lp}$ repulsion, as bond pairs are closer to F-atoms.

(III) All have $\text{sp}^3$ hybridisation and one lone pair.

(IV) $\text{P} = \text{P}^-$

E-12.

E-13. (A) $\text{O} \equiv \equiv \text{C} \equiv \equiv \text{C} \equiv \equiv \text{O}$

(B) Resonance takes place $\text{no resonance}$ Therefore, six Cr – O bond lengths are not equal.

(C) This is an example of 3-centre 2-e bond which is also known as Banana bond. But $\text{Al}_{2}\text{Cl}_6$ 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, $\text{I}^-$ . 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) $\text{KO}_2 \equiv \text{O}_2^{2-}$ B.O = 1.5
$\text{Na}_2 \equiv \text{O}_2^{2-}$ B.O = 1

(D) $\text{C}_2\text{H}_4$ $\equiv \text{C} \equiv \equiv \text{C} \equiv \equiv \text{H}$

(S + P + P) $\rightarrow$ (SP$_3$) $\rightarrow$ (S + P$_x$ + P$_y$) $\equiv \equiv \text{C} \equiv \equiv \text{H}$

xz - plane $\rightarrow$ (xy - plane)
general formula of cyclic silicates is \( [\text{Si}_n\text{O}_{3n}]^{2n-} \)

**PART - II**

### 1.

<table>
<thead>
<tr>
<th>Bond Order</th>
<th>Intermolecular Distance (pm)</th>
<th>Number of unpaired(s)</th>
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</tr>
<tr>
<td>1.0</td>
<td>149</td>
<td>0</td>
<td>(diamagnetic)</td>
</tr>
</tbody>
</table>

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

**B** Helium molecule (He\(_2\))

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\(_2\))

**D** Lithium molecule (Li\(_2\))

Peroxide (O\(_{2+}\))

As all electrons are paired so C\(_2\), Li\(_2\), and O\(_{2+}\) are diamagnetic.

**D** Fluorine molecule (F\(_2\))

### 2.

(D) It is correct statement.

### 3.

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<td>149</td>
<td>0</td>
<td>(diamagnetic)</td>
</tr>
</tbody>
</table>

### 4.

**Oxygen molecule (O\(_2\))**

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

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

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

**Nitrogen molecule (N\(_2\))**

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

Bond order = \( \frac{1}{2}(9 - 4) = 2.5. \)
5. (I) $\text{O}^{2+} : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma 2p)^2 (\pi 2p_x = \pi 2p_y)$ ($\pi^* 2p_x = \pi^* 2p_y$)  
Bond order = $\frac{1}{2}(10 - 5) = 2.5$.

(II) $\text{NO}$ is derivative of $\text{O}_2$ and isoelectronic with $\text{O}^{2+}$:  
so $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma 2p)^2 (\pi 2p_x = \pi 2p_y)$ ($\pi^* 2p_x = \pi^* 2p_y$)  
Bond order = $\frac{1}{2}(10 - 5) = 2.5$.

(III) $\text{N}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_y = \pi 2p_x)$ ($\pi^* 2p_y = \pi^* 2p_x$)  
Bond order = $\frac{1}{2}(9 - 4) = 2.5$.

$\text{O}^{2+}$, $\text{NO}$ and $\text{N}_2^+$ have same bond order i.e. 2.5 and have same magnetic property having one unpaired electron.

10. (A) $\text{N}_2^+ : \text{BO} = 2.5$ (4 electron in antibonding MO) 1 unpaired electron (Paramagnetic)  
$\text{N}_2^- : \text{BO} = 2.5$ (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic)  
(B) $\text{NO} : \text{BO} = 2.5$ (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic), Last electron in antibonding MO. So, easily removed.  
(C) $\text{NO}^+ : \text{BO} = 3$ (0 unpaired electron) diamagnetic [BO ↑ ⇒ BL ↓].  
(D) $\text{He}^2+ : \text{BO} = 0.5$ (1 unpaired electron) paramagnetic [1 electron in antibonding MO].  
$\text{H}^2+ : \text{BO} = 0.5$ (1 unpaired electron) paramagnetic [0 electron in antibonding MO].

**EXERCISE # 2**

11. (a) Hydrogen molecule ($\text{H}_2$) : $\text{H}_2 : (\sigma 1s)^2$  
Its bond order, therefore, is $\frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$  
(b) Cation of hydrogen molecule ($\text{H}_2^+$) : $\text{H}_2^+ : (\sigma 1s)^1$  
Its bond order, therefore, is $\frac{1}{2}(1 - 0) = \frac{1}{2}$  
(c) Helium molecule ($\text{He}_2$) : $\text{He}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$  
Its bond order, therefore, is $\frac{1}{2}(2 - 2) = 0$  
(d) Lithium molecule ($\text{Li}_2$) : $\text{Li}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$  
Its bond order, therefore, is $\frac{1}{2}(4 - 4) = 1$.  
(e) Beryllium ($\text{Be}_2$) : $\text{Be}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x = \pi 2p_y) (\pi^* 2p_x) (\pi^* 2p_y)$  
Its bond order, therefore, is $\frac{1}{2}(6 - 4) = 1$.  
(f) Boron ($\text{B}_2$) : $\text{B}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x = \pi 2p_y) (\pi^* 2p_x) (\pi^* 2p_y)$  
Its bond order, therefore, is $\frac{1}{2}(6 - 6) = 1$.  

13. $^*\sigma 3p$ - - - - -  
$^*\pi 3p$ ↓ ↑ ↓ ↑ ↓  
$\pi 3p$ ↑ ↑ ↓ ↑ ↓  
$\sigma 3p$ ↓ ↑  
$^*\sigma 3s$ ↓ ↑  
$\sigma 3s$ ↓ ↑  
$S_2$ $S_2^+$  
Bond order $S_2 = \frac{8 - 4}{2} = 2$ (paramagnetic with two unpaired electrons)  
$S_2^+ = \frac{8 - 6}{2} = 1$ (diamagnetic, as all electrons are paired).

16. Complex exists as $\text{NO}^+$ and $[\text{BF}_4]^-$. NO$^+$ is isoelectronic with $\text{N}_2$ :  
so $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x = \pi 2p_y,$  
$\sigma 2p_z$, then its bond order is $\frac{10 - 4}{2} = 3$. 

*Resonance*

**Chemical Bonding # 26**
20. (a) 6 shared ‘O’ atoms.

(b) \( HO-S-S-S-OH \)

(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) \( (\text{Si}_3\text{O}_11^{6-})_n \)

(c) \( (\text{Si}_3\text{O}_{10})^{8-} \)

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

(e) \( (\text{Na}^+\text{PO}_3^-)_6 = \text{Na}_6(\text{PO}_3)_6 \)
1. According to the structure of cyclic metaphosphoric acid, \((\text{HPO}_3)_3\), there are three \(\text{P}–\text{O}–\text{P}\) bonds.

2. Molecular orbital electronic configuration of \(\text{O}_2\) is as follows (\(\text{Z}\) is taken as molecular axis).

\[
\begin{align*}
\sigma_{1s^2} & \quad \sigma^*_{1s^2} & \quad \sigma_{2s^2} & \quad \sigma^*_{2s^2} & \quad \sigma_{2p_z^2} & \quad \pi_{2p_y^2} & \quad \pi^*_{2p_y^2} & \quad \sigma_{2p_z^2} \\
\end{align*}
\]

Bond order \(= \frac{10 - 6}{2} = 2\).

As it contains two unpaired electrons in bonding \(\pi\) molecular orbitals \(\text{O}_2\) is paramagnetic.

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

3. There is no S-S bond in \(\text{S}_3\text{O}_9\).

4. \(\text{CN}^-, \text{CO}\) and \(\text{NO}^+\) all have same number of electrons i.e. 14. So all are isoelectronic species. Further all the species are isoelectronic with \(\text{N}_2\) which have molecular orbital electronic configuration as follows

\[
\begin{align*}
\sigma_{1s^2} & \quad \sigma^*_{1s^2} & \quad \sigma_{2s^2} & \quad \sigma^*_{2s^2} & \quad \sigma_{2p_z^2} & \quad \pi_{2p_y^2} & \quad \pi^*_{2p_y^2} & \quad \sigma_{2p_z^2} \\
\end{align*}
\]

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. \(\text{O}_2^-\) is derivative of \(\text{O}_2\) and has 17 electrons. So its molecular orbital electronic configuration is

\[
\begin{align*}
\sigma_{1s^2} & \quad \sigma^*_{1s^2} & \quad \sigma_{2s^2} & \quad \sigma^*_{2s^2} & \quad \sigma_{2p_z^2} & \quad \pi_{2p_y^2} & \quad \pi^*_{2p_y^2} & \quad \sigma_{2p_z^2} & \quad \pi^*_{2p_z^2} \\
\end{align*}
\]

As it contains one unpaired electron in \(\pi^*2p_y\) molecular orbital so it is paramagnetic. Rest all species have paired electrons so diamagnetic.

7. \(\text{O}_2\) bond order = 2 ; \(\text{O}_2^-\) bond order = 1.5 ; \(\text{O}_2^{2-}\) bond order = 1.0 ; \(\text{O}_2^{+}\) bond order = 2.5.

8. In diethyl ether (\(\text{C}_2\text{H}_5\)─\(\overset{-}{\text{O}}\)─\(\text{C}_2\text{H}_5\)) oxygen atom has two lone pairs of electrons, thus acts as lewis base while in anhydrous \(\text{AlCl}_3\) aluminium has vacant 3p-orbital of valence shell and thus acts as Lewis acid. \(\text{AlCl}_3\) accepts a lone pair of electrons from diethyl ether to complete its octet forming a complex

\[\text{C}_2\text{H}_5\overset{-}{\text{O}}\rightarrow\text{AlCl}_3\]

Hence, anhydrous \(\text{AlCl}_3\) is more soluble in diethyl ether by means of solvolysis in comparison to hydrous \(\text{AlCl}_3\) (i.e., \(\text{AlCl}_3\), \(6\text{H}_2\text{O}\)). Hydrous \(\text{AlCl}_3\) is a polar compound, while ether is non-polar, so on basis of Thumb's rule, like dissolve in like solvents. Hence hydrous \(\text{AlCl}_3\) is least soluble in ether.
9. It is peroxodisulphuric acid, the Marshall’s acid and contains one – O – O – linkage as given in structure:

\[
\begin{array}{c}
\text{HO} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{OH} \\
\end{array}
\]

\[(H_2S_2O_8)\]

10. Molecular orbital electronic configuration is \[\sigma_{1s}^2 \sigma^*_{1s}^2 \sigma_{2s}^2 \sigma^*_{2s}^2 \sigma_{2p_x}^2 \pi_{2p_x}^2 \pi^*_{2p_x} \pi_{2p_y}^2 \pi^*_{2p_y} \]

As it contains one unpaired electron it is paramagnetic and bond order = \((10 - 5) / 2 = 2.5\) \((O_2 = 2.0)\).

11. The electronic configuration of \(O_2\) will be:

\[
O_2 = \sigma_{1s}^2 \sigma^*_{1s}^2 \sigma_{2s}^2 \sigma^*_{2s}^2 \sigma_{2p_z}^2 \pi_{2p_z}^2 \pi^*_{2p_z} \]

Now

\[
\text{bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2
\]

Similarly electronic configuration of \(O_2^+\) (in KO) will be

\[
\sigma_{1s}^2 \sigma^*_{1s}^2 \sigma_{2s}^2 \sigma^*_{2s}^2 \sigma_{2p_z}^2 \pi_{2p_z}^2 \pi^*_{2p_z} = \pi^*_{2p_z} \]

Bond order = \[\frac{10 - 7}{2} = \frac{3}{2} = 1.5\]

In \(O_2[AsF_4]^+\), \(O_2^+\) is \(O_2^+\) ·

The electronic configuration of \(O_2^+\) will be

\[
\sigma_{1s}^2 \sigma^*_{1s}^2 \sigma_{2s}^2 \sigma^*_{2s}^2 \sigma_{2p_z}^2 \pi_{2p_z}^2 \pi^*_{2p_z} = \pi^*_{2p_z} \]

Bond order = \[\frac{10 - 5}{2} = 2.5\]

Hence bond order will be \(O_2^- < O_2 < O_2^+\) because Bond order \(\propto \frac{1}{\text{Bond length}}\).

13. NO and NO\(^+\) are derivative of \(O_2\):

\[
\text{NO}^+(\text{isoelectronic with } O_2^+) : (\sigma_1s)^2 (\sigma^*_{1s})^2 (\sigma_2s)^2 (\sigma^*_{2s})^2 (\sigma_2p_x)^2 (\pi_{2p_x}) (\pi^*_{2p_x}) = \pi^*_{2p_x}
\]

Bond order = \[1/2(10 - 5) = 2.5\]

\[
\text{NO}^+(\text{isoelectronic with } O_2^+) : (\sigma_1s)^2 (\sigma^*_{1s})^2 (\sigma_2s)^2 (\sigma^*_{2s})^2 (\sigma_2p_x)^2 (\pi_{2p_x}) (\pi^*_{2p_x}) = \pi^*_{2p_x}
\]

Bond order = \[1/2(10 - 4) = 3\]

Bond order \(\propto 1/\text{bond length}\).

So NO\(^+\) has shorter bond length.


(B) One oxygen atom is shared between two adjacent tetrahedra, \([SiO_4]^{4-}\).

(C) All four oxygen atoms are shared between adjacent tetrahedra, \([SiO_4]^{4-}\).

(D) Two oxygen atoms are shared between adjacent tetrahedra, \([SiO_4]^{4-}\) forming a linear chain.

17.

18. \(He^+ \rightarrow \sigma(1s)^2 \sigma^*(1s)^1\), one unpaired electron.

\(H_2 \rightarrow (1s)^2\), \(\sigma^*(1s)^0\), no unpaired electron.

\(H_2 \rightarrow \sigma(1s)^1\), \(\sigma^*(1s)^0\), one unpaired electron.

\(H_2 \rightarrow \sigma(1s)^1\), \(\sigma^*(1s)^0\), 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 \(O_2^+\) ion there are \(16 + 2 = 18\) electrons. The electronic configuration of \(O_2^+\) ion is

\[KK\sigma(2s)^2 \sigma^*(2s)^2 \pi(2p)^2 \pi^*(2p)^2 p(2p)^2 \pi^*(2p)^2 \pi^*(2p)^2 \pi^*(2p)^2 \]

Here KK represents non-bonding molecular orbital of 1s orbital. \(O_2^+\) contains no unpaired electrons.
The electronic configuration of B₂ molecule is
KK σ(2s)² σ*(2s)² π(2pₓ)¹ π(2pᵧ)¹
It contains 2 unpaired electrons. The electronic configuration of N₂⁺ ion is
KK σ(2s)² σ*(2s)² π(2pₓ)² σ(2pᵧ)² σ*(2pₓ)₁
It contains one unpaired electron.
The electronic configuration of O₂⁺ molecule is
KK σ(2s)² σ*(2s)² π(2pₓ)² π(2pᵧ)² σ(2pₓ)² π*(2pₓ)¹ π*(2pᵧ)¹
It contains 2 unpaired electrons.

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

CO = σ₁s² σ*₁s² σ₂s² σ*₂s² π₂pₓ² π₂pᵧ² σ₂pₓ²
Bond order of CO = 10 – 4 / 2 = 3

NO⁻ = σ₁s² σ*₁s² σ₂s² σ*₂s² π₂pₓ² π₂pᵧ² π₂pₓ² σ₂pₓ²
Bond order of NO⁻ = 10 – 6 / 2 = 2

NO₂⁻ = σ₁s² σ*₁s² σ₂s² σ*₂s² π₂pₓ² π₂pᵧ² σ₂pₓ²
Bond order of NO₂⁻ = 10 – 4 / 2 = 3

CN⁻ = σ₁s² σ*₁s² σ₂s² σ*₂s² π₂pₓ² π₂pᵧ² σ₂pₓ²
Bond order of CN⁻ = 10 – 4 / 2 = 3

N₂ = σ₁s² σ*₁s² σ₂s² σ*₂s² π₂pₓ² π₂pᵧ² σ₂pₓ²
Bond order of N₂ = 10 – 4 / 2 = 3.

21. KO₂ exists as K⁺ & O₂⁻.
In O₂⁻, superoxide ion there are total number of electrons = 16 + 1 = 17.
MOT configuration = σ₁s² σ*₁s² σ₂s² σ*₂s² σ₂pₓ² π₂pₓ² π₂pᵧ² π₂pₓ² π₂pᵧ² σ₂pₓ²
O₂⁻ has one unpaired electron in antibonding π*₂pᵧ¹. So it is paramagnetic.

22. Steric number = 4 ; thus sp³ hybridisation in P₄. As each phosphorus is sp³, so
% p character will be = \( 3 \times 100 = 75 \).

23. O₂⁻(8 + 8 + 2 = 18) : σ₁s² σ*₁s² σ₂s² σ*₂s² σ₂pₓ² π₂pₓ² π₂pᵧ² π₂pₓ² π₂pᵧ² σ₂pₓ² ; all electrons are paired. So diamagnetic.

24. Molecular orbital configuration of O₂⁻

\[ \sigma_1s^2\sigma^*_1s^2\sigma_2s^2\sigma^*_2s^2\sigma_2p_x^2\pi_2p_x^2\pi_2p_y^2\pi^*_2p_x^1\pi^*2p_y^1 \]

\[ \Rightarrow \text{Paramagnetic} \]

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

O₂⁺

\[ \sigma_1s^2\sigma^*_1s^2\sigma^1s^2\sigma_2s^2\sigma^*2s^2\sigma_2p_x^2\pi_2p_x^2\pi^*_2p_y^1 \]

\[ \Rightarrow \text{Paramagnetic} \]

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

N₂⁻

\[ \sigma1s^2\sigma^*1s^2\sigma2s^2\sigma^*2s^2\pi2p_x^2\pi2p_y^2\sigma2p_z^2 \]

\[ \Rightarrow \text{Paramagnetic} \]

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

N₂⁺

\[ \sigma1s^2\sigma^*1s^2\sigma2s^2\sigma^*2s^2\pi2p_x^2\pi2p_y^2\sigma2p_z^1 \]

\[ \Rightarrow \text{Paramagnetic} \]

\[ \text{Bond order} = \frac{9 - 4}{2} = 2.5 \]
\[
\begin{align*}
C_2 & \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x \pi 2p_y \\
& \Rightarrow \text{Paramagnetic} \\
\text{Bond order} &= \frac{8 - 4}{2} = 2 \\
C_2^+ & \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x \pi 2p_y \\
& \Rightarrow \text{Paramagnetic} \\
\text{Bond order} &= \frac{7 - 4}{2} = 1.5 \\
NO & \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x \pi 2p_y \pi^* 2p_x \\
& \Rightarrow \text{Paramagnetic} \\
\text{Bond order} &= \frac{10 - 5}{2} = 2.5 \\
NO^- & \Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x \pi 2p_y \pi^* 2p_x \\
& \Rightarrow \text{Diamagnetic} \\
\text{Bond order} &= \frac{10 - 4}{2} = 3.
\end{align*}
\]

25. NO\(^+\) is derivative of O\(_2\); NO\(^-\) (isoelectronic with O\(_2\)) \(\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x \pi 2p_y \pi^* 2p_x \pi^* 2p_y \)

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

CN\(^-\) is derivative of N\(_2\); CN\(^+\) (isoelectronic with N\(_2\)) \(\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x \pi 2p_y \sigma^* 2p_z \)

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

26. (A) B\(_2\) \(\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x = \pi 2p_y \)

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

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

\[
\begin{align*}
2B + 3Cl_2 & \longrightarrow 2BCl_3; & 2B + 3Ca & \longrightarrow Ca_2B_2 \text{ (boride)} \\
\text{Mixing of 's' and 'p' orbitals takes place.}
\end{align*}
\]

(B) N\(_2\) \(\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x = \pi 2p_y \sigma^* 2p_z \)

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

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

\[
\begin{align*}
N_2 + O_2 & \longrightarrow 2NO; & 6Li + N_2 & \longrightarrow 2Li_3N \\
\text{Mixing of 's' and 'p' orbitals takes place.}
\end{align*}
\]

(C) O\(_2^-\) \(\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x \pi 2p_y = \pi 2p_x \pi^* 2p_y \)

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

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

\[
\begin{align*}
O_2^- & \longrightarrow O_2 + e^-; & O_2^- + e^- & \longrightarrow O_2^{2-} \\
\text{Mixing of 's' and 'p' orbitals does not take place.}
\end{align*}
\]

(D) O\(_2\) \(\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x \pi 2p_y = \pi 2p_x \pi^* 2p_y \)

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

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

\[
\begin{align*}
O_2 & \longrightarrow O_2^+ + e^-; & O_2^+ + e^- & \longrightarrow O_2^{2-} \\
\text{Mixing of 's' and 'p' orbitals does not take place.}
\end{align*}
\]
27. (A) \( \text{N} \quad 1.126 \text{ Å} \quad \text{N} \quad 1.186 \text{ Å} \quad \text{O} \) \\
\( \text{N}_2\text{O} \)

(B) \( \text{N} \quad 1.864 \text{ Å} \quad \text{O} \)

asymmetric form of \( \text{N}_2\text{O}_4 \)

(C) \( \text{O} \quad \text{N} \quad \text{O} \)

\( \text{N}_2\text{O}_4 \)

(D) \( \text{O} \quad \text{N} \quad \text{O} \)

\( \text{N}_2\text{O}_5 \)

28. \( \text{F} \quad \text{B} \quad \text{F} \) \\
Vacant 2p-orbital \\
Filled 2p-orbital \\

Decrease in \( \text{B} \quad \text{F} \) bond length which results in the higher bond dissociation energy of \( \text{B} \quad \text{F} \) in \( \text{BF}_3 \) is due to delocalised \( \pi \)-\( \pi \) bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

29. 

<table>
<thead>
<tr>
<th>Bond Order</th>
<th>Bond Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ( \text{O}_2^+ )</td>
<td>( \frac{10 - 5}{2} = 2.5 )</td>
</tr>
<tr>
<td>(2) ( \text{O}_2^- )</td>
<td>( \frac{10 - 7}{2} = 1.5 )</td>
</tr>
<tr>
<td>(3) ( \text{O}_2^{2-} )</td>
<td>( \frac{10 - 8}{2} = 1 )</td>
</tr>
<tr>
<td>(4) ( \text{O}_2^{2+} )</td>
<td>( \frac{10 - 4}{2} = 3 )</td>
</tr>
</tbody>
</table>

Bond order \( \propto \frac{1}{\text{bond length}} \)

So, \( \text{O}_2^{2-} \) has the shortest bond length.

30. \( \text{B}_2 \); total number of electrons = 10. The MOT electron configuration violating the Hund's rule will be thus:

\[ \sigma^{1s^2} \sigma^*_{1s^2} \sigma_{2s^2}^2 \sigma^*_{2s^2} \sigma_{2p^x}^2 = \pi_{2p_y}^0 \sigma_{2p_z}^0 \]

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 (\( \text{H}_3\text{PO}_4 \)) Dibasic :: \( x = 2 \)
Di meta phosphoric acid (\( \text{H}_5\text{P}_2\text{O}_8 \)) Dibasic :: \( y = 2 \)
Pyro phosphoric acid (\( \text{H}_4\text{P}_2\text{O}_7 \)) tetrabasic :: \( y = 4 \)

Answ. 224

13. (P) Molecular orbital electronic configuration;

\( \text{NO}^+ \) is derivative of \( \text{O}_2 \), so MOT configuration is:

\[ \sigma_{1s^2} \sigma^*_{1s^2} \sigma_{2s^2} \sigma^*_{2s^2} \sigma_{2p^x^2} \pi_{2p_y^2} = \pi_{2p_z^2} \quad (x \text{ is taken as molecular axis}) \]

Bond order = \( \frac{10 - 4}{2} = 3 \)

One \( \sigma \) bond and two \( \pi \) bonds.
(Q) Number of $\sigma$ bonds in NO$^+$ is one and in BF$_4^-$ are four. So total number of $\sigma$ bonds are five.

\[
\begin{array}{c}
\text{F} \\
\text{B} \\
\text{F}
\end{array}
\]

(R) Number of $\pi$ bonds in NO$^+$ are two.

\[
\begin{array}{c}
\text{F} \\
\text{B} \\
\text{F}
\end{array}
\]

(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.

\[
\begin{array}{cccc}
P & Q & R & S \\
3 & 5 & 2 & 4
\end{array}
\]

Ans. 15.

O$_2$[AsF$_6$] $\longrightarrow$ O$_2^+$ $+$ [AsF$_6$]$^-$

O$_2^{2-}$ peroxide ion B.O = $\frac{1}{2}$ (10 – 8) = 1.

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{O}
\end{array}
\]

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

carbon suboxide is C$_3$O$_2$

O = C = C = C = O.

\[
\text{Me}_3\text{Si} \equiv \text{N} \equiv \text{SiMe}_3
\]

Number of l.p is present in N(SiMe$_3$)$_3$ is zero.

16.

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 sideway with an empty d-orbital on the phosphorus atom. The bond angle POP is 127º and there is no P – P bonds.

(i) P = O have bond length of 1.43 Å (8 covalent bonds)
(ii) P – O have bond length of 1.60Å (12 covalent bonds)
(iii) Number of P – O – P linkage = 6.
(iv) Number of lone pair on each phosphorus atom is zero.

\[
\begin{array}{cccc}
\text{(i)} & \text{(ii)} & \text{(iii)} & \text{(iv)} \\
4 & 12 & 6 & 0
\end{array}
\]
**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. 

\[
\begin{align*}
\text{LiCl} & < \text{BeCl}_2 < \text{BCl}_3 < \text{SnCl}_4
\end{align*}
\]

**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 then 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 $\sigma$ and two $\pi$ bonds but C$_2$ contains only two $\pi$ bonds as four electrons are present in bonding $\pi$ molecular orbitals.

(B) Cu$^{2+}$ has higher hydration energy then 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**

1. 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.

2. 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.

3. 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

\[
\text{SiCl}_4 < \text{SnCl}_4 < \text{SnF}_4 < \text{SnCl}_2 < \text{SnF}_2
\]

4. As polarizability of anion increases covalent character increases.

5. Larger anion has higher polarisability.
EXERCISE # 3

1. **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.

2. 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. SnCl₄, PbCl₄, SiCl₄, etc. whereas those which show +2 oxidation state are ionic in nature and behave as reducing agent. e.g. SnCl₂, PbCl₂, 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.

3. High charge and small size of the cations increases polarisation. As the size of the given cations decreases as
   
   \[ K^+ > Ca^{2+} > Mg^{2+} > Be^{2+} \]
   
   Hence, polarising power increases as
   
   \[ K^+ < Ca^{2+} < Mg^{2+} < Be^{2+} \]

4. Covalent character in ionic compounds is governed by Fazan’s Rule. AlCl₃ will show Maximum covalent character on account of higher polarising power of Al³⁺ 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-5. XeF₂

XeOF₂

IOCl₄⁻

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

\[ \text{XeF}_4 \mu = 0 \text{ non polar} \]
A-16. So dipole moment of NH$_3$ is greater than NF$_3$.

A-19. Dipole moment of compound if it would have been completely ionic

$$= (4.8 \times 10^{-10} \text{ esu}) (2.67 \times 10^{-6} \text{ cm}) = 12.8 \text{ D}$$

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. $S_1$: Due to resonance, both bonds are equal.

$S_2$: 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.

$$\delta^- \delta^- \delta^- \delta^-$$

and so on

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 $\pi$ bond. The electrons are delocalised over the whole sheet.
**B-9.** (A) As $\delta^+$ charge on central atom increases, the attraction between $\delta^+$ and $\delta^-$ increases and thus Xe–F bond length decreases. The correct order is $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$. (B) $\text{PH}_5$ can not undergo sp$^3$d hybridisation as there is much large difference in size of s, p and d orbitals. $\text{PH}_5$ does not exist as no partial positive charge develops on P atom. (C) Dipole moment of $\text{CH}_3\text{Cl}$ is greater than $\text{CH}_3\text{F}$ due to greater charge separation on carbon and chlorine atoms in $\text{CH}_2\text{Cl}$. (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**

![Maleic Acid Structure](image)

$\text{O}[\text{AsF}_4] = \text{O}^{2-}$; $\text{B.O.} = 2.5$ so $\text{O}^+ +$ has smaller bond length than $\text{O}^{2-}$

$\text{KO}_4 = \text{O}^{2-}$; $\text{B.O.} = 1.5$

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 $\text{N}_2$ is more than $\text{N}_2^+$. 
$S_4$: 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.

$S_2$: $\text{H}_2^+ : \sigma 1s^1$; $\text{B.O.} = \frac{1}{2}$

$\text{He}_2^+ : \sigma 1s^2\sigma 1s^1$; $\text{B.O.} = \frac{1}{2}$

But $\text{He}_2^+$ 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$_2$O, the bond angle is more than 109°28’ due to steric repulsion.

**C-4.**

As molecular weight increases, magnitude of Van der Waals 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 NH$_3$ = 238.5 K and SbH$_3$ = 254.6 K.

**C-6.**

(A) in $\text{S}_8$ hybridisation of each S-atom is sp$^3$, in $\text{P}_4$ hybridisation of each P-atom is sp$^3$

(B) 177° $\text{F} - S - \text{F} \text{ due to bp-lp repulsions}$

(C) Inter molecular H-bonding (PO$_4^{3-}$ groups are bonded by many H-bonds)

(D)
C-7*. (A) Boiling point of ICl > Br₂ as ICl is polar and Br₂ is non-polar in nature.

(B) pyramidal about each N-atom.

(C) identical due to resonance.

D) \[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\] identical due to resonance.

C-8*. (A) SbH₃ > NH₃ > AsH₃ > PH₃ (order of B.Pt)

(B) As D₂O has higher molecular mass than H₂O so its density is more.

(C) Mn → 4s²3d⁵
   Ca → [Ar] 4s²
   Sr → [Kr]5s²
   Rb → [Kr]5s¹
   Refer notes

(D) H₂ → weak VDW forces
   CO₂ → weak VDW force but stronger than H₂.
   H₂O → H-bonding.

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

(B) CD₃F is more polar than CH₃F. In CD₃F, C–D bond is more polar as deuterium is more electropositive than hydrogen.

(C) Silyl isocyanate (SiH₃NCO) is linear in shape because of pₓ–dₓ delocalisation of lone pair of electrons on nitrogen. While in methyl isocyanate (CH₃NCO) there is no pₓ–dₓ delocalisation of electron as carbon does not have empty d-orbital and thus is bent in shape.

In CH₂=C=C=CH₂, 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. (I)

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$_2$O present, instead of with other HF molecules and H$_3$O$^+$ and F$^-$ are much more likely to be formed.
(C) H$_3$BO$_3$(solid) has intermolecular hydrogen bonding.

C-14. (A) Like hydrated copper sulphate (CuSO$_4$.5H$_2$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)

(B) Structure of anions are different CO$_3^{2-}$ - trigonal planar (sp$^2$)  
\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

SO$_3^{2-}$ - trigonal pyramidal (sp$^3$) (false)

(C) O=\text{Xe}=O no lone pair of electrons (false)

(D) True.  
D$_2$O = 374.4 K; H$_2$O = 373.0 K

C-16. S$_2$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 hydracids, the acidity increases down the group while for oxyacids, the acidity decreases down the group.
C-17*. 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$_2$O 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 H$_2$O > H$_2$Te > H$_2$Se > H$_2$S.

C-28 D is less electronegative than H-atom so the results

PART - II

4. \[
\text{Net dipole moment} = \sqrt{a^2 + a^2 + 2a.a\cos120^\circ}
\]
\[
= \sqrt{2a^2 - a^2} = a
\]

5. IF$_5$ has symmetrical Pentagonal bipyramidal shape.

6. o-nitrophenol has intramolecular H-bonding so it will be vaporised first.

8. D$_2$O has different physical properties than H$_2$O max. density of D$_2$O is at approximately 10°C

10. (A) \[
\begin{array}{c}
\text{sp}^3d; \quad \angle F-I-F = 180^\circ; \quad \mu = 0
\end{array}
\]

(B) \[
\begin{array}{c}
\text{sp}^3d; \quad \text{polar}; \quad \angle F-Cl-F \neq 180^\circ
\end{array}
\]

(C) \[
\begin{array}{c}
\text{sp}^3d, \quad \text{non}-\text{polar}; \quad \angle F-Xe-F = 180^\circ
\end{array}
\]

(D) \[
\begin{array}{c}
\text{sp}^3d, \quad \text{polar}; \quad \angle F-S-F \neq 180^\circ; \quad \text{one lone pair}
\end{array}
\]
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 electronegativity, 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 NH₃. Due to this boiling point of NH₃ is more. For the same reason, boiling point and bond energy are also more for NH₃ than PH₃.

12. (A) CuSO₄.5H₂O SO₄²⁻ is resonance stablized
(B) Ca²⁺ / SO₄²⁻ are held together by electrostatic force of attraction i.e., ionic bond but alternate layers by H – bonds with water molecules
\[
\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}
\]
(C) H₃PO₄ → H–O–P–O–H
(D) Cl–C–H

13. (A) Br₂ 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 Na(OH)₂⁺ and F(H₂O)⁻ exist. Hydrogen bond exist between water molecules. In addition they also experience dispersion London forces.
(D) CH₃NH₂ 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 6H₂O : 1 gas atom (i.e. Xe.6H₂O).
In addition, Xe.6H₂O 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 trimethy phosphate.

12. Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula M[HF₃]; there is a linear symmetrical anion having an over all, F–H–F distance of 2.26 Å.
\[
[F – H \cdots \cdots F]^- \longleftrightarrow [F – \cdots \cdots H \cdots \cdots F]^{-}
\]
\[
F^- + HF \longrightarrow [FHF]^{-}; \Delta H = -161 \pm 8 \text{ kJ mol}^{-1}
\]

EXERCISE # 3

1. Intermolecular forces between H₂S, H₂Se and H₂Te molecules are purely Van der Waals force of attraction while in water there is stronger H-bonding between the water molecules. H-bond is stronger than Van der Waals’s force of attraction and thus more energy is required for converting H₂O(l) to (H₂O)(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 ∝ strength of intermolecular force of attraction.

3. 

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.

5. 

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 - - - - F is strongest.

**SOLUTION OF ADVANCED LEVEL PROBLEM**

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

   $\frac{1.44 \times 10^{-16} \text{ esu cm}}{4.8 \times 10^{-10} \times 1.2 \times 10^{-8} \text{ esu cm}} \times 100 = 20%$

   $\therefore$ % 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
   \( = (4.8 \times 10^{-10} \text{ esu}) \times (2.25 \times 10^{-8} \text{ cm}) = 4.8 \times 2.25 \text{ D} \)
   so % ionic character = \( \frac{9}{4.8 \times 2.25} \times 100\% = 83.33\% \)

5. \[
\mu_R = \sqrt{2\mu_{S-H}^2 + 2\mu_{S-S}^2 \cos 97^\circ} ; \quad \mu_R = \sqrt{2} \times \mu_{S-H} \times \sqrt{1 - 0.12} \\
\mu_R = \sqrt{2} \times \mu_{S-H} \times \sqrt{0.88} ; \quad \mu_{S-H} = \frac{1.5}{\sqrt{2} \times 0.94} \text{ D} \\
(H_{S,H})_{Cal} = \frac{10}{3} \times 10^{-30} \\
(H_{S,H})_{Cal} = 3 \times 0.15 \times 1.6 \times 10 \text{ D} \\
So % ionic character = \frac{1.5}{\sqrt{2} \times 0.94} \left( \frac{1}{0.15 \times 16 \times 3} \right) \times 100 = 16\% 
\]

7. (P) No of \( \pi \)-\( d\pi \) bonds = 6.

(Q) NOHSO\(_4\) exists as NO\(^+\) and HSO\(^-\); NO\(^+\) is derivative of oxygen and isoelectronic with O\(_2^{2+}\). Bond order is \( \frac{1}{2} \) \((10 - 4) = 3\).

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

9. Theoretical value of dipole moment of a 100% ionic character = \( e \times d \)
   \( = (1.60 \times 10^{-19} \text{ C}) \times (1.41 \times 10^{-10} \text{ m}) \)
   \( = 2.26 \times 10^{-29} \text{ Cm} \)
Observed value of dipole moment = 2.60 \times 10^{-30} \text{ Cm}

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 \( \mu = e \times d \)

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

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

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

11. (i) Bond order of \( \text{N}_2 \) = 1/2 \( 10 - 4 \) = 3

Bond order of \( \text{O}_2 \) = 1/2 \( 10 - 6 \) = 2

Bond order of \( \text{F}_2 \) = 1/2 \( 10 - 8 \) = 1

Bond order of \( \text{O}_2^{+} \) = 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:

\[ \text{F}_2 < \text{O}_2 < \text{O}_2^{+} < \text{N}_2^{+} \]

(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

(iii)

So, the increasing order of bond angles is \( \text{XeF}_4 < \text{NH}_3 < \text{BF}_3 > \text{N}_3^- \)

13. (i)

\[ \mu_1 = 3 \mu_{\text{C-Cl}} \times \cos 70.5 + \mu_{\text{CH}_3} = 1.5 + 0.4 = 1.9 \text{ D} \]

\[ \mu_2 = 3 \mu_{\text{C-Cl}} \times \cos 70.5 - \mu_{\text{C-H}} = 1.5 - 0.4 = 1.1 \text{ D} \]

\[ \mu_3 = 3 \mu_{\text{C-H}} \times \cos 70.5 + \mu_{\text{C-Cl}} = 1.9 \text{ D} \]

(ii)

\[ 2\mu_{\text{CH}_3} \cos 60 = 2.5 \text{ D} \]

\[ \mu_{\text{net}} = 2.5 + \mu_{\text{CH}_3} = 2.5 + 0.4 = 2.9 \text{ D} \]
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 (\( \therefore \) 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

\( \therefore \) or h = 63 \( \times \) 76 \( \times \) 13.6 cm = 65116.8 cm = 0.65116 km.

\( \therefore \) The depth of the lake is 0.65116 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, \( \frac{n_2}{n_1} = \frac{T_1}{T_2} \) \( \Rightarrow \) \( \frac{2n/5}{n} = \frac{300}{T_2} \) \( \Rightarrow \) \( T_2 = 750 \) 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.

A-6.

Initially : (A) 76 \( \times \) 45 \( \times \) A = 76 \( \times \) 45 \( \times \) A (B) \( \therefore \) 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 \( P_1 = P_2 + 10 \)

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

\[
76 \times 45 \left[ \frac{45 + x - 4s + x}{(45 - x)(45 + x)} \right] = 10
\]

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. \[ \frac{n_1T_1}{P_1} = \frac{n_2T_2}{P_2} \implies \frac{10 \times 300}{24.6} = \frac{n_2 \times 400}{1} \]
\[ \therefore n_2 = 0.3 \]
\[ \therefore \text{Mass of oxygen left} = 0.3 \times 32 = 9 \text{ g} \]
\[ \therefore \text{Mass of oxygen escaped} = 320 - 9.6 = 310.4 \text{ g}. \]

B-2. \[ PV = nRT \]
\[ P \times 1.5 = \left( \frac{400 \times 10^{-3}}{32} + \frac{60 \times 10^{-3}}{2} \right) \times 0.082 \times 373 \]
\[ \therefore P = 0.867 \text{ atm} \]
\[ \text{initial} \quad 2H_2 + O_2 \rightarrow 2H_2O \]
\[ \text{final} \quad 2H_2 + O_2 \rightarrow 2H_2O \]
\[ = 0.005 \quad 0 \]
\[ = 0.0125 \quad 2 \]
\[ = 0.0125 \quad 2 \]
\[ \therefore m_2 \text{ left} = 0.005 \times 2 = 0.01 \text{ g} \]
\& \[ m_{H_2O} \text{ produced} = 0.025 \times 18 = 0.45 \text{ g} \]
\[ P_{H_2} = \frac{n_{H_2} \times R \times T}{V} = \frac{0.005 \times 0.0821 \times 373}{1.5} = 1.102 \text{ atm}. \]
\[ P_{H_2O} = \frac{n_{H_2O} \times R \times T}{V} = \frac{0.025 \times 0.0821 \times 373}{1.5} = 0.509 \text{ atm}. \]

C-1. At constant volume and temperature \( P \propto W \) (here, volume of balloon is assumed to be constant)
Thus, for \( N_2 \):
\[ P_1 = 2 \text{ atm} \quad P_2 = 1/2 \text{ atm} \quad \text{at } t = 1 \text{ hr} \]
\[ P_1 = \frac{w_1}{P_2} \quad \text{or} \quad P_2 = \frac{w_1}{P_1} \times w_1 \quad \text{or} \quad w_2 = \frac{1}{2} \times 14 = \frac{14}{4} \]
\[ \therefore \text{wt of } N_2 \text{ diffused} = 14 - \frac{14}{4} = 2 \frac{1}{4} \text{ kg} \]
For \( H_2 \):
\[ P_1 = 2 \text{ atm} \quad P_2 = \frac{1}{2} \text{ atm} \quad \text{at } t = t \text{ hr} \]
\[ w_i = 1 \text{ kg} \quad w_i = ? \]
\[ w_2 = \frac{P_2}{P_1} \times w_i = \frac{1}{4} \text{ kg} \]

Hence wt of \( H_2 \) diffused = \( 1 - \frac{1}{4} = \frac{3}{4} \text{ kg} \)

Now, we are to conclude one point as
\[ \frac{r_A}{r_B} = \sqrt{\frac{P_B}{P_A}}, \text{ as per Graham law} \]
\[ \frac{V_A}{V_B} = \frac{P_B}{P_A} \quad \text{or} \quad \frac{V_A \times t_A}{V_B \times t_B} = \frac{P_B}{P_A} \quad \text{or} \quad \frac{V_A}{V_B} \times t_A = \frac{P_B}{P_A} \times t_B \]
\[ \text{or} \quad \frac{V_A \rho_B t_B}{V_B \rho_B t_A} = \frac{P_A}{P_B} \quad \text{or} \quad \frac{w_A \times t_B}{w_B \times t_A} = \frac{P_A}{P_B} \]

For our problem we can write,
\[ \frac{w_{H_2} \times t_{N_2}}{w_{N_2} \times t_{H_2}} = \frac{M_{H_2}}{M_{N_2}} \quad \text{or} \quad \frac{3/4 \times 1}{21/2 \times t} = \frac{2}{8} = \frac{1}{14} \quad \text{or} \quad \frac{6}{21/4} \times \frac{1}{t} = \frac{1}{14} \]
\[ \therefore \quad \text{for } H_2, \text{ 16 mins are required} \quad \text{Ans.} \]
C-3. Change in pressure = 2000-1500 = 500 torr; time-taken = 40 min

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

\[ \frac{\text{rate}_1}{\text{rate}_2} = \frac{\frac{500}{40}}{\frac{500}{80}} = \sqrt{32} \]

\[ \frac{n_{N_2}}{n_x} = \sqrt{\frac{m_x}{M_{N_2}}} \quad \ldots \ldots (i) \]

\[ P \cdot V = n \cdot RT \quad \ldots \ldots (ii) \]

Here \( n = \frac{2.8 \times 4}{0.0821 \times 273} = 0.5 \) and \( n_x + n_{N_2} = 0.5 \) \( \Rightarrow \) \( n_x = 0.1 \)

From (1)

\[ \frac{0.4}{0.1} = \sqrt{\frac{M_x}{28}} \quad \Rightarrow \quad M_x = 448 \]

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

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

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

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

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

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

Volume of one mole of an ideal gas = \( \frac{RT}{P} = \frac{0.082 \times 500}{1} = 41 \) L

So value of \( Z = \frac{V_{n,\text{real}}}{V_{n,\text{ideal}}} = \frac{50}{41} \)

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

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

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

On substitution \[ \frac{304}{728} = \frac{8b}{0.082} \]

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

Now, \[ T_C = \frac{8a}{27Rb} \]
\[ a = \frac{27 \text{RbTC}}{8} = \frac{27 \times 0.0882 \times 4.28 \times 10^{-3} \times 304}{8} = 0.36 \text{ atm litre}^2 \text{ mole}^{-2} \quad \text{Ans.} \]

**E-5.**

\[
\left( P + \frac{n^2 \times 4.2}{(10)^2} \right) (V - nb) = n \text{RT}
\]

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

**F-1.**

\[ \text{CO}_2 + \text{C} \rightarrow 2\text{CO} \]

At \( t = 0 \), \( x \text{ L} \) \( (1 - x) \text{ L} \)

At \( t = 0 \), \( 2x \text{ L} \)

1 - \( x + 2x = 1.6 \)

1 + \( x = 1.6 \)

\( x = 0.6 \text{ L} \)

1 - \( x = 0.4 \text{ L} \)

**F-3.**

In the mix., volume of \( \text{O}_3 = 20 \text{ ml} \)

Volume of \( \text{O}_2 = 80 \text{ ml} \)

on heating \( 2\text{O}_3 \rightarrow 3\text{O}_2 \)

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

total volume = 80 + 30 = 110 ml

increase in volume = 110 - 100 = 10 ml.

**F-6.**

Balanced chemical equation: \( \text{C}_x\text{H}_y + (x + y/4)\text{O}_2 \rightarrow x \text{ CO}_2 + y/2 \text{ H}_2\text{O} \)

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

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

44 a \( \times 1.12 / 22.4 = 2.2 \)

\( a = 1 \)

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

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

18 \( b/2 \times 1.12 / 22.4 = 1.8 \)

\( b = 4 \)

\[ \therefore \text{Hydrocarbon is} \text{CH}_4 \]

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

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

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

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

**PART II**

**A-3.**

Initial \( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \)

\[ \begin{array}{c|c|c}
\text{N}_2 & 1 & 3 \\
\text{H}_2 & 3 & 9 \\
\end{array} \]

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

Mole in I flask = 0.35 + \( n \), \quad Mole in II flask = 0.35 - \( n \)

If new pressure of flask is \( P \) then

for I flask \( P \times V = (0.35 + n) \times R \times 300 \); \quad \text{for II flask} \quad P \times V = (0.35 - n) \times R \times 400

\[ n = 0.5 \]

mole in I flask = 0.40 \quad \text{mole in II flask} = 0.30

\[ 0.5 \times 2V = 0.7 \times 0.0821 \times 300 \text{ (initially)} \quad V = 17.24 \text{ Lt.} \]

\[ P \times 17.24 = 0.30 \times 0.0821 \times 400 \text{ (finally)} \quad P = 0.57 \text{ atm.} \]
A-7. Let vol. of each flask is \( V \) L, Initially
\[
0.5 \times 2V = 0.7 \times 0.0821 \times 300
\]
\( V = 17.24 \) L
Let \( T \) is final temperature of flask when pressure in each flask becomes equal, it happens when
\[
n_{\text{total}} = n_1 + n_2
\]
\[
\frac{P \times (2V)}{R \times T} = \frac{PV}{R \times 400} + \frac{PV}{R \times 300} \quad \Rightarrow \quad \frac{2}{T} = \frac{1}{400} + \frac{1}{300} = \frac{3 + 4}{1200} = \frac{7}{1200}
\]
\[
T = \frac{2400}{7} = 342.85 \text{ K}
\]
\[
P \times 2 \times 17.24 = n_1 \times 0.0821 \times 400
\]
\[
0.5714 \times 17.24 = n_2 \times 0.0821 \times 300
\]
\[
n_1 = 0.3
\]
\[
n_2 = 0.4
\]

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 \( H_2 \) = 20 g in 100 g mixture; Weight of \( O_2 \) = 80 g
\[
\therefore \quad \text{Moles of } H_2 = \frac{20}{2} = 10; \quad \therefore \quad \text{Moles of } O_2 = \frac{80}{32} = \frac{5}{2}
\]
\[
\therefore \quad \text{Total moles} = 10 + \frac{5}{2} = \frac{25}{2}
\]
\[
\therefore \quad P_{H_2} = P \times \text{mole fraction of } H_2 = 1 \times \frac{10}{25/2} = 0.8 \text{ bar}
\]

B-3. Since \( A \) and \( A_2 \) are two states in gaseous phase having their wt ratio 50% i.e. 1 : 1
\[
\text{moles of } A = \frac{96}{2} \times \frac{1}{48} = 1 \quad \text{Moles of } A_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}
\]
\[
\text{Total mole} = \frac{3}{2} \quad P = nRT/V.
\]

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 \( \frac{r_A}{r_B} = \frac{n_A}{n_B} \frac{M_B}{M_A} \)
\[
\frac{16}{3} = \frac{w_A}{w_B} \frac{M_B}{M_A} \frac{M_B}{M_A} \Rightarrow \left( \frac{M_B}{M_A} \right)^{3/2} = 8 \quad \Rightarrow \quad \frac{M_B}{M_A} = 4
\]
\[
\therefore \quad \text{mole ratio} = \frac{8}{3}
\]

D-3. \( m_A = 2 \ m_B \)
\( u_A = 2 \ u_B \)
\( n_A = n_B \)
\( v_A = v_B \)
\[
\frac{P_A V_A}{P_B V_B} = \frac{\frac{1}{3} m_A n_A u_A^2}{\frac{1}{3} m_B n_B u_B^2}
\]
D-4. \[
K.E_{O_2} = \frac{3}{2} \times \frac{N}{32} \times R \times 150 \quad \Rightarrow \quad K.E_{O_2} = \frac{N \times 1}{N \times 2} = \frac{1}{2}
\]

Therefore, (A) option is correct.

D-8. \[
\left(\frac{v_{rms}}{v_{rms}}\right)_1 = \left(\frac{M_1}{M_2}\right) \sqrt{\frac{T_1}{T_2}}
\]

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

E-4. \[
(P + \frac{a}{V^2}) (V) = RT
\]

\[
PV + \frac{a}{V} = RT
\]

\[
PV \quad = RT - \frac{a}{VRT}
\]

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

E-10. \[
P_c = \frac{a}{27b^2} \quad T_c = \frac{64a^2}{27 \times 27R^2b^2}
\]

\[
V_c = 3b \quad \frac{T_c^0}{P_c} = \frac{64a^2}{27 \times 27R^2b^2} \times \frac{27b^2}{a}
\]

\[
T_c = \frac{8a}{27Rb} \quad a = \frac{27R^2T_c^0}{64P_c}
\]

F-3. \[
C_xH_y + O_2 \rightarrow xCO_2 + \frac{y}{2} + H_2O
\]

\[
15 \text{ ml} \quad 357 \times \frac{21}{100} = 75 \text{ ml}
\]

\[\left(x + \frac{y}{4}\right) \times 15 = 75 \quad x + \frac{y}{4} = \frac{75}{15} \quad x + \frac{y}{4} = 5
\]

\[3 + \frac{y}{4} = 5 \quad 15x + 15x + 282 = 327 \quad y = 8 \quad x = 3
\]

Formula = C_3H_8

F-4. \[
C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2} + H_2O
\]

\[
7.5 \text{ ml} \quad 36 \text{ ml}
\]

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

\( y = 4 \)
\( x = 2 \)
So formula = \( \text{C}_2\text{H}_4 \)

F-6. \( \text{C}_2\text{H}_{10} + \frac{13}{2} \text{O}_2 \rightarrow 4 \text{CO}_2 + 5 \text{H}_2\text{O} \)

\( x \text{ ml} \) n-butane
\( y \text{ ml} \) isobutane

Volume of \( \text{O}_2 = x \times \frac{13}{2} + y \times \frac{13}{2} \)

---

**EXERCISE # 2**

**PATR - I**

1. \( \left( \frac{P_1V_1}{T_1} \right)_{\text{inside cylinder}} = \left( \frac{P_2V_2}{T_2} \right)_{\text{outside cylinder}} \)

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

\( V_2 = 51.324 \text{ L} \)

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. \( PV = n_{\text{total}} \cdot RT \)

\( 10^5 \times 0.02 = n_{\text{total}} \times 8.314 \times 300 \)

\( n_{\text{total}} = 0.8 \)

\( \frac{m_{\text{Ar}}}{40} + \frac{m_{\text{Ne}}}{20} = 0.8 \)

m_{\text{Ar}} + m_{\text{Ne}} = 28

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

5. \( u_{\text{av}} = \frac{8RT}{\pi M} \)

For He:

\( 4 \times 10^2 = \frac{8RT}{\pi \times 4 \times 10^{-3}} \quad \text{so} \quad RT = \frac{16 \times 10^4 \times \pi \times 1 \times 10^{-3}}{8} = 80 \pi \)

For Ne:

\( 4 \times 10^2 = \frac{8RT}{\pi \times 20 \times 10^{-3}} \quad \text{so} \quad RT = \frac{16 \times 10^4 \times \pi \times 20 \times 10^{-3}}{8} = 400 \pi \)

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

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

Total K.E. of mixture = 565.71 + 1131.42 J = 1697.13 J/mol

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

\( \text{KE} / \text{mole of mixture} = \frac{1697.13}{2.1} = 808.16 \text{ J/mol} \)
6. For the gaseous mixture
\[ PV = nRT \]
\[ 1 \times 40 = n \times 0.0821 \times 400 \]
\[ n = 1.219 \]
Total mole of mix. = 1.219
Suppose moles of \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \) are \( a \) and \( b \) respectively
\[ a + b = 1.219 \]

\[ \frac{7}{2} \text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2 \]
\[ \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \]
\[ a \quad 7a/2 \quad b \quad 3b \]
moles of \( \text{O}_2 \) required for the combustion of mix. = \( 7a/2 + 3b \)
\[ \frac{7a}{2} + 3b = \frac{130}{32} \]
by solving eq. (1) and (2) we get
\[ a = 0.808 \quad b = 0.4115 \]
mole fraction of \( \text{C}_2\text{H}_6 \) = \( \frac{0.808}{1.219} = 0.66 \); mole fraction of \( \text{C}_2\text{H}_4 \) = \( \frac{0.4115}{1.219} = 0.34 \)

7. Before effusion
Moles of CO = 0.5
Moles of \( \text{CO}_2 \) = 0.5
Total moles diffused out = \( A \)
Let moles of CO effused out = \( a \)
Let moles of \( \text{CO}_2 \) effused out = \( b \)
\[ a + b = A \]
\[ M_1 = \frac{28a + 44b}{a + b} = \frac{28a + 44b}{A} \]
Mean molar mass of residual gases in the vessel
\[ M_2 = \frac{28(0.5 - a) + 44(0.5 - b)}{0.5 - a + 0.5 - b} \]
or \[ M_2 = \frac{36}{1 - A} \]
\[ M_2 (1 - A) = 36 \]
\[ M_1 A + M_2 (1 - A) = 36 \]
Ans.

9. Let moles of \( \text{Ar} \) = \( x \)
Moles of \( \text{O}_2 \) = \( y \)
Moles of \( \text{SO}_2 \) = 1 – \( x + y \)
Total moles of mixture = \( \frac{1 \times 22.4}{0.08 \times 273} \)
\[ 1 - (x + y) = y + x \Rightarrow 1 = 2x + 2y \]
\[ y = 2 \times x \]
\[ 1 = 2x + 4x \]
\[ x = \frac{1}{6} \]
\[ y = \frac{1}{3} \]
\[ M_{\text{mix}} = \frac{\frac{1}{6} \times 40 + \frac{1}{3} \times 32 + \frac{1}{2} \times 64}{\frac{1}{6} + \frac{1}{3} + \frac{1}{2}} = 49.33 \]
\[ f = \frac{pM_{\text{mix}}}{RT} = \frac{1 \times 49.33}{0.0821 \times 273} = 2.2 \text{ g/L} \]

10. (a) By Dalton's partial pressure
\[ P_{\text{N}_2} + P_{\text{H}_2\text{O}} = 760 \text{ mm} \]
From given data \( P_{\text{N}_2} = 745 \text{ mm} \)
So \( P_{\text{H}_2\text{O}} = 760 - 745 = 15 \text{ mm} \)
\% Mole of \( \text{N}_2 = \% \text{ of pressure of } \text{N}_2 = \frac{745}{760} \times 100 = 98.02 \)
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

Mole of H₂O = \( \frac{0.15}{18} \)

Pressure of H₂O (\( P_{H_2O} \)) = 15 mm = \( \frac{15}{760} \) atm

From gas equation \( PV = nRT \)

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

\( V = 10.156 \) litres 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) \( n_{H_2O} \) (vapour) = \( \frac{P_{H_2O}V}{RT} \) = \( \frac{19}{760} \times \frac{0.300}{0.0821 \times 294} \) = 0.31 m mole

(b) \( X_{H_2} = \frac{n_{H_2}}{n_{Total}} = \frac{P_{H_2}}{P_{Total}} = \frac{729}{748} = 0.975 \)

(c) \( P_{Total} = P_{H_2} + P_{H_2O} \) \( \Rightarrow \) 748 = \( P_{H_2} + 19 \)

\( \therefore P_{H_2} = 748 – 19 = 729 \) Torr = \( \frac{729}{760} \) atm

\( n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{729}{760} \times \frac{0.300}{0.0821 \times 294} = 0.0119 \) mol H₂

mass of gas (H₂) = \( n_{H_2} \times M_{gas} = 0.0119 \times 2 = 0.24 \) g

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

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

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

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

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

\( \Rightarrow \) \( PV – Pb = RT \) \( \Rightarrow \) \( \frac{PV}{RT} – \frac{Pb}{RT} = 1 \)

\( \therefore Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} \)

\( Z = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004 \)

15. CaCO₃ (s) \( \rightarrow \) CaO (s) + CO₂(g)

Moles of CaCO₃ used = \( \frac{25}{100} \)

Moles of CaO formed = \( \frac{25}{100} \) = moles of CO₂ formed
Mass of CaO formed = \( \frac{25}{100} \times 56 \text{ g} = 14 \text{ g} \)

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

\[
\left( p + \frac{a n^2}{v^2} \right) (v - nb) = nRT
\]

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

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

**PART - II**

3. \( \text{N}_2 \longrightarrow 2\text{N} \)

at t = 0

\[
\frac{1.4}{28} = \frac{1}{20} = 0
\]

at t = \( t_f \)

\[
\frac{1}{20} = x - 2x
\]

but, \( x = 30\% \) of \( \frac{1}{20} = \frac{3}{200} \)

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. \( \frac{r_{\text{mixture}}}{r_{\text{O}_2}} = \sqrt{\frac{32}{M}} = \frac{20 \times 60}{311} \)

\( M = 2.16 \)

\( \text{V.D.} = 4.32 \)

7. \( \text{HCl} \rightarrow x \quad \text{NH}_3 \rightarrow y \)

\[
\frac{r_{\text{HCl}}}{r_{\text{NH}_3}} = \frac{17}{36.5} \Rightarrow \frac{x}{200-x} = \frac{17}{36.5} \Rightarrow x = 81.13 \text{ cm} \]

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

\[
\frac{r_{\text{NO}_2}}{r_{\text{C}_6\text{H}_5\text{Br}}} = \frac{x}{12-x} = \sqrt{\frac{179}{44}} = 2
\]

\( x = 24 - 2x \)

\( 3x = 24 \)

\( x = 8 = n - 1 \)

\( n = 9^{th} \) Row

10. \( PV = nRT \)

\[ PV = \frac{1}{M} \text{ RT} \]
12. Max capacity of balloon = 600 ml
   \[ P_1V_1 = P_2V_2 \]
   \[ 500 \times 1 = 600 \times P_2 \]
   \[ P_2 = \frac{5}{6} \times 760 \text{ mm} = 633 \text{ mm} \]
   Height above which balloon will burst.
   \[ = (760 - 633) \times 100 \text{ cm} \]
   \[ = 127 \times 100 \text{ cm} = 127 \text{ m} \]

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

17. \[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l) \]
   a+b = 40 \quad a-2b = 10
   a = 30 \text{ ml} \quad b = 10 \text{ ml}
   Mole fraction of \( H_2 = \) volume fraction of \( H_2 = \frac{30}{40} = 0.75 \).

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

II - \[ T_c = \frac{8a}{27b} \]
    \[ T_c \propto a \]
    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. \[ V_c = 3 \times N \times \frac{4}{3} \pi r^3 \times 0.44 \]

27. (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 \( T_2 \text{K} \)
    \[ T_2 = \frac{P_2T_1}{P_1} \quad (V_1 = V_2) = \frac{14.9 \times 300}{12} = 372.5 \text{ K} \]
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, \[r \propto \frac{1}{\sqrt{g}}.\]

(D) From Dalton’s law of partial pressure at constant temperature. \[P = P_1 + P_2 + \ldots\ldots\]
(E) Vander Waal’s equation (real gas equation) \[
\left(\frac{P + \frac{a}{V^2}}{V} - b\right) = RT \quad \text{(For 1 mole)}
\]
(F) \[
\frac{R}{N} = K \quad \text{(Boltzmann constant)}
\]
(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 \(PV = K \quad (T = \text{constant})\) 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 \( V_m \).

\[
\left( P + \frac{a}{V_m^2} \right) (V_m) = RT
\]
\( \Rightarrow \frac{PV_m}{RT} = Z = 1 - \frac{a}{V_mRT} < 1 \)
So, gas is more compressible than ideal gas.

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

\[
\therefore \quad P (V_m - b) = RT
\]
\( \Rightarrow \frac{PV_m}{RT} = Z = 1 + \frac{Rb}{RT} < 1. \)
So, gas is less compressible than ideal gas.

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

(D) At 0ºC \( H_2 \) and He have \( a = 0 \).
So, \( Z = 1 + \frac{Pb}{RT} \) and gas is less compressible than ideal gas.

5. \( P_1 = 75 \text{ cm of Hg, } V_1 = 24 \times A \)
\( P_2 = 75 + 10 + \frac{20.4 \times 10}{13.6} = 100 \text{ cm of Hg} \)
\( \Rightarrow \quad 75 \times 24 = 100 \times x \)
\( x = 18 \text{ cm} \)

6. Case I \quad Case II
\( P_1 = (P_0 + h) \quad P_2 = (P_0 - h) \)
\( P_1V_1 = P_2V_2 \)
Now in both the cases, the gas is the same and temperature is also constant, hence boyles law can be applied.
\( \ell \quad A (P_0 + h) = \ell_A (P_0 - h) \)
\( P_0 = \frac{h(\ell_1 - \ell_2)}{(\ell_2 - \ell_1)} \text{ cm of Hg column.} \)

8. \( Z = \frac{PV_m}{RT} > 1 \)
\( \frac{PV_m}{RT} = \frac{1 \times 22.4}{R \times T} \)
At same pressure = 1 atm.
\[ \frac{V_m}{RT} > \frac{1 \times 22.4}{R \times T} \implies V_m > 22.4 \text{ L at STP for real gas.} \]

For, \( V_m = 22.4 \) L of real gas, we have to increase the pressure.

11. \( P_c, V_c \text{ and } T_c \) are given hence 'a' and 'b' should be calculated using \( P_c \) and \( T_c \) as it is more reliable.

\[
\begin{align*}
P_c &= \frac{a}{27b^2}, \\
T_c &= \frac{8a}{27Rb} \\
P_c &\quad T_c = \frac{R}{8b} \implies b = \frac{300 \times 1}{8 \times 50} = \frac{1}{16} \\
4 \times \frac{4}{3} \pi r^3 \cdot N_A &= \frac{1}{16} \implies r = \left( \frac{3}{256 \pi N_A} \right)^{1/3}
\end{align*}
\]

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

13. \( P \propto \frac{1}{V} \implies PV = K \)

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 \( \propto \frac{1}{\text{Molar mass}} \)

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, \( P_T = 1 \text{ atm}, \quad T = 0^\circ C \)

\[
d_{mix} = \frac{PM_{mix}}{RT} \implies \frac{1.3 \times 0.082 \times 273}{1} \implies M_{mix} = 29.1.
\]
\[ M_{\text{mix}} = 29.1 = \frac{x \times 28 + (100 - x) \times 32}{100} \quad \Rightarrow \quad x = \frac{3200 - 2910}{4} = 72.5\% \]

\[ p_{N_2} = 0.725 \text{ atm.} \]

33. \[ \frac{20 + W_{H_2}}{11} = 2 \quad \Rightarrow \quad W_{H_2} = 2 \text{ g.} \]

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

35. \[ \left( P + \frac{a n^2}{V^2} \right) (V - b) = nRT \]

Unit of \( a \) will be unit of \( \frac{P V^2}{n^2} = \frac{Pa m^6}{mol^2} \).

37. At constant temperature,
\[ P_1 V_1 = P_2 V_2 \]
\[ \frac{875}{760} \times V = P_2 \times \frac{V}{3} \quad \Rightarrow \quad P_2 = \frac{875 \times 3}{760} \text{ atm} = 3.454 \text{ atm.} \]

39. **Case I**
\[ P_1 = (P_0 + h) \]
\[ P_2 = (P_0 - h) \]
\[ P_1 V_1 = P_2 V_2 \]

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

\[ \frac{h(\ell_1 - \ell_2)}{(\ell_2 - \ell_1)} \text{ cm of Hg column.} \]

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

(ii) \[ d = \frac{P M}{RT} \quad \Rightarrow \quad M = \frac{P d R T}{1} = \frac{1.8 \times 0.082 \times 300}{1} = 44.3. \]

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

(iv) \[ P_{\text{total}} = P_{H_2} + P_{O_2} + P_{CO_2} = \left( \frac{2}{2} + \frac{8}{32} + \frac{22}{44} \right) \times \frac{0.082 \times 273}{22.4} = 1.75 \text{ atm.} \]

44. \[ d = \frac{P M_{\text{mix}}}{RT} \quad \Rightarrow \quad M_{\text{mix}} = \frac{d R T}{P} = \frac{1.146 \times 0.082 \times 300 \times 760}{740} \]
\[ x = \frac{289.5 \times 28 + (100 - x) \times 32}{100} \quad \Rightarrow \quad x = 76.25\% \]

45. \[ n = \frac{P V}{R T} \quad \Rightarrow \quad n = \frac{750 \times 200}{760 \times 1000 \times 0.082 \times 293} = 0.0082 \text{ moles.} \]

Weight of gas \[ = x \times 30 + 58 (0.0082 - x) = 0.3846. \]
\[ x = \frac{0.091}{28} = 0.00325. \]

Mole % of butane \[ = \frac{(0.0082 - 0.00325) \times 100}{0.0082} = 60.36\%. \]
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: \( \frac{3RT_H_m}{2} = \sqrt[7]{\frac{3RT_N_N}{28}} \) (because \( U_{rms} = \sqrt[7]{\frac{3RT_m}{M}} \))
   
   So \( \frac{3RT_H_m}{2} = 7 \times \sqrt[7]{\frac{3RT_N_N}{28}} \)
   
   \( \therefore \ T_N_N = 2T_H_H \) or \( T_N_N > T_H_H \).

3. Mass of steam = 1000 \times 0.0006 = 0.6 gm
   
   Mass of water (\( \beta \)) = 0.6 gm
   
   Volume of liquid water = 0.6 cm\(^3\)

4. \( U_{rms} = \sqrt[7]{\frac{3RT}{M}} \) using ideal gas equation,
   
   \( PV = nRT = \frac{w}{M}RT \); \( \frac{RT}{M} - \frac{PV}{w} = \frac{P}{d} \) where \( d \) is the density of the gas
   
   \( \therefore U_{rms} = \sqrt[7]{\frac{3P}{d}} \) at constant pressure, \( U_{rms} \propto \frac{1}{\sqrt{d}} \)

5. We know that, Compressibility factor, \( Z = \frac{P \times V}{RT} \Rightarrow 0.5 = \frac{100 \times V}{0.082 \times 273} \).
   
   \( \therefore V = 0.1119 \) 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 L\(^2\)mol\(^{-2}\).

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) \( \frac{r_1}{r_2} = \sqrt[3]{\frac{M_2}{M_1}} \) or, \( 1.33 = \sqrt[3]{\frac{32}{M_1}} \Rightarrow M_1 = 18.09 \).
   
   (ii) \( V_m = \frac{M_1 \text{ molar density}}{0.36} = 50.25 \times 10^{-3} \text{ m}^3. \)
   
   (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. = \( \frac{3}{2} kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000 \text{ J} = 2.07 \times 10^{-20} \text{ J}. \)
8. \[ U_{av} = \sqrt{\frac{8RT}{\pi M}} \quad \text{and} \quad U_{rms} = \sqrt{\frac{3RT}{M}} \]

\[ \therefore \quad \frac{U_{av}}{U_{rms}} = \sqrt{\frac{8RT}{3RT}} = \sqrt{\frac{8}{3\pi}} = 0.9216 \quad \text{or} \quad U_{av} = 0.9216 \times U_{rms} \]

Given, \( U_{av} = 400 \, \text{m/s} \)

\[ \text{or} \quad U_{rms} = \frac{400}{0.9216} = 434.02 \, \text{m/s} \]

9. \[ u_{rms} = \sqrt{\frac{3RT}{M}} \]

\[ E = \frac{3}{2} RT \quad \therefore \quad RT = \frac{2E}{3} \quad \Rightarrow \quad u_{rms} = \sqrt{\frac{2E}{M}} \]

10. \[ \frac{\text{rate of diffusion}_{2}}{\text{rate of diffusion}_{1}} = \frac{M_1}{M_2} \]

\[ \frac{5 \text{He}}{16 \text{CH}_4} = \frac{5}{4} = 2 \]

11.* The van der 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 increaser in \( P \).

When \( b \) is negligible, then

\[ Z = \frac{pV_m}{RT} = 1 - \frac{a}{VR^2} \]

increasing \( P \) implies decrease in \( V \), which is 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 it’s critical temperature. Hence, the choice (a), (b) and (c) are correct.

12. (A) For \( H_2 \) gas at high pressure \( Z > 1 \).
(B) For any gas at \( P \sim 0, \ Z \sim 1 \) i.e. ideal behaviour.
(C) For \( CO_2 \) gas at normal pressure and temperature \( Z < 1 \).
(D) For any gas at very large molar volume i.e. \( P \sim 0, \ Z \sim 1 \) 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 tempt.

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

15. \[ V_{rms} = V_{mp} \]

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

\[ M_Y = 4. \]

16. (A) Fact \quad \quad (B) \quad P = MV = M \sqrt[3]{\frac{3RT}{M}} = \sqrt{3MRT}\]

(C) Max well distribution \quad (D) Fact
17. \[ P_{He} = 1 - 0.68 = 0.32 \text{ atm} \]
\[ V = ? \]
\[ n = 0.1 \]
\[ V = \frac{nRT}{P} = \frac{0.1 \times 0.0821 \times 273}{0.32} = 7 \]

**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.

5. \[ 2 \text{BCl}_3 + 3 \text{H}_2 \rightarrow 2 \text{B} + 6 \text{HCl} \]
\[ 21.6 \text{ g B} = 2 \text{ mol B} = 3 \text{ mol H}_2 \]
\[ PV = nRT \]
\[ \therefore V = \frac{nRT}{P} = \frac{3 \times 0.0821 \times 273}{1} = 67.2 \text{ L} \]

6. \[ \text{K.E.} = \frac{3}{2} RT \]
\[ E_1 = \frac{3}{2} R 293 \quad \text{and} \quad E_2 = \frac{3}{2} R 313 \quad \Rightarrow \quad E_2 = \frac{313}{293} \times E_1 \]

7. \[ b = 4N \times v \quad \text{i.e., total volume occupied by molecules of one mole of gas in motion.} \]

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 (u) at two temperature \( T_1 \) and \( T_2 \) \( (T_2 > T_1) \) is show below:

![Distribution of molecules](attachment:image.png)

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 \( x_{O_2} \)
\[ \frac{m}{32} + \frac{m}{16} = \frac{m \times 32 + 3m}{32} = \frac{1}{3} \]
Let the total pressure be \( P \).
\[ \therefore \quad \text{Partial pressure of } O_2, \quad P_{O_2} = P \times x_{O_2} \]
\[ P \times \frac{1}{3} = \frac{1}{3} P. \]
CHEMICAL EQUILIBRIUM

EXERCISE # 1

PART - I

A-1. \[ A \xlongequal{K_1} B \]
\[ K_c = \frac{K_1}{K_2} = \frac{b + x}{a - x} \]
\[ a - x \quad b + x \]
\[ x = \frac{K_1 a - K_2 b}{K_1 + K_2} \]
Therefore, (A) option is correct.

A-5. \[ X_2 + Y_2 \xlongequal{} 2XY \]
\[ \frac{1}{3} - x \quad \frac{2}{3} - x \]
\[ 2x \quad 2x = 0.6 \quad \Rightarrow \quad x = 0.3 \]
\[ [x_2] = \frac{1}{3} - 0.3 \quad [y_2] = \frac{2}{3} - 0.3 \]
Therefore, (A) option is correct.

A-9. \[ N_2 + O_2 \xlongequal{} 2NO \]
Initial 2 moles 4 moles
At Eq. \[ 2 - \frac{1}{2} \quad 4 - \frac{1}{2} \]
\[ 2 \times 2 = 1 \text{ mol} \]
Molar concentration of NO at equilibrium = \[ \frac{1}{2.5} = 0.4 \]

B-1. \[ SO_3(g) + CO(g) \xlongequal{} SO_2(g) + CO_2(g) \]
\[ 2 \quad 2 \quad 2 \quad 2 \]
\[ 2+x \quad 2+x \quad 2-x \quad 2-x \]
\[ x = 1 \]
\[ n_{eq} = 3 + 3 + 1 + 1 = 8 \quad n(SO_3) + n(CO_2) = 4 \quad \frac{n(SO_2)}{n(CO)} = \frac{1}{2} < 1 \]
Therefore, (D) option is correct.

B-3. (I) \[ N_2O_4 \xlongequal{} 2NO_2 \]
K_c = 4
at point \[ A \]
\[ Q = \frac{[\text{Product}]}{[\text{Reactant}]} = 0 \]
So, Q have minimum value at point A.

(II) at point \[ [N_2O_4] = [NO_2] = 0.1 \ M \]
\[ Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.1 \times 0.1}{0.1} = 0.1 \]
\[ Q < K_c \]
So, reaction proceeds left to right

(III) \[ K_c = Q \]
at point \[ D & F \].

B-4. \[ 2O_3(g) \xlongequal{} 3O_2(g) \]
K_p = \[ 4 \times 10^{14} \]
\[ p_{O_2} >> p_{O_3} \]
\[ K_p = \frac{p_{O_3}^3}{p_{O_2}^2} \quad p_{O_2} + P_{O_3} = 8 \quad \Rightarrow \quad P_{O_2} \approx 8 \ \text{atm}. \]
\[ 4 \times 10^{14} = \frac{8^3}{p_{O_2}^2} \quad p_{O_2}^2 = 11.3 \times 10^{-7} \]
Therefore, (B) option is correct.

B-6. From given information, \[ Q = \tan 75^\circ = \frac{\text{conc. of isobutane}}{\text{conc. of n-butane}} > K_c = \sqrt{3} \]
so backward reaction
B-7.  
\[ S(s) + S^{2-}(aq) \rightleftharpoons S^{2+}(aq) \]  
\[ K_1 = 12 \]

\[ 2S(s) + S^{2-}(aq) \rightleftharpoons S^{3-}(aq) \]  
\[ K_2 = 132 \]

Now,  
\[ S^{2-}(aq) + S(s) \rightleftharpoons S^{3-}(aq) \]  
\[ K_{eq} = \frac{K_2}{K_1} = \frac{132}{12} = 11 \]

B-9.  
\[ \text{Ni}^{2+} + 6\text{NH}_3 \rightarrow [\text{Ni(NH}_3)_6]^{2+} \]  
\[ K_f = 6 \times 10^8 \]

\[ t = 0 \]  
0.01 mole 0.1 mole 0

At equilibrium  
\[ x = (0.1 - 0.06) \]

\[ 0.1 \]

\[ K_f = \frac{[\text{Ni(NH}_3)_6]^{2+}}{[\text{Ni}^{2+}]^6[\text{NH}_3]^6} = 6 \times 10^8 \]

\[ [\text{Ni}^{2+}] = 4 \times 10^{-8} \]

B-10.  
\[ \text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) \]  
\[ P = \frac{3P}{2} = 12 \]

so  
\[ K_p = \frac{P^2}{P/2} = 2P = 2 \times 8 = 16 \text{ atm.} \]

B-12. \[ K_p = 0.800 \text{ atm} = P_{\text{CO}_2} = \text{maximum pressure of CO}_2 \text{ in the container to calculate maximum volume of container the } P_{\text{CO}_2} = 0.8 \text{ atm and none of CO}_2 \text{ should get converted into CaCO}_3(s).} \]

so  
\[ V(0.800 \text{ atm}) = (10 \text{ L})(0.2 \text{ atm}) \]

so  
\[ v = 2.5 \text{ L} \]

C-3. \[ K_p = 0.667 \text{ atm} \]

so  
\[ \frac{4\alpha^2}{1-\alpha^2} = \frac{2}{3} \]

so  
\[ \alpha = \frac{1}{2} \]

C-10. \[ P_1 = 15 \text{ atm} \quad T_1 = 300 \text{ K.} \]

Equilibrium temperature is 300ºC that is 573 K.

So first of all we have to calculate pressure of NH\(_3\) at 573 K.

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

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

\[ \text{NH}_3(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g). \]

\[ t = 0 \]  
28.65 atm 0 0

\[ t = t_{eq} \]  
\[ [28.65-x] \]

\[ \frac{x}{2} \text{ atm} \]

\[ \frac{3}{2} x \]

But according to question.

\[ P_{\text{total}} = 28.65 - x + \frac{x}{2} + \frac{3}{2}x \]

or  
\[ 28.65 + x = 40.11. \]

\[ x = 11.46. \]

Degree of dissociation of NH\(_3\) = \[ \frac{11.46}{28.65} = 0.4. \]

D-5. \[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O(s)} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O(s)} + 2\text{H}_2\text{O(g)} \]

\[ K_p = 2.25 \times 10^4 \]

\[ K_p = p_{\text{H}_2\text{O}}^2 = 2.25 \times 10^4 \]

\[ p_{\text{H}_2\text{O}} = 1.5 \times 10^{-2} \]
Vapour Pr = \frac{22.8}{760} = 3 \times 10^{-2} \quad \text{R.H.} = \frac{P_{H_2O}}{V.P.} \times 100 = 50\% \\

Therefore, (B) option is correct.

D-7.  
SrCl₂ \cdot 6H_2O(s) \rightleftharpoons SrCl₂ \cdot 2H_2O(s) + 4H_2O(g) \quad K_p = 16 \times 10^{-12} \\
(P_{H_2O})^4 = K_p \quad P_{H_2O} = (K_p)^{1/4} = 2 \times 10^{-3} \text{ atm} \\
H_2O (l) \rightleftharpoons H_2O(g) \quad P_{H_2O} = \frac{7.6}{760} = 1.0 \times 10^{-2} \\
\eta_{H_2O} = \frac{PV}{RT} = \frac{10^{-2} \times 1}{0.082 \times 274} = 4.45 \times 10^{-4} \\
\eta_{H_2O} = \frac{2 \times 10^{-3}}{0.082 \times 274} = 8.9 \times 10^{-5} \quad \therefore \eta_{H_2O} \text{ absorbed} = 3.56 \times 10^{-4} \\
\therefore \text{ wt absorbed} = 6.4 \text{ mg.} \quad \therefore \text{(A) option is correct.}

D-8.  
From thermodynamics.

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

E-7.  
N₂(g) + O₂(g) \rightleftharpoons 2NO(g) \\
1 \text{mole} \quad 2 \text{mole} \quad 3 \text{mole} \\
K_c = \frac{(3)^2}{1 \times 2} = \left(\frac{9}{2}\right). \\
Let \text{ a mole of } O_2 \text{ is added, Then,} \\
N₂(g) + O₂(g) \rightleftharpoons 2NO(g) \\
1 \text{mole} \quad 2 \text{mole} \quad 3 \text{mole} \\
t=0 \quad 1 \quad 2a \quad 3 \quad (2 + a) \quad x \quad (3 + 2x) \\
[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 \\

E-10.  
H₂O(l) \rightleftharpoons H₂O(g) \\
K_p = (P_{H_2O}) \\
When \text{ neon is added at constant pressure, we have to increase volume of the container. So more water will evaporate to maintain equilibrium.}

F-1.  
AB \rightleftharpoons A^+ + B^- \quad AB + B^- \rightleftharpoons AB_2^- \\
K_1 = \frac{[A^+][B^-]}{[AB]} \quad K_2 = \frac{[AB_2^-]}{[AB][B^-]} \\
K_1/K_2 = \frac{[A^+][B^-]}{[AB]} \cdot \frac{[AB][B^-]}{[AB_2^-]} = \frac{[A^+]}{[AB_2^-]} \cdot [B^-]^2 \quad \Rightarrow \frac{[A^+]}{[AB_2^-]} = \frac{K_1}{K_2} \cdot \left(\frac{1}{[B^-]^2}\right) \\
Therefore, (D) option is correct.
F-2. \[ AB \rightleftharpoons A^+ + B^- \quad AB + B^- \rightleftharpoons AB_2^- \]
\[ a-x-y \quad y \quad (y-x) \quad (a-x-y) \quad y-x \quad x \]
\[ K_1 = \frac{y(y-x)}{(a-x-y)} \quad K_2 = \frac{x}{(a-x-y)(y-x)} \]
\[ \frac{K_1}{K_2} = \frac{\left[ \frac{y(y-x)}{(a-x-y)} \right]}{x} \Rightarrow \frac{K_1}{K_2} = \frac{y}{x} (y-x)^2 \]

F-3.\_ \[ AB \rightleftharpoons A^+ + B^- \quad K_1 \]
\[ AB + B^- \rightleftharpoons AB_2^- \quad K_2 \]
\[ \Rightarrow K_1 = (y-x) y \quad K_2 = \frac{x}{y-x} \]
\[ \Rightarrow \frac{K_1}{K_2} = \frac{y}{x} (y-x)^2 \]

F-8. \[ A(s) \rightleftharpoons X + Y \quad \alpha \quad \alpha + \beta \]
\[ B(s) \rightleftharpoons Y + Z \quad \beta + \alpha \quad \beta \]
\[ \Rightarrow K_{P_1} = \alpha (\alpha + \beta) \]
\[ K_{P_2} = \beta (\alpha + \beta) \]
\[ P_{\text{total}} = (\alpha + \beta) + \alpha + \beta = 2 (\alpha + \beta) \]
\[ \Rightarrow 2 (\alpha + \beta) = 50 \Rightarrow \alpha + \beta = 25 \]
\[ \Rightarrow 250 = 25 \alpha \Rightarrow \alpha = 10, \beta = 15 \]
\[ \Rightarrow K_{P_2} = \beta (\alpha + \beta) = 15 \times 25 = 375 \]

PART - II

(7 to 9)
\[ 2A_2(g) \rightleftharpoons A_4(g) \]
\[ 3p - x - y \quad x/2 \]
\[ A_2 + 2C \rightleftharpoons A_2C_2 \]
\[ 3p - y-x \quad P-2y \quad y-z \]
\[ A_2C_2 \rightleftharpoons 2AC \]
\[ y-z \quad 2z \]
\[ \frac{P_{A_4}}{P_{A_2}} = K_{P_1} \Rightarrow (P_{A_4})^2 = \frac{P_{A_4}}{K_{P_1}} = \frac{1}{\frac{2}{81}} = \frac{81}{4} \]
\[ \Rightarrow P_{A_2} = \frac{9}{2} \text{ atm.} \]
\[ \Rightarrow 3p - x - y = \frac{9}{2} \text{ ... (i)} \]
\[ \frac{x}{2} = \frac{1}{2} \text{ ... (ii)} \]
\[ \Rightarrow x = 1 \text{ atm} \]
also given \[ 2Z = \frac{1}{2} \text{ ... (iii)} \]
\[ Z = \frac{1}{4} \text{ atm} \]

\[ P_{\text{total}} = 3p - x - y + \frac{x}{2} + p - 2y + y - z + 2z = 4p - \frac{x}{2} - 2y + z \]

\[ = 4 \times p - 2 \times \frac{1}{2} + 1 \times \frac{1}{4} = \frac{27}{4} \text{ atm.} \]

\[ \Rightarrow P = 2 \text{ atm.} \]

**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.** \[ \frac{n_{A_2}}{n_{AC}} = \frac{P_{A_2}}{P_{AC}} = \frac{3P - x - y}{2z} = \frac{9}{2} = \frac{9}{2} = 9 \]

**Sol. 9.** \[ K_p = \frac{P_{A_2C_2}}{P_{AC}^3} = \left( \frac{3/4}{1/2} \right)^3 = 3 \]

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**EXERCISE # 2**

4. \( H_3BO_3 + \text{glycerine} \rightleftharpoons (H_3BO_3 + \text{glycerine complex}) \)

\[ t = 0 \quad 0.1 \quad a \quad 0 \]

\[ t = \text{eq} \quad 0.04 \quad (a - 0.06) \quad (0.06) \]

Given : \[ \frac{(0.04)}{(a - 0.06)} = 0.9 \]

so, \[ (a - 0.06) = \frac{0.6}{6} = \frac{1}{0.6} \]

Hence, \[ a = \frac{1}{0.6} + 0.06 = 1.73 \text{ M} \]

5. \( 2HI (g) \rightleftharpoons H_2 (g) + I_2 (g) \)

\[ t = 0 \quad a \quad 0 \quad 0 \]

\[ t = (a - 2x) \quad x \quad x \]

Given : \[ \frac{x^2}{(a - 2x)^2} = \frac{1}{54.8} \]

so, \[ \frac{a - 2x}{x} = \sqrt{54.8} \quad \text{and} \quad (a - 2x) = 0.5 \text{ M} \]

so, \[ x = \frac{0.5}{\sqrt{54.8}} = \frac{0.5}{7.40} = 0.0675 \text{ M} \]

6. \( NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \)

\[ 2P_0 \quad P_0 \quad K_p = (2P_0)^2 \times P_0 = 4P_0^3 \]

\[ 3P_0 \quad P' \quad K_p = (3P_0)^2 \times P' = 9P_0^2 \times P' \]

\[ P' = \frac{4}{9} P_0 \]

\[ \frac{P'}{P_0} = \frac{3P_0 + \frac{4}{3} P_0}{3P_0} = \frac{31}{27} \]
9. \[ C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \]
t = 0 \[ \begin{array}{c}
\text{carbon solid will start forming when there will be equilibrium in the container}
\end{array} \]

\[ K_p = \frac{P_{CO} \cdot P_{H_2}}{P_{H_2O}} = 3 \text{ atm} = \frac{(2P)(3P)}{P} = 6 \text{ P} = 3 \text{ atm} \]

So \[ P = \frac{1}{2} \text{ atm} \]

So Total pressure in the container will be \[ P_t = P + 2P + 3P = 6P = 3 \text{ atm} \] \text{ Ans. 3 }

11. \[ \text{LiCl. } 3\text{NH}_3(\text{s}) \rightleftharpoons \text{LiCl. } \text{NH}_3(\text{s}) + 2\text{NH}_3(\text{g}) \]

K_p = 9 atm^2 = P^2_{\text{NH}_3} 

no. of moles of \text{NH}_3 at equilibrium = \frac{3 \times 5}{0.082 \times 313} = 0.5844 

For 0.1 mol of LiCl \text{NH}_3 to convert 0.2 mol of \text{NH}_3 must be needed. Total number of mol of \text{NH}_3 req. = 0.7844.

12. Let initial equilibrium concentration of \text{C} = x M

\[ \begin{array}{c}
\text{t} = t_{\text{eq}}
\end{array} \]

\[ \begin{array}{c}
\text{A} \rightleftharpoons 2\text{B} + \text{C}
\end{array} \]

\[ K_C = \frac{x \times 4^2}{3} = \frac{16x}{3} \]

Now on doubling the volume concentrations will become half of initial so

\[ \text{A} \rightleftharpoons 2\text{B} + \text{C} \]

after doubling volume \[ \frac{3}{2} \]

\[ \begin{array}{c}
\text{Conc. at new equilibrium } (1.5 - a)
\end{array} \]

\[ \text{Hence forward shift.} \]

Now given that \[ (2 + 2a) = 3 \]

so \[ a = 0.5 \]

so \[ [\text{A}] = 1M \quad [\text{B}] = 3 \quad [\text{C}] = \frac{1}{2}(x + 1) \]

so \[ K_C = \frac{(1 + x) \times 9}{2 \times 1} = \frac{16x}{3} \]

so \[ 27x + 27 = 32x \]

so \[ x = \frac{27}{5} = 5.4 \quad \text{and} \quad K_C = \frac{16}{3} \times \frac{27}{5} \times \frac{144}{5} = 28.8 \quad \text{Ans.} \]

13. \[ 2\text{AB}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g}) + \text{B}_2(\text{g}) \]

\[ \begin{array}{c}
t = 0 \quad \text{a} \quad 0 \quad 0
\end{array} \]

\[ a(1-a) \]

\[ (a\alpha) \]

\[ \left( \frac{a\alpha}{2} \right) \]

Total mole = \[ a[1 - \alpha + \frac{\alpha}{2}] \]

\[ a[2 + \alpha] \frac{a[2 + \alpha]}{2} \]

\[ P_{\text{AB}_2} = \frac{a(1-\alpha) \times 2}{a(2 + \alpha)} \times P \quad ; \quad P_{\text{AB}} = \frac{a\alpha \times 2}{a(2 + \alpha)} \times P \]

\[ P = \frac{\left( \frac{a\alpha}{2} \right)}{a(2 + \alpha)} = \left( \frac{\alpha}{2 + \alpha} \right) \times P. \]
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14. \[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

\[ a(1-\alpha) \]

(i) \[ M_{obs} = 38.33 \times 2 = 76.66 \]

(ii) \[ 76.66 = \frac{a(1-\alpha) \times 92 + 2a\alpha \times 46}{a(1+\alpha)} \]

\[ \alpha = 0.2 \]

(iii) \[ \text{% of NO}_2 = \frac{2a\alpha}{a(1+\alpha)} \times 100 = 33.33\% \]

(iv) \[ K_p = \frac{P^2\text{NO}_2}{P\text{N}_2\text{O}_4} = \frac{(\frac{2\alpha}{1+\alpha})^2}{(\frac{1-\alpha}{1+\alpha})^2} = 0.33 \]

16. \[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \]

\[ t = 0 \]

\[ \frac{8.34}{208.5} \quad 0 \quad 0 \]

\[ \text{teq.} \quad (\frac{8.34}{208.5} - x) \quad x \quad x \quad n_x = \left(\frac{8.34}{208.5} + x\right) \]

Given, \((1 \text{ atm})(2.05 \text{ L}) = \left(\frac{8.34}{208.5} + x\right)(0.082 \text{ L atm mole}^{-1} \text{ K}^{-1})(500 \text{ K})\)

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,

\[ \alpha = \frac{0.01}{0.04} = 0.25 = 25\% \]

\[ K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P = \left(\frac{1/16}{1-(1/16)}\right) = \frac{16}{15} \text{ atm.} \]

17. \[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \]

\[ t = 0 \]

\[ a \quad 0 \quad 0 \]

\[ \text{teq} \quad 0.61a \quad 0.39a \quad 0.39a \quad n_x = 1.39a \]

so,

\[ M_{mix} = \frac{208.5 a}{1.39 a} = 150 \]

so, density:

\[ \frac{PM_{mix}}{RT} = \frac{1 \times 150}{0.082 \times 500} = \frac{150}{41} = \text{g/L} \]

19. \[ T = 445^\circ C = 445 + 273 = 718K \]

\[ P = 207 \text{ atm} \]

\[ n = 1 \text{ mole} \]

\[ \text{Ag}_2\text{O} \rightleftharpoons 2\text{Ag} (s) + \frac{1}{2}\text{O}_2 (g) \]
\[ K_p = \sqrt{P_{O_2}} = (207)^{1/2} = 14.39 \]
\[ \Delta G^0 = \Delta G^0 + 2.303 \text{ RT log } K_p \]
But at eq. \( \Delta G = 0 \)
\[ \Delta G^0 = -2.303 \text{ RT log } K_p \]
But for formation
\[ 2\text{Ag} (s) + \frac{1}{2} \text{O}_2 (g) \rightleftharpoons \text{Ag}_2\text{O} (s) \]
\[ K_p = \frac{1}{(P_{O_2})^{1/2}} = \frac{1}{(207)^{1/2}} \]
\[ \Delta G^0 = -2.303 \times 8.312 \times 718 \log \frac{1}{(207)^{1/2}} \]
\[ \Delta G^0 = \frac{2.303 \times 8.312 \times 718}{2} \times \log 207 \]
\[ \Delta G^0 = 6872.17 \log 207 \]
\[ \Delta G^0 = 15915.75 \text{ J} \]
\[ \Delta G^0 = 3789.46 \text{ Cal} \]
\[ \Delta G^0 = 3.789 \text{ KCal} \]
\[ \Delta G^0 = 3.8 \text{ KCal} \]

20. \( \text{So}_2 (g) + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{So}_3 (g) \)
\[ \Delta H^0 = -98.32 \text{ KJ/mole} = -98.32 \times 10^3 \text{ J/mole} \]
\[ \Delta S^0 = -95.0 \text{ J/mole}^{0 \text{ K}} \]
\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 = -98.32 \times 10^3 - [298 \times (-95)] = -98.32 \times 10^3 + 28.310 \times 10^3 \]
\[ \Delta G^0 = -70.01 \times 10^3 \]
\[ \Delta G^0 = -2.303 \text{ RT log } K_p \]
\[ -70.01 \times 10^3 = -2.303 \times 8.312 \times 298 \log K_p \]
\[ 70.01 \times 10^3 = 5.705 \times 10^3 \times \log K_p \]
\[ 12.27 = \log K_p \]
\[ K_p = 1.86 \times 10^{12} \text{ (atm)}^{1/2} \]

21. \( (P_{H_2O})^3 = 10^{-4} \Rightarrow (P_{H_2O})_{eq} = 10^{-2} \text{ atm} \)
\[ P_{H_2O} = \frac{3.8}{760} = \frac{10^{-2}}{2} \]
\[ \Delta P = 0.01 - \frac{0.01}{2} = 5 \times 10^{-3} \]
\[
\text{number of moles of } H_2O \text{ absorbed} = \frac{\Delta PV}{RT} = \frac{5 \times 10^{-3}}{25} \times 15 = 3 \times 10^{-3} \text{ moles} \]
\[ \therefore \text{ moles of CuSO}_4 \cdot 5H_2O \text{ formed} = \frac{3 \times 10^{-3}}{3} = 10^{-3} = x \]
\[ \Rightarrow 10^5x = 10^5 \times 10^{-3} = 100 \]

28. \( \text{A(s)} \rightleftharpoons \text{A}'(g) + H_2S(g) \quad \text{B(s)} \rightleftharpoons \text{B}'(g) + H_2S(g) \)
\[ \text{A(s)} \rightleftharpoons \text{A}'(g) + H_2S(g) \quad P = 50 \text{ mm} \quad \Rightarrow \quad P_{H_2S} = P_{A'} = P/2 = 25 \text{ mm} \]
\[ \text{B(s)} \rightleftharpoons \text{B}'(g) + H_2S(g) \quad P = 68 \text{ mm} \quad \Rightarrow \quad P_{H_2S} = P_{B'} = P/2 = 34 \text{ mm} \]
\[ \text{(i) } K_{p_1} = (25)^2 = 625 \text{ mm}^2 \]
\[ \text{(ii) } K_{p_2} = (34)^2 = 1156 \text{ mm}^2 \]
\[ \text{Ratio of moles is same as that of partial pressure so} \]
\[ \text{A(s)} \rightleftharpoons \frac{\text{A}'(g)}{P_1} + \frac{H_2S(g)}{P_1 + P_2} \]
B(s) \rightleftharpoons B'(g) + H_2S(g)

\[ K_{P_1} = \frac{P_1}{P_2 + P_1} \]

\[ K_{P_2} = \frac{P_2}{P_1} \]

(i) \[ K_{P_1} = \frac{P_2}{P_1} = \frac{625}{1156} \]

(iii) total pressure = \( P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2) \)

\( P_T = 2 \times (\sqrt{K_{P_1} + K_{P_2}}) = 84.4 \text{ mm} \)

29. \[ \begin{align*}
N_2(g) & + 3H_2(g) \rightleftharpoons 2NH_3(g) \\
9P - x - y & \\
13P - 3x - 2y & = 2x
\end{align*} \]

\[ 13P - 3x - 2y = 2P_o \quad \text{then} \] \( 2x = P_o \quad \text{(2)} \)

\[ 9P - x - y = \frac{9P_o}{2} - \frac{P_o}{2} - \frac{3P_o}{2} = \frac{5P_o}{2} \]

\[ 2y = \frac{13 - 7}{2} P_o = 3P_o \]

\[ 13P - 3x - 2y = \frac{13P_o}{2} - \frac{3P_o}{2} - \frac{6P_o}{2} = 2P_o \quad y = \frac{3}{2} P_o \]

\[ K_1 = \frac{(2x)^2}{(9P - x - y)(13P - 3x - 2y)^3} = \frac{P_o^2}{5P_o(2P_o)^3} = \frac{1}{20P_o^2} \]

\[ K_2 = \frac{3}{20P_o^2} \]

30. \[ \text{For I equilibrium } 2NO_2 \rightleftharpoons N_2O_4 \]

\[ K_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = 6.8 \quad \text{.... (1)} \]

\( P_{N_2O_4} = 1.7 \text{ atm} \quad \text{By Eq. (1)} \]

The equilibria are maintained using NO and NO_2 in the ratio 1 : 2

For II equilibrium \[ \begin{align*}
\text{NO} & + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_3 \\
\text{Initial pressures} & \quad P \quad 2P \quad 0 \\
\text{Pressures at equi.} & \quad (P - x) \quad (2P - x - 3.4) \quad x
\end{align*} \]

\( 3.4 \text{ atm of NO}_3 \) are used for I equilibrium to have \( P_{N_2O_4} = 1.7 \text{ atm} \)

At equilibrium \( (P - x) \quad 0.5 \quad x \quad (\therefore P_{NO_2} \text{ is same for both the equilibria since both reactions are at equilibrium at a time.}) \)

Total pressure at equilibrium (Given 5.05 atm)

\[ = P_{NO} + P_{NO_2} + P_{N_2O_3} + P_{N_2O_4} = P - x + 0.5 + x + 1.7 \]
\[ 5.05 = P + 2.20 \]
\[ P = 5.05 - 2.20 \]
\[ P = 2.85 \text{ atm} \]
\[ 2P - x - 3.4 = 0.5 \]
\[ 2 \times 2.85 - x - 3.4 = 0.5 \]
\[ x = 5.70 - 3.90 \]
\[ x = 1.80 \text{ atm} \]
\[ P'_{NO} = 2.85 - 1.80 = 1.05 \text{ atm} \]

Now \( K_p \) for \( NO + NO \rightleftharpoons B_2O_3 \)
\[ K_p = \frac{P'_{NO} \times P'_{NO}}{1.05 \times 0.5} = 3.43 \text{ atm}^{-1} \]

**EXERCISE # 3**

1. Mole of \( \text{NH}_4\text{HS} = \frac{3.06}{18\times 1 + 32} = 0.06 \) mol

\[
\begin{align*}
\text{NH}_4\text{HS}_\text{(s)} & \rightleftharpoons \text{NH}_3\text{g)} + \text{H}_2\text{S}_\text{(g)} \\
t = 0 & 0.06 \text{ mol} \\
t = t_e & 0.06 - 0.3 \times 0.06 = 0.018 \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} \\
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/lt)}^2 \\
(ii) \text{ No effect of addition of } \text{NH}_4\text{HS}_\text{(s)} \text{ on equilibrium as active mass of solid is one.} \\

2. Equilibrium is affected by pressure and temperature but not by catalyst.

3. \( K_p = K_c (RT)^{\Delta n} \) \[ \Rightarrow \]
\[ K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}} \]

4. \( Q_C = \left[ \frac{[C][D]}{[A][B]} \right] < K_c \)
\[ \therefore Q_C \uparrow \text{ with time} \]

5. With change of pressure, \( x \) will change in such a way that \( K_p \) remains a constant.

6. \( \text{N}_2\text{O}_4 \text{(g)} \rightleftharpoons 2\text{NO}_2 \cdot \)
moles \( t=0, \)
\[
\begin{array}{ccc}
\text{moles} & 1 & 0 \\
\text{at eq.} & 1-\alpha & 2\alpha \\
\end{array}
\]
\[ K_p = \left( \frac{2\alpha}{(1+\alpha)} \right)^2 \times \frac{P}{1-\alpha} \left( \frac{1-\alpha}{1+\alpha} \right) P = \frac{4\alpha^2}{1-\alpha^2} \times P. \]

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.
\[ \therefore \alpha \text{ will change as } K_p \text{ is independent of pressure change.} \]
7. In this reaction the ratio of number of moles of reactants to products in 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 in same i.e., 1 : 1, then change in volume will not alter the number of moles.
9. The conversion of SO\textsubscript{2} to SO\textsubscript{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. \[ C_{\text{NO}_2} = 4.8 \times 10^{-2} \text{ mol L}^{-1}, \quad C_{\text{NO}_2} = 1.2 \times 10^{-3} \text{ mol L}^{-1} \]
    
    \[ K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{1.2 \times 10^{-2} \times 1.2 \times 10^{-3}}{4.8 \times 10^{-2}} = 0.3 \times 10^{-2} = 3 \times 10^{-3} \text{ mol L}^{-1} \]

11. \[ P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(g) \quad K_c = \frac{[P_4O_{10}(s)]}{[P_4(s)][O_2(g)]^5} \]

12. \[ \text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \]
    \[ \Delta n = 1 - 2 = -1; \quad K_p = K_c(RT)^{\Delta n} \]
    \[ \frac{K_p}{K_c} = (RT)^{-\Delta n} = \frac{1}{RT} \]

13. \[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4 \times 10^{-4} \]
    \[ \text{NO}(g) \rightleftharpoons \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \quad K_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = \frac{100}{2} = 50 \]

14. \[ K_p = K_c(RT)^{\Delta n} \]
    \[ \Delta n = 3 - 2 = 1. \quad K_p = K_c(0.0821 \times 457)^1 \cdot K_p > K_c. \]

15. \[ \text{Cl}_2(g) + 3\text{F}_2(g) \rightleftharpoons 2\text{ClF}_3(g) \; \Delta H = -329 \text{ kJ} \]
    Favorable conditions: (i) Decrease in temperature, (ii) Addition of reactants, (iii) Increase in pressure i.e., decrease in volume.

16. \[ \text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S(g)} \]
    Initial pressures \[ 0 \quad 0.5 \quad 0 \]
    At equi. \[ 0 \quad 0.5 + x \quad x \]
    Total pressure = 0.5 + 2x = 0.84 \[ \therefore x = 0.17 \text{ atm} \]
    \[ K_p = \frac{P_{\text{NH}_3} \times P_{\text{H}_2\text{S}}}{P_{\text{NH}_4\text{HS}}} = 0.11 \text{ atm}^2. \]

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.

18. Given: \[ \text{PCl}_3(g) \rightleftharpoons \text{PCl}_5(g) + \text{Cl}_2(g) \]
    \[ t = 0 \quad 1 \quad 0 \quad 0 \]
    \[ t_{eq} \quad 1-x \quad x \quad x \]
    Total number of moles = 1 - x + x + x = 1 + x
    Thus partial pressure of PCl\textsubscript{5} = \( \frac{x}{1+x} \) P.

19. \[ \text{SO}_2(g) \rightleftharpoons \text{SO}_3(g) + \frac{1}{2} \text{O}_2(g) \]
    \[ \frac{[\text{SO}_2][\text{O}_2]^{1/2}}{[\text{SO}_3]} = K_c = 4.9 \times 10^{-2} \quad \text{(i)} \]
    \[ \text{SO}_3(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_2(g) \quad \text{(ii)} \]
    \[ \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = K_c = \frac{1}{4.9 \times 10^{-2}} \quad \text{For } 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \]
\[
\frac{[SO_2]^2}{[SO_2][O_2]} = K_c^2 = \frac{1}{4.9 \times 4.9 \times 10^{-4}} = \frac{10000}{24.01} = 416.49
\]

20. \[\Delta G^0 = \Delta H^0 - T \Delta S^0 = -54.07 \times 1000 - 298 \times 10 = -54070 - 2980 = -57050\]
\[\Delta G^0 = -2.303 RT \log K - 57050 = -2.303 \times 298 \times 8.314 \log_{10} K = -5705 \log_{10} K\]
\[\log_{10} K = 10\]

21. At equilibrium \(\Delta G\) (Gibbs energy) = 0 but \(\Delta G^\circ\) (standard Gibbs energy) \(\neq 0\)
As \(\Delta G\) (Gibbs energy) is more negative reaction will be more spontaneous.

22. \(c = a + b\)

23. \[X \rightleftharpoons 2Y \quad Z \rightleftharpoons P + Q\]
\[1 - \alpha \quad 2\alpha \quad 1 - \alpha \quad \alpha \quad \alpha\]
\[K_{p_1} = \frac{(2\alpha)^2}{(1+\alpha)^2} \quad \frac{\alpha}{(1+\alpha)^2}\]
\[K_{p_2} = \frac{\alpha}{(1+\alpha)^2} \quad \frac{(1-\alpha)^2}{(1+\alpha)^2}\]
\[\frac{K_{p_1}}{K_{p_2}} = \frac{4P_{T_1}}{P_{T_2}} \quad \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36}\]

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. \[\text{CO}_2(g) + C(s) \rightleftharpoons 2\text{CO} (g)\]
0.5 atm
0.5–p
2p

Total pressure = 0.5 – P + 2P = 0.8
P = 0.3
\[K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(2P)^2}{(0.5 - P)^2} = \frac{(0.6)^2}{(0.5 - 0.3)^2}\]
\[K_p = 1.8\]

26. \[\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}\]
\[K = 4 \times 10^{-4}\]
\[\text{NO} \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2\]
\[K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50\]
1. (i) $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH} (g)$

\[
0.15 - x \quad a - 2x \quad x \quad \Rightarrow \quad x = 0.08
\]

\[
P = \frac{nRT}{V} = 8.2 \times 2.5 = 0.082 \times 500 = 0.5
\]

\[
K_c = \frac{0.08 \times 0.35}{2.5} = \frac{20000}{343} = 58.3
\]

\[
K_p = 58.3 \times (RT)^2 = \frac{58.3 \times (0.082 \times 500)^2}{41 \times 41} = 0.035
\]

(ii) Total pressure will remain 8.2 atm as catalyst reduces only time taken to achieve equilibrium, does not affect equilibrium condition / concentrations.

2. $2.0 \times 10^{-37} = \frac{x^2}{(0.482)^2 \times (0.933)} \quad \Rightarrow \quad x = 6.6 \times 10^{-20}$

\[
\therefore [\text{N}_2] = 0.0482 \text{ mol L}^{-1} ; [\text{O}_2] = 0.0933 \text{ mol L}^{-1} ; [\text{N}_2\text{O}] = 6.6 \times 10^{-21} \text{ mol L}^{-1}
\]

3. $\text{Ag}^+ (aq) + \text{Fe}^{2+} (aq) \rightleftharpoons \text{Fe}^{3+} (aq) + \text{Ag}(s)$

Millimole before reaction

\[
\begin{align*}
500 \times 0.15 & = 75 \\
500 \times 1.09 & = 545 \\
0 & = 0
\end{align*}
\]

Millimole after reaction

\[
\begin{align*}
(75 - x) & = 0 \\
(545 - x) & = x
\end{align*}
\]

\[
\therefore \text{mM} = \text{Meq. (both Ag}^+ / \text{Ag and Fe}^{2+} / \text{Fe}^{3+} \text{have valency factor unity)}
\]

\[
K_c = \frac{[\text{Fe}^{3+}]}{[\text{Ag}^+][\text{Fe}^{2+}]}
\]

\[
K_c = \frac{x}{(75 - x)(545 - x)} \quad \ldots \quad (1)
\]

\[
\therefore \text{Conc.} = \frac{\text{Millimole}}{\text{Total volume}}
\]

\[
[\text{Ag}^+] = \frac{75 - x}{1000} ; \quad [\text{Fe}^{2+}] = \frac{545 - x}{1000} ; \quad [\text{Fe}^{3+}] = \frac{x}{1000}
\]

Now 25 mL of mixture requires 30 mL of 0.0832 M or $0.0832 \times 5 \text{ N KMnO}_4$.

\[
\therefore \text{Fe}^{2+} \text{ is oxidized by KMnO}_4.
\]

\[
\therefore \text{Milliequivalent of Fe}^{2+} \text{ left at equilibrium in 1000 mL}
\]

\[
= \text{Milliequivalent of KMnO}_4 \text{ for 1000 mL}
\]

\[
= \frac{30 \times 0.0832 \times 5}{25} = 499.2
\]

\[
\therefore 545 - x = 499.2
\]

\[
\therefore x = 545 - 499.2 = 45.8
\]

Thus, by Eq. (1),

\[
K_c = \frac{45.8}{(75 - 45.8)(45.8)} \times \frac{545 - 45.8}{29.2 \times 499.2}
\]

\[
K_c = 3.1420.
\]
4. For the reaction,

\[ \text{Fe}^{2+} + 3\text{dipy} \rightleftharpoons [\text{Fe(dipy)}_3]^{2-} \]

\[ r_{\text{forward}} = K_f = [\text{Fe}^{2+}] [3 \text{dipy}] = 1.45 \times 10^{13} \text{[Fe}^{2+}] \text{[dipy]}^3 \]

\[ r_{\text{backward}} = K_b \times [\text{Fe(dipy)}_3]^3 = 1.22 \times 10^{-4} \text{[Fe(dipy)}_3]^2 \]

At equilibrium \( r_f = r_b \) and \( K_C = \frac{K_f}{K_b} = \frac{[\text{Fe(dipy)}_3]^{2-} / [\text{Fe}^{2+}] \text{[dipy]}^3} \)

Also, stability constant of complex = Equilibrium constt. of reaction = \( \frac{K_f}{K_b} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.188 \times 10^{17} \)

5. (a) \( A \quad + \quad 2B \quad \rightleftharpoons \quad 2C \)

\[ \begin{align*}
2a & \quad 2a \\
2a - x & \quad 2a - 2x \\
2x & \quad 2x
\end{align*} \]

Total moles at equilibrium \( 3a - x \)

Mole fraction of \( C = \frac{2x}{3a - x} = 0.4 \)

\[ 2x = 1.2a - 0.4x \]

\[ x = \frac{1.2a}{2.4} \]

\[ x = \frac{a}{2} \]

Now \( A \quad + \quad 2B \quad \rightleftharpoons \quad 2C \)

\[ \begin{align*}
a & \quad 2a \\
\frac{a}{2} & \quad a \\
a & \quad a
\end{align*} \]

Total moles = \( \frac{5a}{2} \)

\[ P_A = \frac{a}{5a/2} \times 8 = \frac{8}{5} \text{ atm} ; \quad P_B = \frac{a}{5a/2} \times 8 = \frac{16}{5} \text{ atm} \]

\[ P_C = \frac{a}{5a/2} \times 8 = \frac{16}{5} \text{ atm} ; \quad K_P = \frac{(P_C)^2}{(P_B)^2 \cdot P_A} = \frac{5}{8} \]

\( K_P = 0.625 \text{ atm}^{-1} \)

(b) \( A \quad + \quad 2B \quad \rightleftharpoons \quad 2C \)

Mole fraction 0.16 0.32 0.52
Partial pressure 0.16 P 0.32 P 0.52 P

\[ K_P = \frac{(0.52P)^2}{0.16P \times (0.32P)^2} = \frac{5}{8} \]

\[ P = \frac{0.52 \times 0.52 \times 8}{0.16 \times 0.32 \times 0.32 \times 5} = 26.4 \text{ atm} \]

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. \[ Q_c = \binom{3}{10}^4 \binom{3}{10}^4 = \frac{243}{32} \times 10^{-2} = 7.59 \times 10^{-2} > K_c \]

so, reaction will proceed in backward direction.

8. \[ \text{A(g) } \rightleftharpoons \text{B(g) + C(g)} \quad K_c = 4 \]

\[
0.5 - x \quad 1 + x \quad 1 + x \quad 4 = \frac{(1+x)^2}{0.5-x}
\]

\[ x = 0.162 \quad [A] = 0.338 \quad [B] = [C] = 1.162 \]

9. \[ \text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag(CN)}_2]^2- \]

\[
t = 0 \quad 0.1 \quad 0.5 \quad 0
\]

\[ t_{eq} \quad 10^{-6} \quad 0.3 \quad 0.1 \quad K_i = 10^{-9} \times 10^6 \]

\[ \text{Zn}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Zn(CN)}_4]^{2-} \]

\[
t = 0 \quad 0.1 \quad 0.5 \quad 0
\]

\[ eq. \quad 10^{-12} \quad 0.1 \quad 0.1 \quad K_2 = \frac{0.1}{(0.1)^{0.1}} \times 10^{-12} = 10^{15} \]

Subtracting two times 1st reaction from IIrd reaction, we will get the required reaction, so

\[ K_{eq} = \frac{10^{15}}{10^9} \times 10^{12} = \frac{10^3 \times 81}{100} = 810 \quad \text{Ans. 810} \]

10. \[ K_p = \left( \frac{0.55}{0.45} \right)^2 = 1.49 \quad ; \quad K_p = \left( \frac{0.76}{0.24} \right)^2 = 10.03 \]

Higher temperature (\( \therefore K_p > K_p \)).

11. \[ 2\text{HBr(g)} \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g) \quad K_p = \frac{10^{-5}}{1.6} \]

\[ 10^{-2p} \quad p \quad p \]

\[
\left( \frac{p}{10^{-2p}} \right)^2 = \frac{10^{-5}}{1.6} \quad p = 2.5 \times 10^{-2}
\]

\[ (p_{\text{H}_2})_{eq} = (p_{\text{Br}_2})_{eq} = 2.5 \times 10^{-2} \text{ bar} \quad ; \quad (p_{\text{HBr}})_{eq} = 10.0 \text{ bar} \]

12. The equilibrium reaction would involve 2 moles of CO, 1 mole of O\(_2\) and 2 moles of CO\(_2\) as the unit of K\(_c\) is lit/mole.

So the equilibrium equation is

\[ 2\text{CO(g)} + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g) \]

The equation, CO(g) + \( \frac{1}{2} \)O\(_2\) (g) \( \rightleftharpoons \) CO\(_2\) (g) would have an equilibrium constant with units (lit/mole)\(^{1/2}\).

\[ 2\text{CO(g)} + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g) \]

Initial conc. \( \frac{1}{2} = 0.5 \quad \frac{1}{2} = 0.5 \quad 0 \)

Conc. at equil. \( 0.5 - x \quad 0.5 - \frac{x}{2} \quad x \)

\[ \therefore K_c = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 \cdot [\text{O}_2]} = 5 \times 10^3 \]
\[ 5 \times 10^3 = \frac{x^2}{(0.5 - x)^2 \left(0.5 - \frac{x}{2}\right)} \]

Since, the value of equilibrium constant is pretty high so we can assume that almost entire CO goes to CO\(_2\). 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 O\(_2\) at equilibrium would be \(\left(0.25 + \frac{y}{2}\right)\).

\[ 5 \times 10^3 = \frac{(0.5)^2}{y^2 \left(0.25 + \frac{y}{2}\right)} \]

As value of \(y\) is very small, \(\frac{y}{2}\) can be easily ignored with respect to 0.25

\[ 5 \times 10^3 = \frac{(0.5)^2}{y^2 \times 0.25} \]
\[ y = 1.4 \times 10^{-2} \]
\[ [\text{CO}] = y = 1.4 \times 10^{-2} \text{ M.} \]

13. \(\text{CH}_3\text{COOH}(\ell) + \text{C}_2\text{H}_5\text{OH}(\ell) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\ell) + \text{H}_2\text{O}(\ell)\)

\[ \begin{array}{ccc}
1 - 0.5 & 0.5 & 0.5 \\
1 - 0.5 & 1 - 0.5 & 0.5 \\
\end{array} \]

So,
\[ K_c = \frac{0.5 \times 0.5}{0.5 \times 0.5} = 1 \]

Now let a moles of \(\text{CH}_3\text{COOH}\) and \(b\) moles of \(\text{C}_2\text{H}_5\text{OH}\) are taken:

\[ a - \frac{a}{3} \quad b - \frac{a}{3} \quad \frac{a}{3} \quad \frac{a}{3} \]

\[ K_c = \frac{\left(\frac{a}{3} \times \frac{a}{3}\right)}{2a/3 \times \left(\frac{b - \frac{a}{3}}{3}\right)} \quad \text{or} \quad 2\left(\frac{b - \frac{a}{3}}{3}\right) = \frac{a}{3} \]

or \[ 2b = a \quad \text{or} \quad \frac{a}{b} = \frac{2}{1} \]

14. \(\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}\)

\[ K_p = \frac{(30.8)^2}{9.6 \times 2.6} = 38 \]

\[ 25 - x \quad 18 - x \quad 2x = 30.8 \]

\[ 2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2 \quad K_p = \frac{(30.8)^2}{9.6 \times 2.6} = 38 \]

\[ 1 - \alpha \quad \frac{\alpha}{2} \quad \frac{\alpha}{2} \quad \frac{1}{38} = \frac{\alpha^2}{4(1 - \alpha)^2} \quad \Rightarrow \quad \alpha = 0.245 \]

15. \(\text{PCl}_3 \rightleftharpoons \text{PCl}_5 + \text{Cl}_2\)

\[ a \quad 0 \quad 0 \quad (a\alpha) \quad (a\alpha) \]

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 \[ a = \frac{4.5}{208.5} \quad \text{Hence} \quad \alpha = 0.8329 \]

16. \(4\text{PH}_3(\ell) \rightleftharpoons \text{P}_4(\ell) + 6\text{H}_2(\ell)\)

\[ 1 - 0.4 \quad 0.1 \quad 0.6 \]

\[ M_{\text{eq}} = \frac{0.6 \times 34 + 0.1 \times 124 + 0.6 \times 12}{1.3} = 30.76 \]

Vapour density = 15.38
17. \[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3 + \text{Cl}_2 \]

\[ 5(1-\alpha) \quad 5\alpha \quad 5\alpha \]

\[ 4.678 \times 110 = n_{\text{total}} \times 0.082 \times 523 \]

\[ n_{\text{total}} = 11.998 \]

\[ 5(1-\alpha) + 4 = 12 \]

\[ \alpha = \frac{3}{5} = 0.6 \]

\[ P_{\text{eq mix.}} = \frac{4.768}{12} \times 8 = 3.18 \]

\[ K_p = \frac{\alpha^2 P}{1-\alpha^2} = \frac{0.6^2 \times 3.18}{1-0.6^2} = 1.78 \]

18. (a) The given equilibrium is:

\[ \text{CO}_2(g) + \text{C(s)} \rightleftharpoons 2 \text{CO(g)} \]

Initial mole 1 0
Final mole \((1-\alpha)\) 2\(\alpha\)

\[ K_p = \frac{(n_{\text{CO}})^2}{n_{\text{CO}_2}} \times \left[ \frac{P}{\sum n} \right]^{-1} = \frac{(2\alpha)^2}{(1-\alpha)} \times \left[ \frac{5}{1+\alpha} \right] \]

\[ 10 = \frac{20\alpha^2}{(1-\alpha)} \]

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 \(\text{CO}_2\) at equilibrium = 1 - \(\alpha\) = 1 - 0.577 = 0.423.
and mole of \(\text{CO}\) at equilibrium = 2\(\alpha\) = 2 \times 0.577 = 1.154.
Total mole present at equilibrium = 0.423 + 1.154 = 1.577.
At equilibrium, \(PV = nRT\)
\[ P = 5 \text{ atm} ; \quad n = 1.577, \quad T = 817 + 273 = 1090. \]
\[ 5 \times V = 1.577 \times 0.0821 \times 1090. \]
\[ \therefore V = 28.22 \text{ litre.} \]

\[ \therefore [\text{CO}] \text{ at equilibrium} = \frac{1.154}{28.22} = 0.041 \text{ mol litre}^{-1}. \]

\[ \therefore [\text{CO}_2] \text{ at equilibrium} = \frac{0.423}{28.22} = 0.015 \text{ mol litre}^{-1}. \]

(b) For \(\text{CO}_2(g) + \text{C(s)} \rightleftharpoons 2\text{CO(g)}\)

Initial mole 1 0
Final mole \((1-\alpha)\) 2\(\alpha\)

Total mole at equilibrium = 1 - \(\alpha\) + 2\(\alpha\) = 1 + \(\alpha\).

Given
\[ \frac{1-\alpha}{1+\alpha} = \frac{5}{100} \]

\[ \therefore \alpha = \frac{95}{100} \]

\[ K_p = \frac{(n_{\text{CO}})^2}{(n_{\text{CO}_2})} \times \left[ \frac{P}{\sum n} \right]^{-1} \]

\[ 10 = \frac{(2\times\frac{95}{100})^2}{\left( \frac{5}{100} \right)^2} \times \left[ \frac{P}{\frac{105}{100}} \right]^{-1} \]

\[ \therefore P = 0.145 \text{ atm.} \]
19. Pentyne-1 $\xrightleftharpoons{K_{eq}}^{\text{KOH alc.}}$ Pentyne-2 + Pentadiene-1,2.

\[ \text{(A)} \quad \text{(B)} \quad \text{(C)} \]

At eq. 1.3

\[ K_{eq} = \frac{[\text{B}][\text{C}]}{[\text{A}]} = \frac{95.2 \times 3.5}{1.3} = 256.31 \] ......(i)

Now, for $\text{B} \xrightarrow{\text{A}}$ $\text{A}$

\[ K_1 = \frac{[\text{A}]}{[\text{B}]} \]

then from Eqs. (i) and (ii), $K_1 = \frac{[\text{C}]}{[\text{B}]} = \frac{3.5}{256.31} = 0.013$.

:. $\Delta G^0 = -2.303 \text{ RT log}_{10} K = -2.303 \times 8.314 \times 448 \log 0.013 = 16178 \text{ J} = 16.178 \text{ kJ}$.

Stability order for $\text{A}$ and $\text{B}$ is $\text{B} > \text{A}$. Similarly for $\text{B} \xrightarrow{\text{C}}$ $\text{C}$

\[ K_2 = \frac{[\text{C}]}{[\text{B}]} = \frac{K_{eq}[\text{A}]}{[\text{B}]^2} = \frac{256.31 \times 1.3}{95.2 \times 95.2} = 0.037. \]

:. $\Delta G^0 = -2.303 \text{ R log}_{10} K = -2.303 \times 8.314 \times 448 \log 0.037 = 12282 \text{ J} = 12.282 \text{ kJ}$. Thus, stability order for $\text{B}$ and $\text{C}$ is $\text{B} > \text{C}$.

Given the values of $\Delta G^0$ and $\Delta G^0_2$, the total stability order is $\text{B} > \text{C} > \text{A}$.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{C} = \text{CH} \xrightarrow{\text{KOH alc.}} \text{[CH}_3\text{CH}_2\text{CH} = \text{C} = \text{CH}_2 \xrightarrow{\text{KOH}} \text{[CH}_3\text{CH}_2\text{C} = \text{C} - \text{CH}_3. \]

20. $\Delta G^0 = \Delta H^0 - T\Delta S^0$; $K = e^{-\Delta G^0 / RT}$

At 300 K, $\Delta G^0 = (-41.16 - 300 \times -0.0424) \times 1000 = -28440 \text{ J/mol}$
At 1200 K, $\Delta G^0 = (-32.93 - 1200 \times -0.0296) \times 1000 = -2590 \text{ J/mol}$

$K_p (300 K) = 8.935 \times 10^4$
$K_p (1200 K) = 0.37753$

$Q = 1$

at 300 K: $Q < K$, Hence forward direction.
at 1200 K: $Q > K$, Hence backward direction.

21. $\text{CaCl}_2(s) + 2\text{H}_2\text{O(g)} \xrightleftharpoons{K_p} \text{CaCl}_2\cdot2\text{H}_2\text{O(s)}$

0.07 mm of Hg = $0.07 / 760 = 9.21 \times 10^{-5}$ atm

$K_p = 1 / (9.21 \times 10^{-5})^2 = 1.18 \times 10^6 \text{ atm}^{-2}$.

$\Delta G^0 = -RT \ln K_p = -35.489 \text{ kJ}$.

22. $\text{CO(g)} + \text{H}_2\text{O(g)} \xrightleftharpoons{K_p} \text{CO}_2(g) + \text{H}_2(g)$

$\Delta G^0 = (-394.36) - (137.17 - 228.57) = -28.62 \text{ kJ} = -RT \ln k$

$\log K = \frac{-28.62}{8.314 \times 248 \times 2.303} = 5$

$K = 10^5$

$K = \frac{p_{\text{CO}_2} \times p_{\text{H}_2}}{p_{\text{CO}} \times p_{\text{H}_2\text{O}}}$

$\text{CO} + \text{H}_2\text{O} \xrightleftharpoons{} \text{CO}_2 + \text{H}_2$

$1 - x \quad p_{\text{H}_2\text{O}} \quad 1 + x \quad 1 + x$

$10^5 = \frac{(1+x)^2}{(1-x)p_{\text{H}_2\text{O}}} = \frac{(1+x)^2}{(1-x)1.22 \times 10^{-3}}$

$122 = \frac{(1+x)^2}{(1-x)}$

$\Delta G^0_{\text{rxn.}} = -28.62 \text{ kJ}$

KP = $p_{\text{H}_2\text{O}} (\text{vp})$
\[
\begin{align*}
\text{CO} & \quad + \quad \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{CO}_2 & \quad + \quad \text{H}_2 \\
101.325 - x & \quad 3.16 \text{ kp} & \quad 101.325 \text{ kp} - x & \quad 101.325 \text{ kp} - x
\end{align*}
\]

\[\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)\]

\[\Delta G = -8.56\]

\[–8.56 = -2.303 \text{ RT log } kp\]

\[\log kp = 1.5\]

\[kp = 10^5 = \frac{(101.325 + x)(101.325 + x)}{(3.16)(101.325 + x)}\]

\[x = 101.201 \text{ kpa}; \quad P_{\text{CO}} = 0.124 \text{ kPa}; \quad P_{\text{CO}_2} = 202.65 \text{ kPa}\]

23.

\[\begin{align*}
\text{eq.} && \quad \text{initial} \\
20 & \quad 0 & \quad 0 \\
20 - x & \quad x & \quad x
\end{align*}\]

\[0.5 \left(\frac{x}{20 + x}\right)^2 = 0.05 \quad \Rightarrow \quad x = 6.02\]

mole percentage = \(\frac{26.02}{106.02} \times 100 = 24.5\)

\[\Delta H^0 = \Delta G^0 + T \Delta S^0 = 144.01 \text{ kJ}\]

From the equation,

\[\log \left(\frac{0.05}{K_2}\right) = \frac{144.01 \times 1000}{2.303R} \left(\frac{1}{300} - \frac{1}{900}\right)\]

\[\Delta G^0 (300 K) = -R \times 300 \times 2.303 \log K_2 = 103.47 \text{ kJ/mol.}\]

24. (a) Because Fe\(_2\)O\(_3\) is a solid, its "concentration" doesn't change when more Fe\(_2\)O\(_3\) 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 CO. 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, [CO\(_2\)] must decrease and [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\(_2\).

The equilibrium constant K\(_C\) = \(\frac{[NF_2]^2}{[N_2F_4]}\)

will therefore increase with increasing temperature.

(b) The stress here is the removal of NF\(_2\) gas. To offset it, more N\(_2\)F\(_4\) 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 changes in pressure has no effect on the equilibrium.
27. (a) The stress applied to the system is the addition of NH\textsubscript{3}. To offset this stress, some NH\textsubscript{3} reacts to produce N\textsubscript{2} and H\textsubscript{2} until a new equilibrium is established. The net reaction therefore shifts from right to left that is:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

(b) At the instant when some of the NH\textsubscript{3} is added, the system is no longer at equilibrium. The reaction quotient is given by:

\[ Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.65)^2}{(0.683)(8.80)^3} = 2.86 \times 10^{-2} \]

Because this value is greater than 2.37 \times 10^{-3}, the net reaction shifts from right to left until \( Q_c \) equals \( K_c \).

28. \[ \text{NH}_4I(s) \rightleftharpoons \text{NH}_3(g) + \text{HI} \]

\[ \begin{array}{c|c|c} \text{initial eq.} & 150 & 150 \\ \text{final eq.} & 750 & 30 \end{array} \]

\[ \text{HI} (g) \rightleftharpoons \frac{1}{2} \text{H}_2 (g) + \frac{1}{2} \text{I}_2 (g) \]

\[ \text{eq.} \]

\[ \frac{\sqrt{x}}{\sqrt{150 - 2x}} = 2 \quad \Rightarrow \quad x = 60 \]

Final pressure = 750 + 30 + 60 + 60 = 900 mm of Hg.

29. \[ \text{A(g)} \rightleftharpoons \text{B(g)} + 2\text{C(g)} \]

\[ \begin{array}{c|c|c} & 150 & 150 \\ \text{eq.} & 2x - y & 3y + x \\ \end{array} \]

\[ \begin{array}{c|c|c} \text{A(g)} & \text{B(g)} & 2\text{C(g)} \\ \text{eq.} & 2x - y & 3y + x \\ \end{array} \]

\[ n_{eq} = 1 - x + x + 3y + 2x - y + 2y \]

\[ \frac{n_{eq}}{n_i} = \frac{1 + 2x + 4y}{1} = \frac{13}{6} \quad \Rightarrow \quad 2x + 4y = \frac{7}{6} \]

\[ 12x + 24y = 7 \] ..........(i)

\[ 2x + y = \frac{4}{9} \]

\[ 18x - 9y = 4 - 4x \]

\[ \frac{8}{3} (22x - 9y = 4) \] ..........(ii)

\[ \frac{176}{3} x - 24y = \frac{32}{3} \] ..........(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)

\[ 312 \times \frac{1}{4} + 24y = 7 \]

\[ 24y = 4 \]

\[ y = \frac{1}{6} \]
A\textsubscript{(g)} \rightleftharpoons B\textsubscript{(g)} + 2C\textsubscript{(g)}

1 - \frac{1}{4} = \frac{3}{4} \quad \frac{1}{4} + 3 \times \frac{1}{6} = \frac{3}{4} \quad \frac{2}{4} - \frac{1}{6} = \frac{1}{3}

C\textsubscript{(g)} \rightleftharpoons 2D\textsubscript{(g)} + 3B\textsubscript{(g)}

\frac{2}{4} - \frac{1}{6} = \frac{1}{3} \quad \frac{2}{6} = \frac{1}{3} \quad \frac{3}{6} + \frac{1}{4} = \frac{3}{4}

K_{c_1} = \frac{3 \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} \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.

$A \rightleftharpoons B \quad K_{B/A} = x_B / x_A$

$A \rightleftharpoons C \quad K_{C/A} = x_C / x_A$

$K_{B/A} + K_{C/A} = \frac{x_B + x_C}{x_A} = \frac{1 - x_A}{x_A}$

$\Rightarrow \quad x_A = \frac{1}{1 + K_{B/A} + K_{C/A}}$

$x_B = \frac{K_{B/A}}{1 + K_{B/A} + K_{C/A}} \quad x_C = \frac{K_{C/A}}{1 + K_{B/A} + K_{C/A}}$

31. $3A_2\textsubscript{(g)} \rightleftharpoons A_6\textsubscript{(g)} \quad K_p = 1.6 \text{ atm}^{-2}$

$\frac{P_{A_2}^3}{P} = 1.6 \Rightarrow P_{A_2} = \sqrt[3]{1.6 \times 0.2} = 0.5 \text{ atm}$

Also pressure of $A_2$ used for the formation of $A_6 = 0.6 \text{ atm}$

For $A_2\textsubscript{(g)} + C\textsubscript{(g)} \rightleftharpoons A_2C\textsubscript{(g)}$

$t = 0 \quad 2P \quad P \quad 0$

At eq. $2P - P' - 0.6 \quad P - P' \quad P'$

Also for $3A_2\textsubscript{(g)} \rightleftharpoons A_6\textsubscript{(g)}$

$t = 0 \quad 2P \quad 0$

At eq. $2P - P' - 0.6 \quad 0.2$

$2P - P' - 0.6 = 0.5$

(since $P_{A_2}$ at eq. is 0.5 for simulataneous equilibria)

Also pressure of $A_2 + C + A_2C + A_6 = (2P - P' - 0.6) + (P - P') + P' + 0.2$

$= 1.4$

$0.5 + P + 0.2 = 1.4$

$P = 0.7 \text{ atm}$

$\therefore \quad 2P - P' - 0.6 = 0.5$

$\therefore \quad P' = 2 \times 0.7 - 0.6 - 0.5$

$P' = 0.3 \text{ atm}$

$\therefore \quad P_{A_2} = 0.5 \text{ atm, } P_C = 0.7 - 0.3 = 0.4 \text{ atm, } P_{A_2C} = 0.3 \text{ atm}$

Also $K_p$ for $A_2\textsubscript{(g)} + C\textsubscript{(g)} \rightleftharpoons A_2C\textsubscript{(g)}$

$K_p = \frac{P_{A_2C}}{P_{A_2} \times P_C} = \frac{0.3}{0.5 \times 0.4} = 1.5 \text{ atm}^{-1}$
IONIC EQUILIBRIUM

EXERCISE # 1

PART - I

A-1. \( \text{HCl (aq) + CH}_3\text{COOH (aq)} \rightleftharpoons \text{Cl}^- (aq) + \text{CH}_3\text{COOH}_2^+ (aq). \)

\( \text{Acid-1} \quad \text{base-2} \quad \text{base-1} \quad \text{acid-2} \)

A-7.* \( pK_w = -\log K_w = -\log 1 \times 10^{-12} = 12. \)

\( K_w = [H^+][OH^-] = 10^{-12}. \)

\( [H^+] = [OH^-] \Rightarrow [H^+]^2 = 10^{-12}; [H^+] = 10^{-6}; \text{pH} = -\log[H^+] = -\log 10^{-6} = 6. \)

\( \text{H}_2\text{O} \) is neutral because \( [H^+] = [OH^-] \) at 373 K even when \( \text{pH} = 6. \)

(D) is not correct at 373 K. \( \text{Water cannot become acidic.} \)

B-1. (A) At 25ºC, \( [H^+] \) in a solution of \( 10^{-8} \) M \( \text{HCl} > 10^{-7} \) M.

(B) \( [H^+] = 10^{-8} \) M.

(C) \( [OH^-] = 4 \times 10^{-6} \) M \( \Rightarrow [H^+] = 2.5 \times 10^{-9} \) M.

(D) \( [H^+] = 10^{-9} \) M.

B-3. Initial Final

<table>
<thead>
<tr>
<th>pH</th>
<th>( [H^+] )</th>
<th>pH</th>
<th>( [H^+] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>( 10^{-12} ) M</td>
<td>11</td>
<td>( 10^{-11} ) M</td>
</tr>
<tr>
<td>( [OH^-] = 10^{-2} ) M</td>
<td>( [OH^-] = 10^{-3} ) M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Initial No. of mole of \( \text{OH}^- = 10^{-2} \)

Final No. of mole of \( \text{OH}^- = 10^{-3} \)

So no. of mole of \( \text{OH}^- \) removed = \[0.01 - 0.001] = 0.009

B-8. In this solution, source of \( \text{OH}^- \) is water

\( \therefore \quad C\alpha = [\text{OH}^-] \)

\( \alpha = \frac{10^{-9}}{1000/18} = 1.8 \times 10^{-11} \) M

% ionisation = \( 1.8 \times 10^{-9} \) M

B-11. Given density of formic acid = 1.15 g/cm³

\( \therefore \quad \text{Weight of formic acid in 1 litre solution} = 1.15 \times 10^3 \) g

Thus, \( [\text{HCOOH}] = \frac{1.15 \times 10^3}{46} = 25 \) M

Since in case of auto ionisation

\[ [\text{HCOOH}_2^+] = [\text{HCOO}^-] \quad \text{and} \quad [\text{HCOO}^-][\text{HCOOH}_2^+] = 10^{-6} \Rightarrow [\text{HCOO}^-] = 10^{-3} \]

Now % dissociation of \( \text{HCOOH} = \frac{[\text{HCOO}^-] \times 100}{[\text{HCOOH}]} = \frac{10^{-3}}{25} \times 100 = 0.004\% \)

B-13. \( \text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OH}^- \)

\( 1 - \alpha \quad \alpha \quad \alpha \quad \alpha \)

\( K_b = C\alpha^2. \)

\( \therefore \quad a = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{4 \times 10^{-6}}{0.16 \times 1000}} = 0.02 \) or 2%.

C-2. Relative strengths of weak acids = \( \sqrt[\alpha_1]{\frac{K_{a_1}}{K_{a_2}}} \)

Assume \( C_1 \) and \( C_2 \) are same (Although not given).

\( \therefore \quad \text{Relative strength} = \sqrt[\alpha_1]{\frac{K_{a_1}}{K_{a_2}}} = \sqrt[\alpha_1]{\frac{2.1 \times 10^{-4}}{1.1 \times 10^{-5}}} \)

Relative strength for \( \text{HCOOH} \) 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 - log2 = 3 - 0.3 = 2.7**

\[ \alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \quad ; \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2} \]

\[ [\text{HOCl}] = C_1 \alpha_1 = 0.01 \times 10^{-1} = 1 \times 10^{-3} \]

\[ [\text{OH}^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M} \]

\[ [\text{HOC}l^{-}] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M} \]

\[ [\text{CH}_3\text{COOH}] = 10^{-1}(1 - 0.01) \approx 10^{-1} \]

**C-7.**

Initial pH = \( \frac{1}{2} \left( pK_b - \log C \right) = \frac{1}{2} \left( 5 - \log 2 - \log 0.1 \right) = 2.85 \)

After adding NaOH, pOH of solution = 1

Change in pOH = 1.85

D-4.

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

\[ t = 0 \quad 20 \quad 20 \]

\[ t = \text{eq} \quad - \quad - \quad 20 \]

So, \[ [\text{CH}_3\text{COO}^-] = \frac{20}{200} = 0.1 \text{ M} \]

\[ \text{pH} = 7 + \frac{1}{2} \log C = 7 + 2.37 + \frac{1}{2} \log 10^{-1} = 7 + 2.37 - 0.5 = 8.87 \]

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

\[ h = \sqrt{\frac{K_h}{c}} \]

\[ h = \text{degree of hydrolysis where } K_h = \text{Hydrolysis constant} = \frac{K_w}{K_b} \]

\[ h \propto \sqrt{K_h} \]

greater the hydrolysis constant greater the h(degree of hydrolysis).

\[ h \propto \frac{1}{\sqrt{K_b}} \]

greater the $K_b$ lesser the $h$.

Hydrolysis is endothermic, $K_h$ increases with temperature and $h$ also increase with temperature.

\[ h \propto \sqrt{V} \]

$V = $ volume of salt solution hence $h$ increases with dilution. \[ K_h = \frac{K_w}{K_b} \]

Both $K_a$ and $K_c$ change with temperature, hence $K_b$ changes with temperature.

Hence, statement(B) is correct. $h$ increases if $K_b$ decreases, statement(C) correct.

It is found that as temperature increase, $K_a$ and $K_c$ increase but increase in $K_b$ is greater than increase in $K_a$.

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).
D-10. \[ \text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \text{OH}^- \]

\[
[\text{OH}^-] = \frac{K_w C}{K_a} \quad \therefore \quad [\text{H}^+] = \frac{K_a}{\sqrt{\frac{K_w}{C}}} = \sqrt{\frac{K_a K_w}{C}}
\]

or \[ \text{pH} = \frac{1}{2}(\text{pK}_w + \text{pK}_a + \log C) \]

E-2. \[ K_a = 5 \times 10^{-10} \quad \text{pK}_a = 10 \log 5 = 9.3 \]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{\text{CN}^-}{\text{HCN}} \right) \]

\[ 9 = 9.3 + \log \left( \frac{5 \times V_{\text{ml}}}{10 \times 2} \right) \quad \Rightarrow \quad -0.3 = \log \left( \frac{V_{\text{ml}}}{4} \right) \]

\[ 0.3 = \log \left( \frac{4}{V_{\text{ml}}} \right) \quad \Rightarrow \quad \frac{4}{V_{\text{ml}}} = 2 \quad \Rightarrow \quad V_{\text{ml}} = 2 \text{ ml} \]

E-3. \[
\begin{array}{c|c|c}
\text{miliomole} & \text{HCOOH} & \text{KOH} \\
\hline
20 & 10 & \\
10 & - & 10
\end{array}
\]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[\text{HCOO}^-]}{[\text{HCOOH}]} \right) = 3.74 + \log \left( \frac{10}{10} \right) \quad \Rightarrow \quad \text{pH} = 3.74 \]

E-4. \[
\begin{array}{c|c|c|c}
time t = 0 & \text{CH}_3\text{COOH} & \text{NaOH} & \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} \\
\hline
40 \text{ mmole} & 20 \text{ mmole} & \\
time t = t & 20 \text{ mmole} & - & 20 \text{ mmole}
\end{array}
\]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{20}{20} \right) \quad \Rightarrow \quad \text{pH} = \text{pK}_a \quad \Rightarrow \quad [\text{H}^+] = K_a = 1.8 \times 10^{-5} \text{ M} \]

E-6. (a) \[
\begin{array}{c|c|c|c}
\text{NH}_3\text{OH} & \text{HCl} & \rightarrow & \text{NH}_4\text{Cl} + \text{H}_2\text{O} \\
0.2 \text{ M} & 0.1 & 0 & 0 \\
0.1 & 0 & 0.1 & 0.1
\end{array}
\]

\[ \text{pOH} = \text{pK}_b \]

(b) \[
\begin{array}{c|c|c|c}
\text{NH}_3\text{OH} & \text{HCl} & \rightarrow & \text{NH}_4\text{Cl} + \text{H}_2\text{O} \\
0.1 & 0.05 & 0 & 0 \\
0.05 & 0 & 0.05 & 
\end{array}
\]

\[ \text{pOH} = \text{pK}_b + \log \left( \frac{0.05}{0.05} \right) = \text{pK}_b \]

(c) \[
\begin{array}{c|c|c|c}
\text{NH}_3\text{OH} & \text{HCl} & \rightarrow & \text{NH}_4\text{Cl} + \text{H}_2\text{O} \\
0.3 & 0.15 & 0 & 0.15 \\
0.15 & 0 & 0.15 & 
\end{array}
\]

\[ \text{pOH} = \text{pK}_b \]

So all solution have same pH

E-9. Maximum buffer capacity of a solution is given by, buffer capacity = 2.303 \[ \frac{ab}{a+b} \]. Hence the result.

and \[ a = b = 0.5, \quad \text{BC} = 2.303 \times \frac{(0.5)^2}{1} = 0.57 \]

E-10. Mole of \text{NaOH} is required for 1 lit solution = x

Mole of \text{NaOH} is required for 100 ml of solution = 0.1 x

Now, \[ 0.1x = 1 \times V \quad \Rightarrow \quad V = 0.1x \text{ lit} = 100x \text{ ml} \]

F-4. \[ \text{pK}_a = 5.45 \]

\[ \text{pH} = \text{pK}_{\text{hin}} + \log \left( \frac{[\text{Base form}]}{[\text{Acid form}]} \right) \quad \Rightarrow \quad \text{pH} = \text{pK}_{\text{hin}} = 5.45 \]
For a Buffer solution
\[
\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \quad \Rightarrow \quad 5.45 = 4.75 + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}])}
\]
\[
0.7 = \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \quad \Rightarrow \quad 5 = \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}.
\]

**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.

\[
[\text{OH}^-] = K_b = 1 \times 10^{-5}.
\]

\[
\text{pOH} = 5
\]

\[
\text{pH} = 9.
\]

**F-8.** \( K_s = \frac{[\text{H}^+][\text{In}^-]}{[\text{HN}]} \)

\[
1 \times 10^{-5} = \frac{[\text{H}^+][\text{In}^-]}{20} \quad \Rightarrow \quad [\text{H}^+] = \frac{1}{4} \times 10^{-5}
\]

\[
\text{pH} = 5.6.
\]

**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

\[
K_a = \frac{C \alpha^2}{(1 - \alpha)}
\]

when \( \alpha << 1 \) then \( \alpha = \frac{K_a}{C} \)

as C increases \( \alpha \) decreases

as C is tending to zero \( \alpha \) will be unity

(c) At \( \frac{1}{4} \)th neutralisation

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

\[
\begin{pmatrix} 0.1 \times 3 \\ 4 \end{pmatrix} \quad \begin{pmatrix} 0.1 \times 1 \\ 4 \end{pmatrix}
\]

\[
\text{pH} = \text{pK}_s + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pK}_s + \log \left( \frac{1}{3} \right)
\]

At \( \frac{3}{4} \)th neutralisation

\[
\text{pH} = \text{pK}_s + \log 3
\]

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)\(_2\) = \( 2.56 \times 10^{-13} \)

\[
4 s_1^3 = 2.56 \times 10^{-13} \quad \Rightarrow \quad s_1 = 4 \times 10^{-6} \text{ M}
\]

\( K_{sp} \) of Al(OH)\(_3\) = \( K_{sp} = 4.32 \times 10^{-34} \)

\[
27 s_2^4 = 4.32 \times 10^{-34} \quad \Rightarrow \quad s_2 = 2 \times 10^{-9} \text{ M}
\]

\[
\frac{s_1}{s_2} = \frac{4 \times 10^{-5}}{2 \times 10^{-9}} = 2 \times 10^4
\]
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 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 AgNO$_3$ = $s_4 = \frac{x}{0.05}$

So $s_1 > s_3 > s_2 > s_4$

H-8. Solubility of BaSO$_4$ = $\sqrt{K_{sp}} = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}$ M

$\therefore$ wt. of BaSO$_4$ = $1.05 \times 10^{-5} \times 233 = 244.37 \times 10^{-5}$ g/litre.

$\therefore$ Volume of water needed to dissolve 1g BaSO$_4$ is equal to $\frac{1}{244.37 \times 10^{-5}} = 410$ litre

H-10. Ca$_3$(PO$_4$)$_2$ + 6HCl → CaCl$_2$ + 2H$_3$PO$_4$

soluble

I-2. $K_{sp}$ (BaCrO$_4$) = $2.4 \times 10^{-10}$ M

$[\text{CrO}_4^{2-}] = 6 \times 10^{-4}$

$K_{sp}$ (BaCrO$_4$) = [Ba$^{2+}$][CrO$_4^{2-}$] = $2.4 \times 10^{-10}$

$[\text{Ba}^+] = 4 \times 10^{-7}$ M Ans.

I-3. pH = 4 $\Rightarrow$ $[\text{H}^+] = 10^{-4}$ M $\Rightarrow$ $[\text{OH}^-] = 10^{-10}$ M

Al$^3$ $\text{(OH)}_3$ $\rightarrow$ Al$^{3+}$ + 3 OH$^-$

$K_{sp}$ (Al$^3$) = [Al$^{3+}$][OH$^-]^3$

$[\text{Al}^{3+}] [\text{OH}^-]^3 = 1 \times 10^{-33}$

$[\text{Al}^{3+}](10^{-10})^3 = 1 \times 10^{-33}$ $\Rightarrow$ $[\text{Al}^{3+}] = 10^{-3}$ M

I-7. $\text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^-$

$\text{AgCNS} \rightarrow \text{Ag}^+ + \text{CNS}^-$

$(x + y) \times \ x \quad (x + y) \quad y$

$K_{sp}$ (AgCl) $\frac{x}{y} = \frac{[\text{Cl}^-]}{[\text{CNS}^-]}$

So $\frac{[\text{Cl}^-]}{[\text{CNS}^-]} = \frac{x}{y} = \frac{1.8 \times 10^{-10}}{1.6 \times 10^{-17}}$

$= 1.125 \times 10 = 11.25$

$\Rightarrow \frac{x}{y} = 11.25 \quad x = 11.25$

$K_{sp}$ (AgCl) = [Ag$^+$][Cl$^-$] = $(x + y) \times = 1.8 \times 10^{-10}$

$12.25 \times 11.25 \times = 1.8 \times 10^{-10}$

$y^2 = \frac{1.8 \times 10^{-10}}{12.25 \times 11.25}$

$y^2 = 1.3 \times 10^{-12}$

$y^2 = 1.3 \times 10^{-12}$

$y = 1.14 \times 10^{-6}$

$x = 11.25 \times 1.14 \times 10^{-6} = 12.83 \times 10^{-6}$

$[\text{Ag}^+] = [x + y] = 12.83 \times 10^{-6} + 1.14 \times 10^{-6} = 13.97 \times 10^{-6} = 1.4 \times 10^{-5}$ M

I-8.* [Ag$^+$] ion required to precipitate Cl$^-$ ion = $\frac{K_{sp}}{[\text{Cl}^-]} = \frac{10^{-10}}{0.05} = 2 \times 10^{-9}$ mol/L.

[Ag$^+$] ion required to precipitate I$^-$ ion = $\frac{K_{sp}}{[I^-]} = \frac{4 \times 10^{-16}}{0.05} = 8 \times 10^{-15}$ mol/L.

Since [Ag$^+$] ion conc. required to precipitate AgI is less than the [Ag$^+$] ion conc. required to precipitate AgCl, AgI precipitates first.

Hence choices (A),(B) and (D) are correct while (C) is incorrect.
For precipitation of Ag₂CO₃,

\[ [\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{6.9 \times 10^{-12}}{[10^{-5}]^2} = 6.9 \times 10^{-2} \]

and for precipitation of BaCO₃,

\[ [\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ba}^+]^2} = \frac{8.1 \times 10^{-9}}{[10^{-4}]^2} = 8.1 \times 10^{-5} \]

(i) \( \text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3]^{-} \quad K_r = 3.5 \times 10^{-3} \).

(ii) \([\text{Ag(NH}_3]^{-} + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3]_{2}^{-} \), \( K_r = 1.8 \times 10^{-3} \).

On the basis of above reaction,

\[ K_1 = \frac{[\text{Ag(NH}_3]^{-}}{[\text{Ag}^+][\text{NH}_3]} \quad ; \quad K_2 = \frac{[\text{Ag(NH}_3]_{2}^{-}}{[\text{Ag(NH}_3]^{-}][\text{NH}_3]} \]

For the formation of \( \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3]_{2}^{-} \)

Formation constant

\[ K_f = \frac{[\text{Ag(NH}_3]_{2}^{-}}{[\text{Ag}^+][\text{NH}_3]^2} \]

\[ K_f = K_1 \times K_2 = 3.5 \times 10^{-3} \times 1.8 \times 10^{-3} = 6.3 \times 10^{-6} \]

In AgNO₃ solution, the solubility of AgCN will decrease as compared to pure water because of common ion effect of Ag⁺ ion. In NH₃ solution and buffer of pH = 5, the solubility of AgCN will increase due to complex formation in case of NH₃ solution and hydrolysis of CN⁻ ions in case of buffer of pH = 5.

(a) \( \text{Zn(OH)}_{2} \rightleftharpoons \text{Zn}^{2+} + 2\text{OH}^- \)

\[ S \quad 2S \]

\[ 4S^2 = 4.1 \times 10^{-16} \]

\[ S = 2.172 \times 10^{-6} \text{ mol/L} \]

\[ p\text{OH}^- = 5.362 \]

\[ p\text{H}^+ = 8.64 \]

(b) \( \text{Zn(OH)}_{2} \rightleftharpoons \text{Zn}^{2+} + 2\text{OH}^- \)

\[ K_{sp} = 4.1 \times 10^{-17} \]

\[ \text{Zn}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_{4}^{2-} \quad K_r = 3 \times 10^{15} \]

\[ \text{Add} \quad \text{Zn(OH)}_{2} + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)}_{4}^{2-} \quad K = 0.123 \]

\[ K_r \text{ is v. large almost all the dissolved salt will form the complex.} \]

\[ \text{Hence} \quad \frac{[\text{Zn(OH)}_{4}^{2-}]}{[\text{OH}^-]^2} = 0.123 \quad \Rightarrow \quad \frac{x}{(0.1 - x)^2} = 0.123 \text{ (if x is the solubility)} \]

\[ i.e. \quad x^2 - 8.33x + 0.01 = 0 \quad \Rightarrow \quad x = 1.2 \times 10^{-3} \text{ mol/L} \]

For SrF₂ in pure water

\[ 4s_i^3 = K_{sp} \]

For SrF₂ in 0.1 M NaF solution

\[ s_i (0.1)^2 = K_{sp} \quad \Rightarrow \quad 4s_i^3 = s_i (0.01) \]

\[ 4s_i^3 = s_i \times \frac{256}{10^6} (0.01) \quad \Rightarrow \quad s_i = 8 \times 10^{-4} \text{ M} \]

\[ K_{sp} = 4s_i^3 = 2.048 \times 10^{-9} \]

Also, \( [\text{Sr}^{2+}] = 0.0011 = 11 \times 10^{-4} \text{ M} \)

\( [\text{Sr}^{2+}] = 2 \times 10^{-4} \text{ M} \)

\( [\text{F}^-] \text{ needed for this precipitation} = 2 \times 9 \times 10^{-4} = 18 \times 10^{-4} \text{ M} \)

\( \text{NaF needed for 100 ml solution} = \frac{5 \times 10^{-3} \times 42}{10} = 0.021 \text{ g} \)
6. \[ \text{SrF}_2 \rightarrow \text{Sr}^{2+} + 2\text{F}^- \]

\[ s \]

\[ 2s \]

F\(^-\) will react with H\(^+\) to produce HF

\[ \text{F}^- + \text{H}^+ \rightleftharpoons \text{HF} \]

\[ K = \frac{1}{K_a} = \frac{[\text{HF}]}{[\text{H}^+][\text{F}^-]} = \frac{7}{10^{-5}} \]

\[ \therefore [\text{HF}] = 7 \times 10^6 [\text{F}^-] \quad [\text{H}^+] \]

\[ = 7 \times 10^5 [\text{F}^-] \times 10^{-5} = 7 [\text{F}^-] \]

Here

\[ [\text{F}^-] + [\text{HF}] = 2s \]

\[ [\text{F}^-] = s \]

\[ \frac{K_{sp}}{s} = \left( \frac{s}{4} \right)^2 \times 2.048 \times 10^{-6} \]

\[ \therefore s = 3.2 \times 10^{-3} \text{ mol/L} \]

11. (A) \[ [\text{H}^+] \] in HCl solution = \(10^{-5}\) M

\[ [\text{H}^+] \] in \(\text{H}_2\text{S}\) solution = \(\sqrt{K_a \times C} = 10^{-4}\) M

so \[ [\text{H}^+] \] in HCl solution < \[ [\text{H}^+] \] in \(\text{H}_2\text{S}\) solution

& \[ [\text{OH}^-] \] in HCl solution > \[ [\text{OH}^-] \] in \(\text{H}_2\text{S}\) solution

& degree of dissociation of water in HCl solution > degree of dissociation of water in \(\text{H}_2\text{S}\) solution

pH of HCl solution > pH of \(\text{H}_2\text{S}\) solution.

(B) At pH = 4.74 in \(\text{CH}_3\text{COOH}\) solution, \([\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]\)

\[ \therefore \text{degree of dissociation of CH}_3\text{COOH} = \frac{1}{2} \]

At pH = 9.26, i.e., pH = 4.74 in \(\text{NH}_4\text{OH}\) solution, \([\text{NH}_4^+] = [\text{NH}_4\text{OH}]\)

\[ \therefore \text{degree of dissociation of CH}_3\text{COOH} = \text{degree dissociation of NH}_4\text{OH} \]

degree of dissociation of water in \(\text{CH}_3\text{COOH}\) solution > degree of dissociation of water in \(\text{NH}_4\text{OH}\) solution.

(C) \[ [\text{H}^+] \] in \(\text{CH}_3\text{COOH}\) solution = \(\sqrt{1.8 \times 10^{-5} \times 0.1} = 1.8 \times 10^{-3}\) M

\[ [\text{H}^+] \] in HCOOH solution = \(\sqrt{1.8 \times 10^{-4} \times 1} = 1.8 \times 10^{-2}\) M

so, degree of dissociation of \(\text{CH}_3\text{COOH} = \text{degree dissociation of HCOOH}.\)

(D) \[ [\text{H}^+] \] in \(\text{HA}_1\) solution = \(\sqrt{10^{-5} \times 0.1} = 10^{-3}\) M

\[ [\text{H}^+] \] in \(\text{HA}_2\) solution = \(\sqrt{10^{-6} \times 0.01} = 10^{-4}\) M

so \[ [\text{OH}^-] \] in solution of \(\text{HA}_1 < [\text{OH}^-] \) in solution of \(\text{HA}_2\)

pH in solution of \(\text{HA}_1 < \text{pH in solution of HA}_2\)

& degree of dissociation of water \(\text{HA}_1 < \text{degree of dissociation of water HA}_2\).

12. (A) \[ \text{H}_2\text{C}_2\text{O}_4^- + \text{OH}^- \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \]

m.moles

50

25

Buffer solution pH = pK_{a1}

(B) \[ \text{H}_2\text{C}_2\text{O}_4^- + \text{OH}^- \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \]

m.moles

50

50

Amphiprotic, pH = \(\frac{pK_{a1} + pK_{a2}}{2} = \frac{13}{2} = 6.5\).

(C) \[ \text{H}_2\text{C}_2\text{O}_4^- + \text{OH}^- \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \]

m.moles

50

25

Buffer solution pH = pK_{a2}.\]
(D) $H_2C_2O_4 + OH^- \rightarrow HC_2O_4^- + H_2O$

m.moles

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<thead>
<tr>
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<th>$H_2O_4^-$</th>
<th>$OH^-$</th>
<th>$HC_2O_4^-$</th>
<th>$C_2O_4^{2-}$</th>
<th>$H_2O$</th>
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Salt hydrolysis, pH > 7.

EXERCISE # 2

4. $H_2O \rightleftharpoons H^+ + OH^-
\begin{align*}
\text{t} &= 0 \\
C' &= C(1-\alpha) \\
C &= C_\alpha
\end{align*}
So, $[H^+] = [OH^-] = C_\alpha = \frac{10^{10}}{18} \times 3.6 \times 10^{-3}$
\[
\therefore \quad \text{pH} = 7 - \log 2 = 6.7 \quad \text{and} \quad K_w = [H^+] [OH^-] = 4 \times 10^{14}
\]

6. (i) $[\text{TIOH}] = \frac{2.21 \times 2}{221} = 5.0 \times 10^{-3}.$ (mol. wt. TIOH = 221).
\[
\therefore \quad \text{pOH} = \log [\text{OH}^-] = -\log 5.0 \times 10^{-3} = 2.3; \\
\therefore \quad \text{pH} = 11.7.
\]

(ii) $[\text{Ca(OH)}_2] = \frac{0.37 \times 10^{10}}{74 \times 500} = 0.01 \text{ M}.$
\[
\therefore \quad [\text{OH}^-] = 2 \times 0.01 \text{ M} = 0.02 \text{ M} \\
\therefore \quad \text{pOH} = -\log [\text{OH}^-] = 1.7; \\
\therefore \quad \text{pH} = 12.3.
\]

(iii) $[\text{NaOH}] = \frac{0.32 \times 10^{10}}{40 \times 200} = 0.04 \text{ M}.$
\[
\therefore \quad \text{pOH} = -\log [\text{OH}^-] = 1.4; \\
\therefore \quad \text{pH} = 12.6.
\]

(iv) $[\text{HCl}] \text{ formed} = \frac{1 \times 12}{1000} = 12 \times 10^{-3} \text{ M.}$ (M$_1$V$_1$ = M$_2$V$_2$)
\[
\therefore \quad \text{pH} = 1.92.
\]

10. (a) $\text{HN}_3 \rightleftharpoons H^+ + N_3^-$
\[
\begin{align*}
\text{c} &\quad \text{c} \quad \text{c} \quad \text{c} \quad \text{c} \\
[1-\alpha] &\quad \alpha &\quad \alpha &\quad \alpha &\quad \alpha \\
\text{c} \quad \text{c} \quad \text{c} \quad \text{c} \quad \text{c}
\end{align*}
\]
\[
\frac{c\alpha^2}{1-\alpha} = K_a
\]
\[
\therefore \quad \alpha < < 1 \
\therefore \quad \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{2 \times 10^{-5}}{0.1}} = 1.4 \times 10^{-3}
\]
\[
[H^+] = c\alpha = 1.41 \times 10^{-4}. \\
\text{pH} = 3.85 \\
\text{pOH} = 10.15
\]

(b) $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = 0.141 > 0.1$
\[
\alpha \text{ cannot be neglected.}
\]
\[
\frac{c\alpha^2}{1-\alpha} = K_a
\]
\[
\alpha = \frac{-K_a + \sqrt{K_a^2 + 4cK_a}}{2c}
\]
\[
\alpha = 0.13. \\
[H^+] = c\alpha = 1.3 \times 10^{-2}.
\]
14. \[
C = \frac{1.725}{138} \left( \frac{\alpha^2}{1-\alpha} \right) = 10^{-3}
\]
\[
12.5 \times 10^{-3} \left( \frac{\alpha^2}{1-\alpha} \right) = 10^{-3}
\]
\[
\alpha = 0.245
\]
\[
[H^+] = 12.5 \times 10^{-3} \times 0.245 = 3.07 \times 10^{-3}
\]
pH = 3 - log 3.07 = 2.52

15. (i) \[
\text{CH}_3\text{COOH} = 0.2 \text{ M}
\]
\[
[H^+] = \sqrt{K_a \times C} = \sqrt{2 \times 10^{-5} \times 0.2} = 4 \times 10^{-6} = 2 \times 10^{-3}
\]
pH = 3 - log 2 = 2.7
\[
C \alpha = [H^+] \quad \Rightarrow \quad \alpha = \frac{2 \times 10^{-3}}{2 \times 10^{-1}} \quad \Rightarrow \quad \alpha = 0.01
\]

(ii) \[
\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-
\]
\[
\begin{align*}
0.1 & \quad 0.1 & \quad 0.1 \\
\text{CH}_3\text{COOH} & \rightleftharpoons \text{CH}_3\text{COO}^- & + \text{H}^+ \\
0.2 & \quad 0.1 & \quad 0.1 + 0.2 \alpha &= 0.1 \\
0.2 (1 - \alpha) & \quad 0.2 \alpha
\end{align*}
\]
\[
K_a = \frac{0.2 \alpha \times 0.1}{0.2} = 2 \times 10^{-5} \quad \alpha = 2 \times 10^{-4}
\]

(iii) \[
[\text{CH}_3\text{COO}^-] = 0.2 \times 2 \times 10^{-4} = 4 \times 10^{-4}
\]

(iv) \%

21. \[
\text{C}_5\text{H}_5\text{NH}^+\text{Cl}^-
\]
It is salt of SAWB
\[
pH = 7 - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log C \quad \Rightarrow \quad pH = 7 - \frac{1}{2} \text{pK}_b - \frac{1}{2} \log 0.25
\]
\[
\Rightarrow \quad \text{pK}_b = 9.1
\]
\[
K_b = \text{Antilog} (-9.1) = 8 \times 10^{-10}
\]

24. (a) We have pH = -log\[\text{salt}] - log\[\text{acid}]
\[
\therefore \quad \text{pH} = - \log 1.8 \times 10^{-5} + \log \left( \frac{4.1 \times 60}{82 \times 4} \right) = 4.74 + \log \left( \frac{3}{4} \right) = 4.62
\]

(b) \[
\text{pOH} = - \log \text{K}_b + \log \left[\text{salt}\right]\
\]
\[
\therefore \quad \text{pOH} = - \log 1.8 \times 10^{-5} + \log \left( \frac{2.5}{0.5} \right) = 4.74 + \log 5 = 5.43
\]
\[
\therefore \quad \text{pH} = 14 - \text{pOH} = 8.57
\]

25. \[
\text{pH} = \text{pK}_a + \log \left( \frac{50 \times C}{50 \times 0.2} \right) \quad \Rightarrow \quad 4 = 5 + \log \left( \frac{50 \times C}{50 \times 0.2} \right)
\]
\[
\Rightarrow \quad \log \left( \frac{C}{0.2} \right) = -1 \quad \Rightarrow \quad \frac{C}{0.2} = 0.1 \quad \Rightarrow \quad C = 0.02 \text{ M}
\]
26. \[ \text{NaCN} + \text{HCl} \rightarrow \text{HCN} + \text{NaCl} \]

\[ \begin{array}{c|cc}
0.01 & x \text{ mole} & 0 \\
(0.01-x) & 0 & x \text{ mole} \\
\end{array} \]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{0.01-x}{x} \right) \Rightarrow 8.5 = 9.4 + \log \frac{0.01-x}{x} \]

\[ \Rightarrow \log \left( \frac{x}{0.01-x} \right) = 0.9 \Rightarrow \frac{x}{0.01-x} = 8 \Rightarrow x = 8.9 \times 10^{-3} \text{ mole} \]

28. \[ \text{pOH} = 4.74 + \log \frac{0.1}{0.1} = 4.74 \]

\[ \therefore \quad \text{pH} = 9.26 \]

(a) \[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

\[ \begin{array}{c|cc}
t = 0 & 0.1 \text{ mole} & 0.05 \text{ mole} \\
0.05 \text{ mole} & 0.1 \text{ mole} & 0.15 \text{ mole} \\
\end{array} \]

\[ \text{pOH} = 4.74 + \log \frac{0.05}{0.15} = 4.26 \]

\[ \therefore \quad \text{pH} = 9.74 \]

(b) \[ \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \]

\[ \begin{array}{c|cc}
t = 0 & 0.1 \text{ mole} & 0.05 \text{ mole} \\
0.05 \text{ mole} & 0.1 \text{ mole} & 0.15 \text{ mole} \\
\end{array} \]

\[ \text{pOH} = 4.74 + \log \frac{0.15}{0.05} = 5.22 \]

\[ \therefore \quad \text{pH} = 8.78 \]

29. A buffer solution show best buffering action when the pH of solution is near to Ka of acid component of buffer solution

There for the above buffer can be best prepared by taking \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \)

(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

\[ [\text{H}_2\text{PO}_4^-] = 0.1 \text{ M} = 5 \text{ milimole}, \quad [\text{HPO}_4^{2-}] = 0.06 = 3 \text{ milimole} \]

milimole of NaOH added = \( 20 \times 0.01 = 2 \)

\[ \begin{array}{c|cc}
\text{H}_2\text{PO}_4^- & \text{OH}^- & \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O} \\
5 & 2 & 3 \\
3 & 0 & 5 \\
\end{array} \]

\[ \text{pH} = \text{pK}_{a2} + \log \left( \frac{5}{3} \right) = 7.44. \]

30. \( K_b (\text{NH}_3) = 1.8 \times 10^{-5} \)

\[ \text{CH}_3\text{COOCH}_3 (aq) + 2\text{H}_2\text{O} (aq) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{H}_3\text{O}^+ (aq) + \text{CH}_3\text{OH} (aq) \]

\[ [\text{NH}_4^+] = 0.1 \text{ M}, \quad [\text{NH}_3] = 0.06 \text{ M}, \quad [\text{CH}_3\text{COOCH}_3] = 0.02 \text{ M} \]

\[ \text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.74 + \log \frac{0.1}{0.06} \]

\[ (\text{pOH})_{\text{initial}} = 4.74 + 0.22 = 4.96 \quad \therefore \quad (\text{pH})_{\text{initial}} = 9.04 \]

\[ \text{NH}_3 (aq) + \text{H}^+ (aq) \rightarrow \text{NH}_4^+ (aq) \]

\[ \begin{array}{c|cc}
0.06 & 0.02 & 0.1 \text{ mole} \\
0.04 & - & 0.12 \text{ mole} \\
\end{array} \]
(pOH)_{final} = 4.74 + \log \left( \frac{0.12}{0.04} \right) = 4.74 + \log 3 = 4.74 + 0.48 = 5.22

\therefore \quad (pH)_{final} = 8.78

\Delta pH = 9.04 - 8.78 = 0.26

Yes this is satisfactory buffer.

33. For this indicator, pH = pK_b = 2

Now, at [H^+] = 4 \times 10^{-3} M,

K_w = \frac{[Hln]}{[ln^-]} \Rightarrow \frac{[Hln]}{[ln^-]} = 0.4

\therefore \quad \% of Hln = \frac{[Hln]}{[ln^-] + [Hln]} \times 100 = \frac{0.4}{1.4} \times 100 = 28.57 \%.

37. NH_4OH + HCl \rightarrow NH_4Cl + H_2O

Milimole

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at mid point

Milimole = N_i \times V_{HCl} = 2.25

V_{HCl} = \frac{2.25}{0.1} = 22.5

[NH_4Cl] = \frac{2.25}{37.5} = 0.06 M and pK_b = 5 - \log 1.8 = 4.74

\therefore \quad \text{pH} = 7 - \frac{1}{2} \log C = 7 - \frac{4.74}{2} - \frac{1}{2} \log 0.06 = 5.24

38. HCOOH + OH^- \rightarrow HCOO^- + H_2O

\begin{align*}
t = 0 & \quad 20 \text{ mmol} & \quad 10 \text{ mmol} \\
& \quad 10 & \quad 0 & \quad 10
\end{align*}

\therefore \quad \text{pH} = 3.7

At end point [HCOONa] = \frac{20}{40} = \frac{1}{2} M

\therefore \quad \text{pH} = 7 + \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 \quad \text{Molar mass of base} = 45

(b) BOH + HCl \rightarrow BCl + H_2O

\begin{align*}
t = 0 & \quad 5.6 & \quad 0.14 \times 20 \\
& \quad 5.6 & \quad 2.8 & \quad 0 & \quad 0 \\
& \quad 2.8 & \quad 0 & \quad 2.8
\end{align*}

Basic buffer

pH = 10.7 \quad \text{So} \quad \text{pOH} = 3.3

pOH = pK_b = 3.3

K_b = \text{Antilog} (-3.3) = \text{Antilog} (1 - 0.3) \times 10^{-4} = 5 \times 10^{-4}

44. Let V ml of each is mixed.

\begin{align*}
[Cu^{2+}] = \frac{0.002 \times V}{2V} = 0.001 & \quad \text{and} \quad [IO_3^-] = \frac{0.002 \times V}{2V} = 0.001 \\
K_{sp} = (0.001)^2 \times 10^{-3} \times 10^{-6} = 10^{-9} & \quad K_p < K_{sp} \rightarrow \text{NO PPT formation}
\end{align*}
45. FeSO₄ + Na₂S → FeS + Na₂SO₄  
\[ \text{a} \quad \text{a} \]

\[ K_{sp} = \left(\frac{a}{2}\right)^2 = 6.25 \times 10^{-18} \]

\[ a^2 = 4 \times 6.25 \times 10^{-18} = 4 \times 625 \times 10^{-20} \]

\[ a = 2 \times 25 \times 10^{-10} = 5 \times 10^{-9} \text{ M} \]

46. CaF₂ ⇌ Ca²⁺ + 2F⁻  
Let Solubility is s mole/lit  
CaF₂ ⇌ Ca²⁺ + 2F⁻  
\[ s \quad 2s \]

The F⁻ react with H⁺ to produce HF  
F⁻ + H⁺ ⇌ HF  

\[ K_1 = \frac{1}{K_a} = \frac{[HF]}{[F^-][H^+]} \Rightarrow [HF] = \frac{[F^-][H^+]}{K_a} = \frac{[F^-][H^+]}{3.45 \times 10^{-4}} \]

\[ [HF] = 2.9 \times 10^3 [F^-] [H^+] \]

At pH = 7  
\[ [HF] = 2.9 \times 10^{-4} [F^-] \]

But the solution contain [HF + F⁻] = 2 [Ca²⁺]  
\[ [2.9 \times 10^{-4} + 1] [F^-] = 2s \]

\[ K_{sp} = 4s^3 = 0.4 \times 10^{-11} \quad s = (10 \times 10^{-12})^{1/3} = 2.15 \times 10^{-4} \]

(a) At pH = s  
\[ [HF] = 2.9 \times 10^3 [F^-] \cdot 10^{-5} = 2.9 \times 10^{-2} [F^-] \]

\[ [F^-] + HF = 2s \Rightarrow [F^-] + 0.029 [F] = 2s \]

\[ [F^-] (1.029) = 2s \Rightarrow [F^-] = \frac{2s}{1.029} \]

\[ [F^-] = 2s \]

\[ s = (10.6 \times 10^{-12})^3 = 2.2 \times 10^{-4} \]

48. concentration of H₂S = 0.1 M  
So concentration of MBr₂ = 0.05 M

Ksp of (MS) = [M²⁺][S⁻²] = 6 \times 10^{-21}

\[ [S²⁻] = \frac{100 \times 6 \times 10^{-21}}{5} = 120 \times 10^{-21} = 1.2 \times 10^{-19} \text{ M} \]

Precipitation of MS will start when H₂S provide 1.2 \times 10^{-19} M ion of S⁻²

For H₂S  
\[ H₂S \rightleftharpoons 2H^+ + S²⁻ \]

\[ K = K_{1} \cdot K_{2} = \frac{[H⁺]^2 [S⁻²]}{[H₂S]} \]

\[ 10^{-7} \times 1.2 \times 10^{-13} = \frac{[H⁺]^2 \times 1.2 \times 10^{-19}}{0.1} \]

\[ [H⁺]^2 = 10^{-2} \]

So [H⁺] = 0.1 M  
\[ \therefore \quad \text{pH} = 1 \]

49. (1) [NaI] = 0.1 M  
NaI → Na⁺ + I⁻  
0.1 M 0.1 M 0.1 M

(2) Na₂SO₄ → 2Na⁺ + SO₄²⁻  
0.1 0.2 0.1

For precipitation of PbI₂  
Ksp (PbI₂) = [Pb⁺²][I⁻²] = 9 \times 10^{-9}  
\[ \Rightarrow \quad [Pb⁺²] \times (0.1)^2 = 9 \times 10^{-9} \]

\[ \Rightarrow \quad [Pb⁺²] = 9 \times 10^{-7} \]

For Precipitation of PbSO₄  
Ksp (PbSO₄) = [Pb⁺²][SO₄²⁻] = 1.8 \times 10^{-8}  
\[ \Rightarrow \quad [Pb⁺²] \times 0.1 = 1.8 \times 10^{-8} \]

\[ \Rightarrow \quad [Pb⁺²] = 1.8 \times 10^{-7} \]

For Precipitation of PbSO₄ required conc. of Pb⁺² is less  
So PbSO₄ 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
\[K_{sp}(\text{PbSO}_4) = [\text{Pb}^{2+}] [\text{SO}_4^{2-}] = 1.8 \times 10^{-8} = (9 \times 10^{-7}) [\text{SO}_4^{2-}] = 1.8 \times 10^{-8} [\text{SO}_4^{2-}] = \text{0.02 M}\]

50. Let solubility of CaC\(_2\)O\(_4\) is \(s\) mole/lit
\[
\text{CaC}_2\text{O}_4 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{C}_2\text{O}_4^{2-} (aq)
\]
\(\text{C}_2\text{O}_4^{2-}\) react with \(\text{H}^+\) to produce \(\text{HC}_2\text{O}_4^-\) & \(\text{H}_2\text{C}_2\text{O}_4\)
\[
\text{H}^+ + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{HC}_2\text{O}_4^- \quad K_1' = \frac{1}{K_2}
\]
\[
\frac{1}{K_2} = \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+] [\text{C}_2\text{O}_4^{2-}]} \Rightarrow [\text{HC}_2\text{O}_4^-] = \frac{[\text{H}^+] [\text{C}_2\text{O}_4^{2-}]}{K_2}
\]
Again this \(\text{HC}_2\text{O}_4^-\) react with \(\text{H}^+\) as.
\[
\text{HC}_2\text{O}_4^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 \quad K_1' = \frac{1}{K_1}
\]
\[
\frac{1}{K_1} = \frac{[\text{H}_2\text{C}_2\text{O}_4]}{[\text{HC}_2\text{O}_4^-] [\text{H}^+]} \Rightarrow [\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{HC}_2\text{O}_4^-] [\text{H}^+]}{K_1}
\]
Putting the value of \([\text{HC}_2\text{O}_4^-]\) \[\Rightarrow [\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}^+] [\text{C}_2\text{O}_4^{2-}]}{K_1 K_2}
\]
Now \([\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] = s\)
\[
[C_2O_4^{2-}] \left[ 1 + \frac{[H^+]^2}{K_2} + \frac{[H^+]^2}{K_1 K_2} \right] = s ; \quad [C_2O_4^{2-}] \left[ 1 + \frac{10^{-4}}{5 \times 10^{-5}} + \frac{10^{-8}}{25 \times 10^{-7}} \right] = s
\]
\[
[C_2O_4^{2-}] = \left( \frac{s}{3} \right) \Rightarrow s = 2.7 \times 10^{-9}
\]
\[
s^2 = 2.7 \times 10^{-9} \Rightarrow s = 9 \times 10^{-5} \text{ M}
\]

52. \(K_a([\text{Ag (CN)}_2^-] = 1 \times 10^{-21}\) \(K_a([\text{Ag (CN)}_2^-] = 1 \times 10^{21}\)
Initial \([\text{Ag}^+]\) = \(9 \times 10^{-4}\) M \(\Rightarrow [\text{Ag}^+] = 1 \times 10^{-4}\) M
Almost all \(\text{Ag}^+\) get precipitated,
\[
\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag (CN)}_2^-]
\]
t = 0 \(9 \times 10^{-4}\) b \(\Rightarrow [\text{Ag (CN)}_2^-] = 9 \times 10^{-4}\)
\(t = t_Q \quad 1.0 \times 10^{-19} \quad (b - 18 \times 10^{-4}) \quad 9 \times 10^{-4}\)
\[
K_i = \frac{(1 \times 10^{-19}) (b - 18 \times 10^{-4})^2}{1 \times 10^{21}} \Rightarrow b = 4.8 \times 10^{-3}
\]
So Amount of \(\text{CN}^-\) added = \(4.8 \times 10^{-3}\) mole

54. Given,
\[
\text{Ag}^+ \rightleftharpoons [\text{Ag (CN)}_2^-] + [\text{CN}^-] ; \quad K_{sp} = [\text{Ag}^+] [\text{CN}^-] = 1.2 \times 10^{-17}
\]
\[
[\text{Ag (CN)}_2^-] \rightleftharpoons [\text{Ag}^+] [\text{CN}^-] ; \quad K_i = \frac{[\text{Ag (CN)}_2^-]}{[\text{Ag}^+] [\text{CN}^-]^2} = 7.1 \times 10^{19}
\]
Let x mole of AgI be dissolved in CN⁻ solution then,

Now AgI(s) ⇌ [Ag(CN)₂⁻] + I⁻
mole before reaction 1 0 0
mole after reaction (1−2x) x x
By Eqs. (1) and (2),

\[ K_{eq} = K_{sp} \times K_f = \frac{[Ag(CN)_2\text{]}[I\text{]}^\text{–}}{[CN\text{]}} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19} \]

\[ K_{eq} = 8.52 \times 10^2 \]

\[ \therefore K_{eq} = 8.52 \times 10^2 = \frac{x \times (1-2x)^2}{(1-2x)^2} = \frac{x^2}{1-2x} = 29.2 \]

Thus,

x = 29.2 − 52.4x
or
x = 0.49 mole

---

EXERCISE # 3

1. (A) \[ A_pB_q(s) \rightleftharpoons pA^{\text{aq}} + qB^{\text{aq}} \]
   \[ L_s = (pS)^q \cdot (qS)^p \]
   \[ pS = qS \]

2. (a) \[ \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^{-} + \text{H}^+ \]
   conc. 0.1 (1−\(\alpha\)) 0.1\(\alpha\) (0.1 + 0.1\(\alpha\)) approximations
   Let \(1-\alpha \approx 1\) and \(1+\alpha \approx 1\)
   \[ K_a = \frac{[\text{CH}_3\text{COO}^{-}][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \]

or \[ 1.75 \times 10^{-5} = \frac{[\text{CH}_3\text{COO}^{-}] \cdot 0.1}{0.1} . \]

or \[ [\text{CH}_3\text{COO}^{-}] = 1.75 \times 10^{-5} . \]

or \[ 0.1 \alpha = 1.75 \times 10^{-5} . \]

or \[ \alpha = 0.0175\% . \]

or \[ \text{pH} = -\log[H^+] = -\log(0.1) \]

or \[ \text{pH} = 1 \]

(b) \[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]
   m mole before reaction 100 50 100
   m mole after reaction 0 50 50
   \[ \text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} \]
   (buffer sol.)
   pH = \(pK_a + \log \frac{[\text{CH}_3\text{COO}^{-}]}{[\text{CH}_3\text{COOH}]}\) = \(-\log(1.75 \times 10^{-5}) = 4.757\) Ans.

3. Solution is acidic in nature but not a buffer solution.

4. \(\text{HSO}_4^{-}\) – can accept and donate a proton. \[ \text{HSO}_4^{-} + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4 ; \text{HSO}_4^{-} \rightarrow \text{H}^+ + \text{SO}_4^{2-} \]

5. \[ \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \]
   \[ K_{sp} = [\text{Mg}^{2+}] \cdot [\text{OH}^-]^2 \]
   \[ K_{sp} = s(2s)^2 = 4s^3 \]

6. At 25°C, Ionic product of water \(K_w\) = \(1 \times 10^{-14}\). So \(pK_w = 14\)
   \[ [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14} \]
   or \[ -\log[H^+] - \log[OH^-] = 14 \]
   \[ \text{pH} + \text{pOH} = 14 \]
   It is neutral compound, so in it \(\text{pH} = \text{pOH} = 7\) at 25°C. On decreasing the temperature, \(K_w\) decreases, so \(pK_w\) increases. Hence at 4°C \(pK_w\) is higher than 25°C and at higher \(pK_w\), 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. $\text{AB}_s \rightleftharpoons \text{A}^2+ + 2\text{B}^- \quad s = 1.0 \times 10^{-5} \text{ mol L}^{-1}$  
   $K_{sp} = [\text{A}^2+] [\text{B}]^2 = 1.0 \times 10^{-5} \times (2.0 \times 10^{-5})^2 = 4.0 \times 10^{-15}$

9. We know for acids, pH must be less than 7.

10. When rain is accompanied by a thunderstorm,  
    $$\text{N}_2 + \text{O}_2 \rightarrow \text{NO} \rightarrow \text{NO}_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$$

11. $\text{NaX} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{HX}$
    In it HX is weak acid, so NaX is a salt of weak acid and strong base.
    $\therefore$ 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 $K_h = \text{Ch}^2$
    $C = \text{molar concentration}$
    $h = \text{degree of hydrolysis}$
    $\Rightarrow 1 \times 10^{-9} = 0.1 \times h^2$
    or $h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8}$
    $h = 1 \times 10^{-4}$
    $\therefore$ percentage hydrolysis of NaX salt = $1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01\%$

12. $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$
    0.1 V 0.1 V m. moles
    $\text{--} \rightarrow \text{--} \rightarrow 0.1$ V
    $[\text{A}^-] = \frac{0.1V}{2V} = \frac{0.1}{2}$ M
    $\text{pH} = 7 + \frac{1}{2} (\text{pK}_a + \log c) = 7 + \frac{1}{2} (6 - \log 5.6) + \frac{1}{2} \log \left(\frac{0.1}{2}\right) \approx 9$

13. Conjugate base is formed by the removal of $\text{H}^+$ from acid
    $\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}^+$

14. $\text{MX}_4^-(\text{solid}) \rightleftharpoons \text{M}^{1+}(\text{aq}) + 4\text{X}^- (\text{aq})$
    Solubility product, $K_{sp} = s \times (4s)^4 = 256 \text{ s}^5$
    $\therefore s = \left(\frac{K_{ps}}{256}\right)^{1/5}$

15. $\text{CH}_3\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-.$
    Initial moles 0.1 0.08
    moles after reaction 0.02 0
    0.08 mole in 1 lt
    $K_b = \frac{[\text{OH}^-][\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]}$
    or, $5 \times 10^{-4} = \frac{[\text{OH}^-] \times 0.08}{0.02}$
    or, $[\text{OH}^-] = \frac{5}{4} \times 10^{-4}$.
    $\therefore [\text{H}^-] = \frac{K_w}{[\text{OH}^-]}$
    or, $[\text{H}^-] = \frac{10^{-14} \times 4}{5 \times 10^{-4}} = 8 \times 10^{-11}$ M.

16. Conjugate base of $\text{OH}^-$
    $\text{OH}^- \rightleftharpoons \text{O}^2^- + \text{H}^+$

17. $\text{MX}_2^{(aq)} \rightleftharpoons \text{M}^{2+} (\text{aq}) + 2\text{X}^- (\text{aq})$
    $K_{sp} = s \times (2s)^2 = 4s^3 \quad \Rightarrow \quad 4 \times 10^{-12} = 4s^3 \quad \Rightarrow \quad s^3 = 1 \times 10^{-12}$
    $\Rightarrow \quad s = 1 \times 10^{-4} \text{ M} \quad \Rightarrow \quad [\text{M}^{2+}] = 1 \times 10^{-4} \text{ M}$

18. $\text{pH} = -\log[H^+] \Rightarrow [H^+] = \text{antilog} (-\text{pH}) = \text{antilog} (-5.4) = 3.98 \times 10^{-6}$
19. \[ \text{H}_2\text{A} \rightleftharpoons \text{H}^+ + \text{HA}^-; \quad K_1 = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = 1 \times 10^{-5} \]

\[ \text{HA}^- \rightleftharpoons \text{H}^+ + \text{A}^{2-}; \quad K_2 = 5 \times 10^{-10} = \frac{[\text{H}^+][\text{H}^2\text{A}^-]}{[\text{HA}^-]} \]

\[ K = \frac{[\text{H}^+]^2[\text{H}^2\text{A}^-]}{[\text{H}_2\text{A}]} = K_1 \times K_2 = 1 \times 10^{-5} \times 5 \times 10^{-15} \]

20. For acidic buffer, pH = \( pK_a + \frac{[\text{A}^-]}{[\text{HA}]} \)

when the acid is 50% ionised, \([\text{A}^-] = [\text{HA}]\) or pH = \( pK_a + \log 1 \) or pH = \( pK_a \)
given \( pK_a = 4.5 \)

\[ \therefore \text{pH} = 4.5 \]

\[ \text{pOH} = 14 - 4.5 = 9.5 \]

21. \( \text{AgIO}_3(s) \rightleftharpoons \text{Ag}^+(aq) + \text{IO}_3^-(aq) \) \[ [s = \text{Solubility}] \]

\[ K_{sp} = s \]

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.} \]

22. \( \text{BOH} + \text{HCl} \rightarrow \text{BCl} + \text{H}_2\text{O} \) (in titration)

\( \text{B}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH} + \text{H}^+ \)

For titration

\[ \frac{N_{\text{acid}}}{V_{\text{acid}}} = \frac{N_{\text{base}}}{V_{\text{base}}} \]

\[ \frac{2}{15} \times V = 2.5 \times \frac{2}{5} \]

\[ V = 3 \times 2.5 = 7.5 \text{ mL} \]

In resulting solution

\[ [\text{B}^+] = \frac{2 \times 2.5}{10} = \frac{2}{20} = 0.1 \]

\[ K_w = \frac{10^{-14}}{10^{-12}} = 10^{-2} \]

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 \( h > 0.1 \))

or \( h = 0.27 \)

\[ [\text{H}^+] = 0.1 \times 0.27 = 2.7 \times 10^{-2} \]

23. \( \text{MX} \)

\[ s_1^2 = 4 \times 10^{-8} \]

\[ s_2^2 = 2 \times 10^{-4} \]

\[ s_3^2 = 2 \times 10^{-5} \]

\[ s_4^3 = 3.2 \times 10^{-14} \]

\[ s_5^3 = 8 \times 10^{-15} \]

\[ s_6^3 = 2 \times 10^{-5} \]

\[ s_7^3 = 2 \times 10^{-5} \]

\[ s_8^4 = 2.7 \times 10^{-15} \]

\[ s_9^4 = 10^{-16} \]

\[ s_{10}^4 = 10^{-4} \]

\[ \Rightarrow s_1 > s_2 > s_3 \]

\[ \Rightarrow \text{MX} > s_1 > s_2 > s_3 \]

24. \( \text{pH} = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b = 7 + \frac{4.8}{2} - \frac{4.78}{2} = 7.01 \)

25. Given \( K_a = 10^{-4} \)

\[ pK_a = 4 \]

\[ C = 0.01 \text{ M} \]

\[ \text{pH} = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \frac{1}{2} (4) + \frac{1}{2} (-2) = 8 \]

\text{Ans.}
26. $\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \\
1 \times 10^{-6} \text{M} \quad 1 \times 10^{-4} \text{M} \quad 1 \times 10^{-4} \text{M}$

$K_{sp}[\text{BaCO}_3] = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$
$5.1 \times 10^{-9} = [\text{Ba}^{2+}] \times 1 \times 10^{-4}$
$[\text{Ba}^{2+}] = 5.1 \times 10^{-5} \text{M}$

27. (C) $\text{HNO}_3 + \text{CH}_3\text{COONa}$ mixture can act as buffer solution if volume of $\text{HNO}_3$ solution taken is lesser than volume of $\text{CH}_3\text{COONa}$ solution because of following reaction:
$\text{CH}_3\text{COONa} + \text{HNO}_3 \rightarrow \text{CH}_3\text{COOH} + \text{NaNO}_3$

(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 II$^{\text{nd}}$ equation $\text{H}_2\text{PO}_4^-$ give $\text{H}^+$ ion to the $\text{H}_2\text{O}$ therefore in the II$^{\text{nd}}$ equation it act as an acid.

30. $\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$  $K_1 = 4.2 \times 10^{-7}$

$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$  $K_2 = 4.8 \times 10^{-11}$

$K_1 >> K_2$

$\therefore \quad [\text{H}^+] = [\text{HCO}_3^-]$  

$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$

but  $[\text{H}^+] = [\text{HCO}_3^-]$

$[\text{CO}_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

31. $K_{sp} = [\text{Ag}^+][\text{Br}^-] = 5.0 \times 10^{-13}$

$[\text{Ag}^+] = 0.05 \text{ M}$

$[0.05][\text{Br}^-] = 5.0 \times 10^{-13}$

$[\text{Br}^-] = \frac{5.0 \times 10^{-13}}{0.05} = 1 \times 10^{-11} \text{ M}$

moles of $\text{KBr} = M \times V = 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$

weight of $\text{KBr} = 1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9} \text{ g}$

32. $K_{sp} = 1.0 \times 10^{-11} = (\text{Mg}^{2+})(\text{OH}^-)^2$

$1.0 \times 10^{-11} = (0.001)(\text{OH}^-)^2$

$(\text{OH}^-) = 10^{-4}$

$P_{\text{OH}} = 4$

$P_{\text{H}} = 14 - 4 = 10$.

33. $\text{AgCl} (\text{s}) \leftrightarrow \text{Ag}^+ + \text{Cl}^-$  $K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$

$\text{CuCl} (\text{s}) \leftrightarrow \text{Cu}^+ + \text{Cl}^-$  $K_{sp}(\text{CuCl}) = 10^{-6}$

$Z (Z + Y) = 1.6 \times 10^{-10}$

$Y (Z + Y) = 10^{-6}$

$\Rightarrow (Z + Y)^2 = 1.6 \times 10^{-10} + 10^{-6}$  $\Rightarrow (Z + Y)^2 = 10^{-6}$

$\Rightarrow Z + Y = 10^{-3}$  $\Rightarrow Z (Z + Y) = 1.6 \times 10^{-10}$

$\Rightarrow Z \times 10^{-3} = 1.6 \times 10^{-10}$  $\Rightarrow Z = 1.6 \times 10^{-7}$

$\Rightarrow x = 7$

34. $\text{O}^2- (\text{base}) + \text{H}_2\text{O} (\text{acid}) \rightarrow \text{OH}^- (\text{C.B}) + \text{OH}^- (\text{C.A.})$

$\text{O}^2-$ acts as Lewis base.
1. \[ \text{C}_6\text{H}_5\text{OH} + \text{C}_5\text{H}_5\text{N} \rightleftharpoons \text{C}_6\text{H}_5\text{O}^- + \text{C}_5\text{H}_5\text{NH}^+ \]
   \[ K_n = \frac{K_aK_b}{K_w} = 2.34 \times 10^{-5} \]
   \[ K_n \text{ being small and thus neutralisation does not proceed very far towards completion.} \]

2. Since \([\text{H}^+] = \sqrt{K_w}, \text{ therefore}\]
   \[ \text{pH} = -\log [\text{H}^+] = -\frac{1}{2} \log K_w \]
   Thus, the calculated values of pH at the given temperatures are as follows.
   \[
   \begin{array}{c|c}
   \text{Temperature} & \text{pH} \\
   \hline
   0^\circ C & -\frac{1}{2} \log (0.114 \times 10^{-14}) = 7.472 \\
   10^\circ C & -\frac{1}{2} \log (0.292 \times 10^{-14}) = 7.267 \\
   25^\circ C & -\frac{1}{2} \log (1.008 \times 10^{-14}) = 7.002 \\
   40^\circ C & -\frac{1}{2} \log (2.919 \times 10^{-14}) = 6.767 \\
   50^\circ C & -\frac{1}{2} \log (5.474 \times 10^{-14}) = 6.631 \\
   \end{array}
   \]

3. For a solution to have twice alkalinity, we have
   \[ [\text{OH}^-] = 2.0 \times 10^{-7} \text{ M} \]
   Thus,
   \[ \text{pOH} = -\log ([\text{OH}^-]/[M]) = -\log (2.0 \times 10^{-7}) = 7 - 0.301 = 6.699 \]
   and hence
   \[ \text{pH} = 14 - \text{pOH} = 7.301 \]

4. (a) meq. of \([\text{H}^+] = 10 \times 0.1 + 40 \times 0.2 \times 2 = 17. \]
   
   \[ [\text{H}^+] = \frac{17}{50} = 0.34 \]
   \[ \text{pH} = 0.47 \]

   (b) \[ [\text{H}^+] = \frac{10 - 9.9}{109.9} = \frac{0.1}{109.9} = 9.1 \times 10^{-4} \]
   \[ \text{pH} = 4.0 - \log 9.1 = 3.04 \]

   (c) \[ \text{pV} = nRT \]
   \[ n = \frac{(740 - 23.7)}{760} \times 100 \times \frac{1}{0.0821 \times 298} \times 10^{-3} = 3.85 \times 10^{-3} \text{ M} \]
   \[ [\text{HCl}] = 3.85 \times 10^{-3} \text{ M} = [\text{H}^+] \]
   \[ \text{pH} = 3 - \log 3.85 = 2.41 \]

   (d) pH of Final Solution = 1
   \[ \text{pH} = 1 \]
   \[ [\text{H}^+] = 10^{-1} \]
   \[ \text{Initial} \rightarrow \text{M} = \frac{P \times d \times 10}{\text{M.W.}} = \frac{36.5 \times 10 \times 1.25}{36.5} = M = 12.5 \]
   \[ N_1V_1 = N_2V_2 \Rightarrow 12.5 \times V_1 = 10^{-1} \times 2.5 \]
   \[ V_1 = \frac{2.5}{125} = 0.02 \text{ lit} = 20 \text{ ml} \]

5. \[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]
   \[ \frac{c(1-\alpha)}{c\alpha} \]
   \[ \text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_a + \log \frac{c\alpha}{c(1-\alpha)} \]
\[ \text{pH} = \text{pK}_a + \log \left( \frac{\alpha}{1 - \alpha} \right) = \text{pK}_a - \log \left( \frac{1 - \alpha}{\alpha} \right) \]

\[ \log \left( \frac{1 - \alpha}{\alpha} \right) = \text{pK}_a - \text{pH}. \quad \Rightarrow \quad \left( \frac{1 - \alpha}{\alpha} \right) = 10^{(\text{pK}_a - \text{pH})} \quad \Rightarrow \quad \alpha = \frac{1}{1 + 10^{(\text{pK}_a - \text{pH})}} \]

(b) \( \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \)

\[ C_0 - x \quad x + y \quad x \]

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad x + y \quad y \]

\[ K_a = \frac{[\text{H}^+] x}{C_0 - x} \cdot \quad [\text{H}^+] y = 10^{-14} = K_w \quad \text{Where} \quad [\text{H}^+] = x + y. \]

\[ y = \frac{K_W}{[\text{H}^+]}, \quad x = \frac{K_a C_0}{K_a + [\text{H}^+]}. \]

\[ [\text{H}^+] = x + y = \frac{K_W}{[\text{H}^+]}, \quad + \frac{K_a C_0}{K_a + [\text{H}^+]}:\]

\[ 10^{-3} = 10^{-11} + \frac{0.1 K_a}{K_a + 10^{-3}} \]

\[ K_a + 10^{-3} = 100 K_a \]

\[ K_a = \frac{10^{-3}}{99} = 10^{-5}. \]

(c) \( \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \)

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{C^2 \alpha^2}{C(1 - \alpha)} \]

with an error of 10\% \( C(1 - \alpha) \quad \text{or} \quad C - C\alpha = 0.90 \ C. \)

or

\[ K_a = \frac{(0.10 C)^2}{0.90 C} = \frac{C}{90} \quad \text{or} \quad C = 90 K_a. \]

6. \( \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{(CH}_3\text{)}_2\text{NH}_3^+ + \text{OH}^- \)

\[ K_b = \frac{[\text{(CH}_3\text{)}_2\text{NH}_3^+][\text{OH}^-]}{[\text{(CH}_3\text{)}_2\text{NH}_2]} = \frac{c\alpha c\alpha}{c(1 - \alpha)} = \frac{c\alpha^2}{c(1 - \alpha)} = \frac{c\alpha^2}{1 - c(1 - \alpha)} \]

\[ 5.4 \times 10^{-4} = 0.02 \times \alpha^2. \]

\[ \alpha = 0.164. \]

Since \( \alpha > 0.1, \) 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)} \]

Now \( \alpha = 0.151 \)

In presence of NaOH, the dissociation of diethylamine will decrease due to common ion effect. Thus \( 0.1 + ca = 0.1 + c\alpha \approx \text{and} \quad 0.1 & (1 - \alpha) \approx 1 \)

Thus \( K_b = 5.4 \times 10^{-4} = \frac{c\alpha \times (0.1 + c\alpha)}{c(1 - \alpha)} = \alpha \times 0.1. \)

or \( \alpha = 5.4 \times 10^{-3} = 0.0054. \)

7. \( \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \)

\[ 1 \quad 0 \quad 0 \quad 1 - \alpha \quad \alpha \quad \alpha \]

\( (\text{pK}_a = - \log K_a = 4.74, \quad \therefore \quad K_a = 1.82 \times 10^{-5}) \)
\[ K_a = \frac{c\alpha^2}{(1-\alpha)} = c\alpha^2 \quad (1-\alpha \approx 1). \]

\[ \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = 0.019 \text{ or } 1.9\%. \]

Always calculate first by \( K_b = c\alpha^2 \), if \( \alpha > 10\% \) then use again.

(a) If \( H^+ \) are already present (due to HCl)

\[
\begin{align*}
\text{CH}_3\text{COOH} & \rightleftharpoons \text{CH}_3\text{COO}^- + H^+ \\
1 & 0 \quad 0.01 \\
c(1-\alpha) & c\alpha & [0.01+c\alpha].
\end{align*}
\]

\[
K_b = \frac{[\text{CH}_3\text{COO}^-][H^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha \times (0.01 + c\alpha)}{c(1-\alpha)}
\]

Since presence of \( H^+ \) will favour the reverse reaction or \( \alpha \) will decrease.

i.e., \( 0.01 + c\alpha = 0.01 \) and \( 1-\alpha = 1 \) (due to common ion effect).

\[ \therefore \quad 1.82 \times 10^{-5} = \frac{0.05 \times \alpha \times 0.01}{0.05}. \]

\[ \therefore \quad \alpha = 1.82 \times 10^{-3} = 0.0018. \]

(b) Similarly solve for 0.1 M HCl

\[ \alpha = 0.00018. \]

8. \[ K_a = \frac{c\alpha^2}{1-\alpha} \]

\[ 40 \alpha^2 + \alpha - 1 = 0 \]
\[ \alpha = 0.146 \]
\[ [H^+] = C\alpha = 1.75 \times 10^{-3} \text{ M} \]
\[ \text{pH} = 2.76 \]

9. \[ \text{HA} \rightleftharpoons H^+ + A^- \]
\[ c - x \quad x \quad x \]
\[ [H^+] = x = 1.5 \times 10^{-3} \text{ M} \]
\[ K_a = \frac{x^2}{c-x} \]
\[ 2.5 \times 10^{-3} = \frac{(1.5 \times 10^{-3})^2}{c-1.5 \times 10^{-3}}. \]
\[ c = 2.4 \times 10^{-3} \text{ M}. \]

10. \[ \text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2. \]

\[ \text{concentration} \quad \text{H}_3\text{BO}_3 = c = 2 \times \frac{1}{27.6} \times \frac{1000}{100} = 0.725 \]
\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]
\[ [H^+] = \sqrt[K_a]{c} = \sqrt{7.3 \times 10^{-10} \times 0.725} = 2.3 \times 10^{-5}. \]
\[ \text{pH} = -\log[H^+] = 4.64. \]

11. \[ K_a = c\alpha^2 = 0.1 \times (0.01)^2 = 10^{-5}. \]
\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]
\[ 0.1(1-\alpha) \quad 0.1 \alpha \quad 0.1 \alpha + 0.2 \]
\[ 10^{-5} = \frac{0.1 \alpha \times (0.1 \alpha + 0.2)}{0.1} \]
\[ \alpha = 5 \times 10^{-5} \quad (\text{Therefore, } 0.1\alpha \text{ is neglected}). \]
12. \( \text{HSac} \rightleftharpoons \text{H}^+ + \text{Sac}^- \)

\[
\begin{array}{ccc}
0.002 \times 10^3 & 10^{-2} & 0 \\
8 \times 10^{-3} & 10^{-2} & 0 \\
8 \times 10^{-3} (1 - \alpha) & 10^{-2} & 8 \times 10^{-3} \alpha
\end{array}
\]

\[ K_a = \frac{10^{-2}(8 \times 10^{-3} \alpha)}{8 \times 10^{-3} (1 - \alpha)} = 2 \times 10^{-12} \quad \Rightarrow \quad \alpha = 2 \times 10^{-10} \]

\[ [\text{Sac}^-] = 8 \times 10^{-3} \times 2 \times 10^{-10} = 16 \times 10^{-13} = 1.6 \times 10^{-12} \text{ M} \]

13. \( \text{C}_6\text{H}_5\text{OH} \) (Phenol) \( \rightleftharpoons \) Weak acid \( K_a = 1 \times 10^{-10} \)

\[
\begin{array}{ccc}
\text{C}_6\text{H}_5\text{OH} & \text{C}_6\text{H}_5\text{O}^- + \text{H}^+ \\
\text{C} & 0 & 0 \\
\text{C} - \text{C} \alpha & \text{C} \alpha & \text{C} \alpha
\end{array}
\]

\[ K_a = C \alpha^2 = 1 \times 10^{-10} \]

\[ \alpha = \sqrt[2]{\frac{1 \times 10^{-10}}{0.05}} = \sqrt{2} \times 10^{-5} \quad \alpha = 4.47 \times 10^{-5} \]

\[ [\text{C}_6\text{H}_5\text{O}^-] = 4.47 \times 10^{-5} \times 0.05 = 2.42 \times 10^{-6} \]

\[ [\text{C}_6\text{H}_5\text{ONa}] = 0.01 \text{ M} \]

\[
\begin{array}{ccc}
\text{C}_6\text{H}_5\text{ONa} & \text{C}_6\text{H}_5\text{O}^- + \text{Na}^+ \\
0.01 & 0.01 & 0.01 \\
0.05 (1 - \alpha) & 0.01 & 0.05 \alpha
\end{array}
\]

\[ [0.05\alpha] 0.01 = 1 \times 10^{-10} \quad \alpha = 10^{-4} \]

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, \[ K_a = 10^{-10} = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \]

\[ \therefore \quad [\text{B}^-] = 3.33 \times 10^{-3} \text{ M} \]

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, \[ K_a = 2.4 \times 10^{-4} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \]

\[ \therefore \quad [\text{HCOO}^-] = 3 \times 10^{-3} \text{ M} \]

for HOCN, \[ K_a = 4 \times 10^{-6} = \frac{[\text{H}^+][\text{OCN}^-]}{[\text{HOCN}]} \]

\[ \therefore \quad [\text{OCN}^-] = 5 \times 10^{-3} \text{ M} \]

16. \( \text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- \)

\[
\begin{array}{ccc}
0.01 & 0.01 & 0.01 \\
0.01 & 0 & 0.01 \\
0.01 (1 - \alpha) & 0.01 \alpha & 0.01 + 0.01 \alpha
\end{array}
\]

\[ K_a = \frac{0.01 \alpha \times [0.01 + 0.01 \alpha]}{0.01 (1 - \alpha)} = 2 \times 10^{-2} \]

\[ 0.01 \alpha^2 + 0.01 \alpha = 2 \times 10^{-2} \]

\[ 10^{-2} \alpha^2 + 10^{-2} \alpha = 2 \times 10^{-2} \]

\[ \alpha^2 + \alpha - 2 = 0 \]
\[ \alpha = \frac{-2 \pm \sqrt{1 + 8}}{2} = \frac{-2 + 3}{2} \implies \alpha = 0.56 \]

\[ [H^+] = 10^{-2} + 10^{-2} \times 0.56 = 1.56 \times 10^{-2} \text{ M} \]

\[ [\text{CHCl}_2\text{COO}^-] = 0.01 \] \[ \alpha = 5.6 \times 10^{-3} \text{ M} \]

17. Dissociation of \( H_2S \) can be represented as

(a) \( H_2S \rightleftharpoons H^+ + HS^- \)

(b) \( HS^- \rightleftharpoons H^+ + S^{2-} \)

From the first ionisation of \( H_2S \):

\[ \frac{[H^+][HS^-]}{[H_2S]} = K_a^1 \]

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 \( H_2S \):

\[ \frac{[H^+][S^{2-}]}{[HS^-]} = K_a^2 \text{ or } \frac{0.2 \times [S^{2-}]}{5 \times 10^{-8}} = 1.3 \times 10^{-13} \]

\[ [S^{2-}] = 3.25 \times 10^{-20} \text{ M} \]

18. \( \text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + H^+ \)

\[ 0.1 - x \quad x - y \quad x + y + z \]

\( \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + H^+ \)

\[ x - y \quad y - z \quad y + x + z \]

\( \text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-} + H^+ \)

\[ y - z \quad z \quad x + y + z \]

\[ K_{a1} = \frac{(x - y)(x + y + z)}{0.1 - x} = \frac{x^2}{0.1 - x} \quad (y + z \text{ are very small compared to } x) \]

\[ 7.5 \times 10^{-3} = \frac{x^2}{0.1 - x} \quad \implies \quad x = 0.024 \text{ M} \]

\[ K_{a2} = \frac{(y - z)(x + y + z)}{x - y} = \frac{y \times y}{x} = y \quad \implies \quad y = 6.2 \times 10^{-8} \quad \text{(here } z < < y) \]

\[ K_{a3} = \frac{z(x + y + z)}{y - z} = \frac{z \times x}{y} \quad \implies \quad z = K_{a3} \frac{y}{x} = 9.3 \times 10^{-19} \text{ M} \]

\[ : [\text{H}_3\text{PO}_4] = 0.1 - x = 0.076 \text{ M} \]

\[ [H^+] = [\text{H}_2\text{PO}_4^-] = x = 0.024 \text{ M} \]

\[ [\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M} \]

\[ [\text{PO}_4^{3-}] = z = 9.3 \times 10^{-19} \text{ M} \]

\[ [\text{OH}^-] = K_w / [H^+] = 4.17 \times 10^{-13} \text{ M} \]

19. Given,

\[ \frac{\text{wt. of } \text{NH}_3}{\text{wt. of solution}} = \frac{10}{100} \]

\[ \text{wt. of } \text{NH}_3 = \frac{100 \text{ g solution}}{100} \] \[ \therefore \text{M}_{\text{NH}_3} = \frac{(10 \times 1000)}{[17 \times (100/0.99)]} \quad (\because V = \text{mass} / \text{density}) \]

Now \( \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \)

Before dissociation

\[ 1 \quad 0 \quad 0 \]

After dissociation

\[ (1 - \alpha) \quad \alpha \quad \alpha \]

\[ [\text{OH}^-] = C \alpha = C \sqrt{(K_b / C)} = \sqrt{(K_b \times C)} \]

\[ \therefore C = 5.82 \text{ M and } K_b = K_w / K_a = 10^{-14} / (5 \times 10^{-10}) = 2 \times 10^{-5} \]

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\[ [\text{OH}^-] = \sqrt{2 \times 10^{-5} \times 5.82} = 1.07 \times 10^{-2} \text{ M} \]

\[ [\text{H}^+] = 10^{-14/1.07} \times 10^{-2} = 0.9268 \times 10^{-12} \text{ M} \]

\[ \text{pH} = -\log [\text{H}^+] = -\log 0.9268 \times 10^{-12} = 12.0330 \]

20. \( \text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^- \)

\[ c(1 - h) \quad \text{ch} \quad \text{ch} \quad \text{ch} \quad \text{where h is degree of hydrolysis} \]

\[ [\text{OH}^-] = ch; \]

\[ \text{Also; } h = \sqrt{\frac{K_w}{c \cdot K_a}} = \sqrt{\frac{10^{-14}}{4.5 \times 10^{-4} \times 0.04}} = 2.36 \times 10^{-4} \]

\[ [\text{OH}^-] = 0.04 \times 2.36 \times 10^{-5} \quad \text{or} \quad \text{pOH} = 6.025 \]

\[ \text{Also} \quad h = \sqrt{\frac{K_h}{c \cdot K_a}} = \sqrt{\frac{10^{-14} \times 0.02}{5 \times 10^{-5}}} = 2 \times 10^{-6} \]

\[ \text{or} \quad \text{pH} = 14 - \text{pOH} = 7.975 \]

21. \( \text{Asc}^- + \text{H}_2\text{O} \rightleftharpoons \text{HAsc} + \text{OH}^- \)

\[ c(1 - h) \quad \text{ch} \quad \text{ch} \quad \text{ch} \quad \text{where h is degree of hydrolysis} \]

\[ [\text{OH}^-] = ch; \]

\[ \text{Also; } h = \sqrt{\frac{K_h}{c \cdot K_a}} = \sqrt{\frac{10^{-14}}{2 \times 10^{-6}}} = 5 \times 10^{-9} \text{ M} \]

\[ [\text{OH}^-] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3} \text{ M} \]

\[ \text{So} \quad [\text{OH}^-] = 10^{-6} \text{ M} \]

22. \( \text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^- \)

\[ c(1 - h) \quad \text{ch} \quad \text{ch} \quad \text{ch} \quad \text{where h is degree of hydrolysis} \]

\[ [\text{OH}^-] = ch; \]

\[ \text{Also; } h = \sqrt{\frac{K_h}{c \cdot K_a}} = \sqrt{\frac{10^{-14}}{2 \times 10^{-6}}} = 5 \times 10^{-9} \text{ M} \]

\[ [\text{OH}^-] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3} \text{ M} \]

\[ \text{So} \quad [\text{OH}^-] = 10^{-6} \text{ M} \]

24. (a) Let V mL of NH\text{$_3$OH} be mixed with NH\text{$_3$Cl} to have a buffer of pH 8.65. The total volume after mixing becomes (V + 30) mL.

\[ \text{m mole of NH}_3\text{OH} = 0.3 \times V \]

\[ \therefore \quad [\text{NH}_3\text{OH}] = \frac{0.3 \times V}{(V + 30)} \]

\[ \text{m mole of NH}_3\text{Cl} = 0.2 \times 30 \]

\[ \therefore \quad [\text{NH}_3\text{Cl}] = \frac{0.2 \times 30}{(V + 30)} \]

Also pOH of buffer mixture is given by:

\[ \text{pOH} = \text{pK}_b + \log \left( \frac{[\text{Salt}]}{[\text{Base}] \cdot c} \right) \]

\[ \text{or} \quad 14 - 8.65 = 4.74 + \log \left( \frac{0.2 \times 30}{(V + 30)} \right) \frac{(0.3 \times V)}{(V + 30)} \]

\[ \therefore \quad \text{pOH} = 14 - \text{pH} \]
0.6 = log $\frac{6}{0.3V}$.

\[ \therefore V = 5 \text{ mL.} \]

Similarly calculate \( \left(14 - 10 = 4.74 + \log \frac{0.2 \times 30}{0.3 \times V_i/(V_i + 30)} \right) \) for pH = 10 ;

\[ V = 111.11 \text{ mL.} \]

(b) HA \[\rightleftharpoons H^+ + A^-\]

\[ t = 0 \quad \begin{align*} & 0.2 - x \quad x \quad 0.1 + x 
\end{align*} \]

\[ K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x(0.1+x)}{(0.2-x)} \]

\[ \Rightarrow 0.05 = \frac{x^2 + 0.1x}{0.2 - x} \]

\[ \Rightarrow 0.01 - 0.05x = x^2 + 0.1x \]

\[ x^2 + 0.15x - 0.01 = 0 \]

\[ x = 0.05 \text{ M} \]

(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.

NaCN + HCl \[\rightarrow\] NaCl + HCN

Mole added 0.01 a 0 0
Mole after reaction (0.01-a) 0 a a

This is buffer of HCN + NaCN

Let a mole of HCl be used for this purpose

\[ \therefore \text{pH} = -\log K_a + \log \frac{0.01-a}{a} \]

\[ 8.5 = -\log (4 \times 10^{-10}) + \log \frac{0.01-a}{a} \]

\[ a = 8.89 \times 10^{-3} \text{ mole of HCl} \]

(e) We know,

\[ \text{pOH} = -\log K_b + \log \frac{[\text{Base}]}{[\text{Salt}]} \]

\[ 5 = 4.7 + \log \frac{a}{b} \]

\[ \frac{a}{b} = 2 \quad \therefore a = 2b \]

Given \( a + b = 0.6 \)

\[ 2b + b = 0.6 \]

\[ 3b = 0.6 \]

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,
\[
\begin{align*}
[NH_3] &= \frac{0.1}{1} \\
[NH_4^+] &= \frac{0.1}{1}
\end{align*}
\]
\[
pH = - \log 1.8 \times 10^{-5} + \log \frac{[\text{Salt}]}{[\text{Base}]} = - \log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.74
\]
\[\therefore \quad pH = 9.26\]

(i) Now 0.02 mole of HCl are added then
\[
\begin{align*}
\text{HCl} + \text{NH}_4\text{OH} &\rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O} \\
\text{Mole before reaction} &\quad \text{0.02} \quad \text{0.1} \quad \text{0} \quad \text{0.1} \\
\text{Mole after reaction} &\quad \text{0} \quad \text{0.08} \quad (0.1 + 0.02) \\
\therefore \quad \text{Volume} = 1 \text{ litre}
\end{align*}
\]
\[\therefore \quad [\text{NH}_4\text{OH}] = \frac{0.08}{1} \quad \text{and} \quad [\text{NH}_4\text{Cl}] = \frac{0.12}{1}
\]
\[\therefore \quad pOH_1 = - \log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08} = 4.92
\]
\[\therefore \quad pH_1 = 9.08
\]
\[\therefore \quad \text{Change in pH} = pH_1 - pH_1 = 9.26 - 9.08 = + 0.18
\]
\[\therefore \quad \text{Change in pH} = 0.18 \text{ unit i.e., pH increases}
\]

(ii) Now 0.02 mole of NaOH are added
\[
\begin{align*}
\text{NaOH} + \text{NH}_4\text{Cl} &\rightarrow \text{NaCl} + \text{NH}_3\text{OH} \\
\text{Mole before reaction} &\quad \text{0.02} \quad \text{0.1} \quad 0 \quad 0.1 \\
\text{Mole after reaction} &\quad \text{0} \quad \text{0.08} \quad 0.02 \quad 0.12
\end{align*}
\]
\[\therefore \quad pOH_2 = - \log 1.8 \times 10^{-5} + \log \frac{0.08}{0.12} = 4.57
\]
\[\therefore \quad pH_2 = 9.43
\]
\[\therefore \quad \text{Change in pH} = pH - pH_2 = 9.26 - 9.43 = - 0.18
\]
\[\therefore \quad \text{Change in pH} = 0.18 \text{ unit i.e., pH increases}
\]

(b) \[
\begin{align*}
\text{HCOONa} + \text{HCl} &\rightarrow \text{HCOOH} + \text{NaCl} \\
\text{Initially mM} &\quad 6.25 \quad 0.25 \quad 0 \quad 0 \\
\text{Finally mM} &\quad 6 \quad 0 \quad 0.25 \quad 0.25
\end{align*}
\]
\[\therefore \quad pH = 3.75 + \log \frac{6}{0.25} = 3.75 + \log 24 = 5.13
\]

Also \[\text{[HCOOH]} = \frac{0.25}{60} = 4.17 \times 10^{-3} \text{ M}\]

(c) Let Acid is H$_2$A
\[
\begin{align*}
\text{H}_2\text{A} &\rightarrow K_{a1} \text{ HA}^- \\
\text{HA}^- &\rightarrow K_{a2} \text{ A}^{2-}
\end{align*}
\]
For HA$^-$, \quad \text{pK}_{a2} = 9.7
and \quad \text{pK}_{b} = 11.7 \quad \text{So pK}_{a1} = 14 - 11.7 = 2.3
\[
\begin{align*}
\text{HA}^- + \text{HCl} &\rightarrow \text{H}_2\text{A} + \text{Cl}^- \\
t = 0 &\quad 10 \text{ milimole} \quad x \text{ milimole} \quad 0 \quad 0 \\
(10 - x) &\quad 0 \quad x \quad x
\end{align*}
\]
This solution Act as Buffer solution
\[
\begin{align*}
\text{So} \quad pH = \text{pK}_{a1} + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]} &\Rightarrow 2.6 = 2.3 + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]}
\end{align*}
\]
\[0.3 = \log \frac{(10 - x)}{x} \quad \Rightarrow \quad 2 = \left[ \frac{10 - x}{x} \right] \quad \Rightarrow \quad 2x = 10 - x
\]
\[3x = 10 \quad \Rightarrow \quad x = 3.33 \text{ milimole} \]
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
\[
\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-
\]
t=0 300 150 150
so \(\text{pH} = \text{pK}_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10.3\).

(b) Mole balance equation
\[
[\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]
\[
\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] \left(1 + \frac{K_{a1}[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2} + \frac{K_{a1}K_{a2}[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2}\right)
\]
\[
\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] \left(1 + \frac{4.9 \times 10^{-7}}{10^{-8}} + \frac{4.9 \times 10^{-7} \times 10^{-12}}{(10^{-8})^2}\right)
\]
\[
\Rightarrow [\text{HCO}_3^-]_0 = [\text{H}_2\text{CO}_3] (1 + 49 + 4.9 \times 10^{-3})
\]
\[
\Rightarrow [\text{H}_2\text{CO}_3] = \frac{[\text{HCO}_3^-]_0}{50}
\]
\[
\Rightarrow n_{\text{H}_2\text{CO}_3} = \frac{0.0005}{50} = 10^{-5} \text{ mole.}
\]
\[
[\text{HCO}_3^-] = \frac{K_{a1}[\text{H}_2\text{CO}_3]}{[\text{H}^+]} 
\]
\[
\Rightarrow n_{\text{HCO}_3^-} = \frac{4.9 \times 10^{-7} \times 10^{-5}}{10^{-8}} = 4.9 \times 10^{-4} \text{ mole}
\]
\[
[\text{CO}_3^{2-}] = \frac{K_{a1}K_{a2}[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2}
\]
\[
\Rightarrow n_{\text{CO}_3^{2-}} = \frac{4.9 \times 10^{-7} \times 10^{-12} \times 10^{-5}}{(10^{-8})^2} = 4.9 \times 10^{-4} \text{ mole}
\]

27. \(\text{pH}_1 = \text{pK}_a + \log \frac{x}{a}\)
\(\text{pH}_2 = \text{pK}_a + \log \frac{y}{a}\).
\(\text{pH}_2 - \text{pH}_1 = 0.6 = \log \frac{y}{x}.\)
\(y = x \times 10^{0.6} = 4x.\)
\(x : y = 1 : 4.\)

28. \(\text{pK}_a = 11 - \log 4.7 = 11 - \log 4.7 = 11 - 0.672 = 10.328\)
\(\text{pH} = \text{pK}_a + \log \left(\frac{n_{\text{Na}_2\text{CO}_3}}{0.3}\right) = 10 + 10.328 + \log \left(\frac{n_{\text{Na}_2\text{CO}_3}}{0.3}\right)\)
\[
\log \frac{0.3}{n_{\text{Na}_2\text{CO}_3}} = 0.328 \Rightarrow \frac{0.3}{n_{\text{Na}_2\text{CO}_3}} = 2.13
\]
\(W_{\text{Na}_2\text{CO}_3} = \left[\frac{0.3}{2.13}\right] \times 106 = 14.94 \approx 15 \text{ gram}\)
29. For sodium butyrate

\[ \text{pH} = 7 + \frac{1}{2} \log C = 7 + \left( \frac{5 - \log 1.5}{2} \right) + \frac{1}{2} \log (0.1) \]

\[ = 7 + 2.41 - 0.5 = 8.91 \]

For indicator

\[ K_{\text{In}} = \frac{[H^+] [\text{In}^-]}{[\text{In}]} \]

\[ \Rightarrow \frac{[\text{In}^-]}{[H^+]} = \frac{K_{\text{In}}}{3.16 \times 10^{-10}} = 0.257 \]

30. **Case I:**

\[ \text{BOH} + \text{HCl} \rightarrow \text{BCl} + \text{H}_2\text{O} \]

Millimole before reaction

<table>
<thead>
<tr>
<th></th>
<th>BOH</th>
<th>HCl</th>
<th>BCl</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimole</td>
<td>a</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Millimole after reaction</td>
<td>(a - 0.5)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ \therefore \text{pH} = 10.04 \]

\[ \therefore \text{pOH} = 3.96 \]

**Case II:**

\[ \text{BOH} + \text{HCl} \rightarrow \text{BCl} + \text{H}_2\text{O} \]

Millimole before reaction

<table>
<thead>
<tr>
<th></th>
<th>BOH</th>
<th>HCl</th>
<th>BCl</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimole</td>
<td>a</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Millimole after reaction</td>
<td>(a - 2)</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

\[ \therefore \text{pH} = 9.14 \]

\[ \therefore \text{pOH} = 4.86 \]

\[ K_b = 1.81 \times 10^{-5} \]

31. \[ \text{pH of CH}_3\text{COOH} = \frac{1}{2} (pK_a - \log c) \]

\[ 3 = \frac{1}{2} (pK_a - \log 0.1) \]

\[ \therefore pK_a = 5 \]

\[ \frac{1}{4} \text{ stage of neutralisation} : \text{pH} = 5 + \log \frac{1/4}{3/4} = 4.52 \]

\[ \frac{3}{4} \text{ stage of neutralisation} : \text{pH} = 5 + \log \frac{3/4}{1/4} = 5.48 \]

32. We know that pH of a mixture of solution containing weak acid and strong base can be calculated as below

\[ \text{pH} = 7 + \frac{1}{2} \log C = 7 + \frac{1}{2} \log \frac{[\text{In}^-]}{[\text{In}]} \]

\[ = 7 + \frac{1}{2} \times 4.72 + \frac{1}{2} \log 0.05 \]

\[ = 7 + 2.36 - 0.65 = 8.71 \]

33. \[ \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^- \]

Thus,

\[ K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} \]

\[ = \frac{2.4 \times 10^{-14}}{0.24} = 10^{-5} \times [\text{OH}^-] \]

\[ \therefore [\text{OH}^-] = 10^{-2} \text{ M} \]
34. Let $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3 + \text{KCl}$

\[ x \text{g} \quad y \text{g} \]

At 1st equivalent point

\[ \text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl} \]

Milimole HCl consumed = $0.15 \times 10 = 1.5$

\[ Y \frac{106}{1000} \times 1 \times 10^3 = 1.5 \]

\[ y = \frac{1.5 \times 106}{1000} = 0.159 \text{ g} \]

At 2nd equivalent point

m. eq. of Na$_2$CO$_3$ + m. eq. of NaHCO$_3$ = m. eq. of HCl = $35 \times 0.15$

\[ \Rightarrow \frac{x}{84} + \left( \frac{1.5 \times 10^{-3}}{106} \right) \times 2 = 0.15 \times 35 \times 10^{-3} \]

\[ \Rightarrow \frac{x}{84} + 3 \times 10^{-3} = 0.15 \times 35 \times 10^{-3} \]

\[ x = \frac{(2.25 \times 84)}{1000} = 0.189 \text{ g} \]

mass of KCl = 0.152 g

mass % of Na$_2$CO$_3$ = $\frac{0.159 \times 100}{0.5} = 31.8$ %

mass % of NaHCO$_3$ = $\frac{0.189 \times 100}{0.5} = 37.8$ %

mass % of KCl = $\frac{0.152 \times 100}{0.5} = 30.4$ %

35. Let Molarity of $\text{C}_6\text{H}_4(\text{OH})\text{COOH} = M_1$

\[ \text{C}_6\text{H}_4(\text{OH})\text{COOH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5(\text{OH})\text{COONa} \]

At end point

No. of eq. of $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ = No. of eq. of NaOH = $16.24 \times 0.02$

\[ 25 \times M_1 = 0.3248 \Rightarrow M_1 = \frac{0.3248}{25} = 0.013 \]

Half neutralization

\[ \text{C}_6\text{H}_4(\text{OH})\text{COOH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5(\text{OH})\text{COONa} \]

\[ \begin{array}{ccc}
0.3248 & 0.1624 & 0 \\
0.1624 & 0 & 0.1624 \\
\end{array} \]

\[ \text{pH} = \text{pK}_{a1} + \log \frac{[\text{C}_6\text{H}_5(\text{OH})\text{COONa}]}{[\text{C}_6\text{H}_5(\text{OH})\text{COOH}]} \Rightarrow 4.7 = \text{pK}_{a1} \Rightarrow K_{a1} = 2 \times 10^{-5} \]

Complete neutralization

\[ \text{C}_6\text{H}_5(\text{OH})\text{COOH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5(\text{OH})\text{COONa} + \text{H}_2\text{O} \]

\[ \begin{array}{ccc}
0.3248 & 0.3248 & 0 \\
0 & 0 & 0.3248 \\
\end{array} \]

\[ [\text{C}_6\text{H}_5(\text{OH})\text{COONa}] = \frac{0.3248}{41.24} = 7.88 \times 10^{-3} \]

$\text{C}_6\text{H}_5(\text{OH})\text{COONa}$ This species is amphiprotic species.

So 

\[ \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} \Rightarrow 7.5 = \frac{4.7 + \text{pK}_{a2}}{2} \]

\[ 15 - 4.7 = \text{pK}_{a2} \Rightarrow \text{pK}_{a2} = 10.3 \Rightarrow K_{a2} = 5 \times 10^{-11} \]

36. $\text{[Sr(OH)}_3] \rightarrow \text{Sr}^{2+} + 2\text{OH}^–$

\[ \text{[Sr(OH)}_3] = \frac{19.23}{121.62 \times 1} = 0.158 \text{ M} \]

$\therefore \text{[OH}^–] = 2 \times 0.158 \text{ M} = 0.316 \text{ M}$
or \( pOH = 0.5 \). \( \therefore \) \( pH = 13.5 \)

\[ [Sr^{2+}] = 0.158 \text{ M} \]

37. (a) \( \text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-} \)

\( [\text{Sr}^{2+}] = 0.158 \text{ M} \).

(i) 
\[ K_{sp} = s \times s \]
\[ \therefore s = \sqrt{K_{sp}} = \sqrt{1.6 \times 10^{-9}} = 4 \times 10^{-5} \text{ mol litre}^{-1} \]

(ii) In presence of 0.10 M \( \text{BaCl}_2 \), let \( s \) mol/litre \( \text{BaSO}_4 \) is dissolved

\[ K_{sp} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] \]
\[ 1.6 \times 10^{-9} = (0.1 + s) (s) \]
\[ (0.1 + s) = 0.1 \text{ as } s \ll 0.1 \]
\[ s = 1.6 \times 10^{-4} \text{ M} \]

(b) For \( \text{CaSO}_4 \), let solubility be \( s \) mol/litre

\[ s = \sqrt[3]{K_{sp}} = \sqrt[3]{9 \times 10^{-6}} = 3 \times 10^{-2} \text{ mol litre}^{-1} \]

Thus, \( 3 \times 10^{-2} \) mole of \( \text{CaSO}_4 \) is soluble in water = 1 litre

\[ \frac{1}{136} \text{ mole (1 g) of } \text{CaSO}_4 \text{ is soluble in } \frac{1}{136 \times 3 \times 10^{-3}} = 2.45 \text{ litre water} \]

(c) Let solubility of \( \text{Mg(OH)}_2 \) be \( s \) mol litre\(^{-1} \)

\[ \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \]
\[ [\text{Mg}^{2+}] [\text{OH}^-]^2 = K_{sp} \]
\[ 4s^3 = 8.9 \times 10^{-12} \]
\[ s = 1.305 \times 10^{-4} \text{ mol litre}^{-1} \]
\[ [\text{OH}^-] = 2 \times 1.305 \times 10^{-4} \text{ mol litre}^{-1} \]
\[ pOH = 3.58 \]
\[ \therefore \text{pH} = 10.42 \]

38. (a) For \( \text{Ag}_2\text{CrO}_4 (s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} \)

\[ K_{sp} = 4s^3 \]
\[ \Rightarrow s = 2 \times 10^{-4} \text{ mol/lt.} \]

Now,
\[ \text{m. moles of } \text{CrO}_4^{2-} = \text{m. moles of } \text{Pb}^{2+} \]
\[ 50 \times 2 \times 10^{-4} = 20 X \]
\[ \therefore X = 5 \times 10^{-4} \text{ M.} \]

(b) \( \text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2 \).

\[ \frac{10}{101} - x \times \frac{1}{101} - 2x \approx 0. \]
\[ [\text{Pb}^{2+}] = \left( 10 - \frac{1}{2} \right) \times \frac{1}{101} = \frac{9.5}{101} = 9.4 \times 10^{-2} \text{ M.} \]

(c) Taking density of water to be 1 g/cc.

\[ [\text{CaSO}_4] = \frac{136}{10^{-5}} \times \frac{1000}{136} = 10^{-10} \text{ M.} \]

Concentration of \( \text{CaSO}_4 \) in saturated solution = \( \sqrt{K_{sp}} = 3 \times 10^{-3} \).

\[ M_1 V_1 = M_2 V_2 \]
\[ 10^{-10} \times V_1 = 3 \times 10^{-3} \times V_2 \]
\[ \frac{V_2}{V_1} = \frac{1}{3} \Rightarrow \frac{V_1 - V_2}{V_1} = 0.67 \]
39. \[ \text{PbBr}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Br}^- \]
\[
\begin{align*}
0.8 \text{ s} &\quad 2 \times 0.8 \text{ s} \\
8 \times 10^{-5} &\quad 4 \times (0.8)^2 \times \text{s}^3 \\
\Rightarrow s &= 5 \times 10^{-3} \text{ mol/lt.} \\
\text{solubility of salt} &= 5 \times 10^{-3} \times 368 = 1.84 \text{ g/lt.}
\end{align*}
\]

40. (a) \[
\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}.
\]
\[
\text{BaCrO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{CrO}_4^{2-}.
\]
\[
[\text{Ba}^{2+}] = 1.4 \times 10^{-5} = \sqrt{K_{sp1} + K_{sp2}}
\]
\[
\therefore K_{sp1} + K_{sp2} = (1.4 \times 10^{-5})^2
\]
\[
K_{sp1} \quad \text{&} \quad K_{sp2} = 2.5
\]
\[
\text{On solving, } K_{sp1} = 5.6 \times 10^{-11}
\]
\[
K_{sp2} = 1.4 \times 10^{-10}
\]
\[
\text{Solubility of BaSO}_4 \text{ in 0.01 M Na}_2\text{SO}_4 = \frac{5.6 \times 10^{-11}}{0.01} = 5.6 \times 10^{-9} \text{ M.}
\]

(b). milli moles of I\(^-\) = 25 \times 2 \times \frac{7.1 \times 10^{-9}}{4}.

milli moles of Ag\(^+\) = 13.3 \times M.

Ag\(^+\) (aq) + I\(^-\) (aq) \longrightarrow AgI (s)

Equating both M = 4.55 \times 10^{-3}.

(c). [F\(^-\)] concentration when [Sr\(^{2+}\)] is 2.5 \times 10^{-3}.

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 g.

41. Given,
\[
\begin{align*}
\text{MBr}_2(g) &\rightleftharpoons \text{MBr}_2(aq) \rightleftharpoons \text{M}^{2+} + 2\text{Br}^- \\
\text{MBr}_2 + \text{H}_2\text{S} &\rightarrow \text{MS} + 2\text{HBr}
\end{align*}
\]
\[
K_{sp} \text{ of MS} = [\text{M}^{2+}][\text{S}^-]^2
\]
\[
6 \times 10^{-21} = [0.05][\text{S}^-]^2
\]
\[
\therefore [\text{S}^-] = 1.2 \times 10^{-10} \text{ M}
\]

Thus, MS will be precipitated if H\(_2\)S provides 1.2 \times 10^{-10} M ions of S\(^2-\).

Now for H\(_2\)S
\[
\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^- \]
\[
K_1 \times K_2 = \frac{[\text{H}^+]^2[\text{S}^-]}{[\text{H}_2\text{S}]}
\]
\[
10^{-7} \times 1.3 \times 10^{-13} = \frac{[\text{H}^+]^2[1.2 \times 10^{-19}]}{[0.1]}
\]
\[
\therefore [\text{H}^+] = 1.04 \times 10^{-1} \quad \text{and pH} = 0.983
\]

42. Volume of both AgNO\(_3\) & HCN are equal so. There concentration is half

[AgNO\(_3\)] = 0.01 M \quad [HCN] = 0.01 M

HCN \rightleftharpoons \text{H}^+ + \text{CN}^- \quad K_a = 4 \times 40^{-10} \quad \text{...... (i)}

Ag\(^+\) + CN\(^-\) \rightleftharpoons AgCN \quad K = \frac{1}{K_a} \quad \text{...... (ii)}

on adding equation (i) & equation (ii)

Ag\(^+\) + HCN \rightleftharpoons H^+ + AgCN \quad K' = 10^6
As the value of $K'$ is very high so almost all $\text{Ag}^+ \text{ & HCN}$ converted in product

\[
\text{Ag}^+ + \text{HCN} \rightleftharpoons \text{H}^+ + \text{AgCN(s)} \quad K' = \frac{K_a}{K_{sp}} = 1 \times 10^6
\]

\[
\begin{array}{c|c|c|c|c|c|c}
 & 0.01 & 0.01 & 0 & 0 \\
\hline
x & x & \approx 0.01 & \approx 0.01 \\
\end{array}
\]

\[
K' = \frac{0.01}{(x)^2} = 10^6
\]

\[
X^2 = 10^{-6} \quad \Rightarrow \quad X = 10^{-4}
\]

Conc. of $\text{[Ag}^+\text{]} = 10^{-4}$

43. For the precipitation of $\text{Mg(OH)}_2$

$[\text{Mg}^{2+}] [\text{OH}^-]^2 = K_{sp}$

$[\text{OH}^-] = 5 \times 10^{-5}$.

For $\text{NH}_3 - \text{NH}_4^+$ buffer solution,

\[
K_b = \frac{[\text{NH}_3][\text{NH}_4^+]}{[\text{NH}_2\text{OH}]} \Rightarrow [\text{NH}_3] = \frac{(5 \times 10^{-6})(0.4)}{2 \times 10^{-5}} = 0.1 \text{ M}.
\]

44. Let final concentration of $\text{SO}_4^{2-}$ in solution $= [\text{SO}_4^{2-}]_{\text{left}} = x$

Mole balance equation for $\text{SO}_4^{2-}$:

\[
[\text{SO}_4^{2-}]_{\text{initial}} = [\text{SO}_4^{2-}]_{\text{left}} + [\text{SO}_4^{2-}]_{\text{combined}}
\]

\[
\begin{array}{c|c|c|c|c|c|c}
 & 0.3 \times 10^{-3} & 0.1 = [\text{SO}_4^{2-}]_{\text{left}} + [\text{SO}_4^{2-}]_{\text{combined}} \\
\hline
0.1 = x + [\text{Ca}^{2+}]_{\text{combined}} + [\text{Sr}^{2+}]_{\text{combined}} \\
\Rightarrow 0.1 = x + ([\text{Ca}^{2+}]_{\text{initial}} - [\text{Ca}^{2+}]_{\text{left}}) + ([\text{Sr}^{2+}]_{\text{initial}} - [\text{Sr}^{2+}]_{\text{left}}) \\
\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{K_{sp \text{ of CaSO}_4}}{[\text{SO}_4^{2-}]_{\text{left}}}\right) + \left(\frac{0.2}{3} - \frac{K_{sp \text{ of SrSO}_4}}{[\text{SO}_4^{2-}]_{\text{left}}}\right) \\
\Rightarrow 0.1 = x + \left(\frac{2.4 \times 10^{-5}}{x}\right) + \left(\frac{7.6 \times 10^{-7}}{x}\right)
\end{array}
\]

\[
3x^2 + 0.1x + 7.428 \times 10^{-5} = 0
\]

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 $= \frac{100}{350} \times 2 \times \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}} = 8.68 \times 10^{-3}$. 

$[\text{SO}_4^{2-}]$ concentration $= \frac{100}{350} \times \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}} = 4.34 \times 10^{-3}$. 

$[\text{Pb}^{2+}] = \frac{250}{350} \times \sqrt[3]{2.8 \times 10^{-13}} = 3.78 \times 10^{-7}$. 

$[\text{CrO}_4^{2-}] = 3.78 \times 10^{-7}$. 

$[\text{Ag}^+][\text{CrO}_4^{2-}] = 2.85 \times 10^{-11} > K_{sp}$ of $\text{Ag}_2\text{CrO}_4$. 

$[\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.64 \times 10^{-9} < K_{sp}$ of $\text{PbSO}_4$. 

Only $\text{Ag}_2\text{CrO}_4$ will precipitate.
46. \[ \text{[Ag}^+\text{]} [\text{Cl}^-] = 1.75 \times 10^{-10} \]
\[ \text{[Ag}^+\text{]} [\text{Br}^-] = 5.25 \times 10^{-13} \]

\[ \Rightarrow \quad \text{[Br}^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times [\text{Cl}^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times (0.075) = 2.25 \times 10^{-4} \text{ M.} \]

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.

For \[ \text{Ca(OH)}_2 \xrightleftharpoons{} \text{Ca}^{2+} + 2\text{OH}^- \]

Then,

\[ 4s^3 = 4.42 \times 10^{-5} \]

\[ \therefore \quad s = 3^{\sqrt{\frac{4.42 \times 10^{-5}}{4}}} = 0.0223 \text{ M.} \]

Now Ca (OH)\(_2\) + NaOH are mixed

\[ \therefore \quad \text{Solution has Ca}^{2+} \text{ and OH}^- \text{ out of which some Ca}^{2+} \text{ are precipitated} \]

On mixing,

\[ [\text{Ca}^{2+}] = \frac{0.0223 \times 500}{1000} = 0.01115 = 111.5 \times 10^{-4} \text{ M} \]

\[ [\text{OH}^-] = \frac{0.0223 \times 2 \times 500}{1000} + \frac{500 \times 0.4}{1000} = 0.2223 \text{ M} \]

\[ [\text{from Ca(OH)}_2] [\text{from NaOH}] \]

\[ [\text{Ca}^{2+}]_\text{left} [0.2223]^2 = 4.42 \times 10^{-5} \]

\[ [\text{Ca}^{2+}]_\text{left} = \frac{4.42 \times 10^{-5}}{[0.2223]^2} = 8.94 \times 10^{-1} \text{ mol litre}^{-1} \]

\[ \therefore \quad \text{Mole of Ca(OH)}_2 \text{ precipitated} = \text{Mole of [Ca}^{2+}] \text{ precipitated} \]

\[ = 111.5 \times 10^{-4} - 8.94 \times 10^{-4} = 102.46 \times 10^{-4} \]

\[ \therefore \quad \text{Wt. of Ca(OH)}_2 \text{ precipitated from Ca(OH)}_2 \text{ solution} \]

\[ = 102.46 \times 10^{-4} \times 74 = 7582.04 \times 10^{-4} \text{ g} = 759 \text{ mg} \]

(b) For \[ \text{CaSO}_4 \xrightleftharpoons{} \text{Ca}^{2+} + \text{SO}_4^{2-} \]

\[ [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = K_{\text{sp}} \]

Let \[ [\text{SO}_4^{2-}] = a, \text{just sufficient to precipitate CaSO}_4 \text{ from a solution having [Ca}^{2+}] = 0.005 \text{ M} \]

Then,

\[ [0.005][a] = 2.4 \times 10^{-5} \]

\[ \therefore \quad a = \frac{2.4 \times 10^{-5}}{0.005} = 4.8 \times 10^{-3} \text{ mol litre}^{-1} \]

(c). The minimum [OH\(^-\)] at which there will be no precipitation of Mg(OH)\(_2\) obtained by

\[ K_{\text{sp}} = [\text{Mg}^{2+}] [\text{OH}^-]^2 \]

\[ 6.0 \times 10^{-12} = [0.05][\text{OH}^-]^2 \]

\[ \therefore \quad [\text{OH}^-] = 1.34 \times 10^{-5} \text{ M} \]

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\(_4\)Cl and NH\(_4\)OH i.e.,

\[ \text{NH}_4\text{OH} \xrightleftharpoons{} \text{NH}_4^+ + \text{OH}^- \]

\[ \text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

For \[ \text{NH}_4\text{OH} \]

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \]

In presence of NH\(_4\)Cl; all the \[ [\text{NH}_4^+] \] are provided by NH\(_4\)Cl since common ion effect decreases dissociation of NH\(_4\)OH.

\[ \therefore \quad 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][1.34 \times 10^{-5}]}{[0.05]} \]
\[ \text{[NH}_4^+\text{]} = 0.067 \text{ M} \]

or

\[ \text{[NH}_4\text{Cl]} = 0.067 \text{ M} \]

(d). \[ \text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad \text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^- \]

\[ K_{sp} (\text{AgCl}) = \frac{x}{(x+y)} = 1 \times 10^{-10} \quad y = x \]

\[ K_{sp} (\text{AgI}) = \frac{x}{(x+y)} = 1 \times 10^{-17} \quad y = x \]

\[ x = 1.8 \times 10^6 \quad y = 1.8 \times 10^5 \]

\[ \text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad \text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^- \]

\[ x^2 = 10^{-10} \quad y = 8.5 \times 10^{-17} \]

(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. Concentration of \( \text{CaCO}_3 \) = \[ \left[ \frac{7 \times 10^{-3}}{100} \right] \] mole/lit = \( 7 \times 10^{-5} \) mole/lit

\[ K_{sp} \text{ of } \text{CaCO}_3 = 49 \times 10^{-5} \text{ mole/lit} \]

when only \([\text{Ba}^{2+}]\) is 90% precipitated then only \( \text{CaCO}_3 \) starts precipitation then if & solution contain a mole/lit of \([\text{Ca}^{2+}] \) & \([\text{Ba}^{2+}] \)

\[ [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 49 \times 10^{-10} \]

\[ [\text{CO}_3^{2-}] = \left[ \frac{49 \times 10^{-10}}{a} \right] \]

Now for \( \text{BaCO}_3 \)

\[ K_{sp} = [\text{Ba}^{2+}] [\text{CO}_3^{2-}] = \frac{a \times 10}{100} \times \frac{49 \times 10^{-10}}{a} = 4.9 \times 10^{-10} \]

49. \[ \text{Al(OH)}_3 (s) \rightleftharpoons \text{Al}^{3+} + 3 \text{OH}^- \quad K_{sp} = 5 \times 10^{-33} \]

\[ [\text{Al(OH)}_4]^- \rightleftharpoons \text{Al}^{3+} + 4 \text{OH}^- \quad K_d = 1 \times 10^{-34} \]

\[ \text{Al(OH)}_3 (s) + \text{OH}^- \rightleftharpoons [\text{Al(OH)}_4]^- , K_t = \frac{K_{sp}}{K_d} \]

\[ 1 \times 10^{-3} \quad 0 \]

\[ 0 \quad 1 \times 10^{-3} \]

\[ K_t = \frac{[\text{Al(OH)}_4]^-}{[\text{OH}^-]} = \frac{5 \times 10^{-33}}{1 \times 10^{-34}} = 50 \quad [\text{OH}^-] = \frac{1 \times 10^{-3}}{50} = 2 \times 10^{-5} \]

\[ \text{pOH} = 5 - \log 2 = 4.7 \quad \Rightarrow \quad \text{pH} = 14 - 4.7 = 9.3 \quad \Rightarrow \quad \text{pH} = 9.3 \]

(b) \[ \text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3 \text{OH}^- \]

\[ 5 \times 10^{-3} \]

\[ [\text{Al}^{3+}] [\text{OH}^-]^3 = K_{sp} \quad \Rightarrow \quad [\text{OH}^-]^3 = \frac{5 \times 10^{-33}}{5 \times 10^{-3}} \]

\[ [\text{OH}^-]^3 = 1 \times 10^{-30} \quad \Rightarrow \quad [\text{OH}^-] = 10^{-10} \quad \Rightarrow \quad \text{pOH} = 10 \quad \Rightarrow \quad \text{pH} = 4 \]

50. \[ \text{Cu}^{2+} + 4 \text{NH}_3 (\lambda) \rightleftharpoons [\text{Cu(NH}_3)_4]^{2+} ; \quad K_f = 5.6 \times 10^{11} \]

Initial mole 0.005 0.5

0 = 0.2

\[ K_f \text{ is large and thus all the Cu}^{2+} \text{ will give } [\text{Cu(NH}_3)_4]^{2+} \]

Let \( \text{Cu}^{2+} \) left is \( a \), then

\[ [\text{Cu(NH}_3)_4]^{2+} = 0.005 \text{ mole} = \frac{0.005}{0.5} \text{ M} \quad (0.005 >> a) \]
\[ [\text{Cu}^{2+}] = \frac{a}{0.5} \text{ M} \quad \text{(Let)} \]

\[
[\text{NH}_3] = 0.2 - 4 \times 0.005 + 2a
= 0.2 - 0.02 + 2a
\quad \text{(0.18 >> 2a)}
\]
\[
= 0.18 \text{ mole} = \frac{0.18}{0.5} \text{ M}
\]

\[
\therefore \quad K_f = 5.6 \times 10^{11} = \frac{[\text{Cu(NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{0.005}{0.5} \times \left( \frac{0.18}{0.5} \right)^4
\]

\[
\therefore \quad [\text{Cu}^{2+}] = 1.06 \times 10^{-12} \text{ M}
\]

51. 
\[
\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+}(aq.) + 2\text{OH}^-(aq.) \quad K_{sp} = 1.2 \times 10^{-17} \quad \text{...... (i)}
\]
\[
\text{Zn}^{2+} + 4\text{OH}^- \rightleftharpoons [\text{Zn(OH)}_4]^{2-} \quad K_f = 10^{16} \quad \text{...... (ii)}
\]
\[
2 \times \text{[eq.(i) & eq.(ii)]}
\]
\[
2\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+} + [\text{Zn(OH)}_4]^{2-} \quad K' = (K_{sp})^2 \quad K_f \Rightarrow \quad K' = 1.44 \times 10^{-18}
\]
\[
2\text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+} + [\text{Zn(OH)}_2]^{2-} \quad K' = 1.44 \times 10^{-16}
\]
\[
\left( \frac{s}{2} \right) \left( \frac{s}{2} \right) = 1.44 \times 10^{-18}
\]
\[
\left( \frac{s^2}{4} \right) = 1.44 \times 10^{-18}
\]
\[
\text{But} \quad K_{sp} [\text{Zn(OH)}_2] = [\text{Zn}^{2+}] [\text{OH}^-]^2 = 1.2 \times 10^{-17}
\]
\[
\Rightarrow \quad (1.2 \times 10^{-9}) [\text{OH}^-]^2 = 1.2 \times 10^{-17}
\]
\[
[\text{OH}^-] = 10^{-8} \text{ M}
\]
EXERCISE # 1

PART - I

A-2. \[ \text{In } S_2\text{Cl}_2 \]
\[ 2 \times 35.5 \text{ g } \text{Cl} = 2 \times 32 \text{ g } \text{S} \]
\[ \therefore 35.5 \text{ g } \text{Cl} = 32 \text{ g } \text{S} \]
\[ \therefore \text{Equivalent mass of } \text{S in } S_2\text{Cl}_2 \text{ is 32.} \]

A-11. Moles of pure NaOH required = \[ \frac{N \times V_1}{V.f} = \frac{0.5 \times 70}{1} = 35 \]
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_1 = 1/2 x 1
\[ \text{eq. } \times \text{ eq. mass } = \text{mass (g)} \]
\[ \frac{1}{2} \times 36.5 = 18.25 \text{ (g)} \]
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. \[ \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_4 \]
the total change in oxidation number = \[ 4 \times 2 = 8 \]
\[ \because \quad E_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{\text{mol. wt.}}{V.f} = \frac{M}{8} \]

C-3. Eq. of \[ \text{Na}_2\text{CO}_3 \] = Eq. of \[ \text{H}_2\text{SO}_4 \]
\[ \frac{1.06}{100} \times 2 = \frac{25}{1000} \times N \]
\[ N = 0.8 \text{ N} \]

C-4. \[ \text{H}_2\text{C}_2\text{O}_4 \quad \text{NaOH} \]
\[ M = \frac{63 \times 1000}{126 \times 100} \quad M = \frac{40 \times 1000}{40 \times 100} \]
\[ M = 5 \quad M = 10 \]
\[ N = 10 \quad N = 10 \]
\[ V = 125 \text{ mL} \quad V = 125 \text{ mL} \]
\[ N_1V_1 = 1250 \text{ milli equivalent} \quad N_2V_2 = 1250 \text{ milli equivalent} \]
so, resulting solution will be neutral.

C-9. \[ \text{eq}_{\text{HNO}_3} = \text{eq}_{\text{NaOH}} \]
\[ \frac{18.9}{63} \times 1 \times V_1 = \frac{3.2}{40} \times 1 \times V_2 \]
\[ \frac{V_1}{V_2} = \frac{4}{15} \]

C-10. \[ \text{eq}_{\text{acid}} = \text{eq}_{\text{base}} \ (V.F = 1 \text{ for both}) \]
\[ \text{CHCl}_2\text{COOH} + \text{NH}_3 \rightarrow \text{CHCl}_2\text{COONH}_4 \]
From reaction, m.moles of \[ \text{NH}_3 \] = m.moles of dichloroacetic acid = 100
\[
\text{Moles of NH}_3 = \frac{100}{1000} = 0.1
\]

**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.

\[\therefore \text{New oxidation number of A} = -n + 3 = 3 - n.\]

**D-7.**  \[K_2Cr_2O_7 + Sn^{2+} \rightarrow Sn^{4+} + Cr^{3+}\]

\[Sn^{4+} + Fe^{2+} \rightarrow Sn^{2+} + Fe^{3+}\]

Milli equivalent of \(K_2Cr_2O_7\) in 10 mL solution = \[\frac{4.9}{(294/6) \times 0.1} \times 10 = 10\]

so, milli mole of \(Fe^{3+} = \frac{10}{1} = 10\) (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 \(Cr^{2+}\) = \[\frac{0.1}{2}\] moles of Zn

\[(\text{v.f. of Zn} = 2 & \text{v.f. of Cr}^{3+} = 1)\]

\[= \frac{6.54}{2} \text{ g} = 3.27 \text{ g}\]

(C) \(CrO_4^{2-} \rightarrow Cr_2O_7^{2-}\)

in both ions, chromium is in +6 oxidation state.

(D) Given reaction is correct.

**D-11.**  \[MnO_4^- + 5e^- + 8 H^+ \rightarrow Mn^{2+} + 4 H_2O\]

\[\Rightarrow 1 \text{ mole of MnO}_4^- \text{ accepts 5 mole of } e^-\]

\[\Rightarrow 0.2 \text{ mole of MnO}_4^- \text{ accepts 1 mole of } e^-\]

\[\Rightarrow 0.6 \text{ mole of MnO}_4^- \text{ accepts 3 mole of } e^-\]

\[\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-\]

\[\Rightarrow 1 \text{ mole of Fe}^{2+} \text{ will liberate 1 mole of } e^-\]

\[\text{Cr}_2O_7^{2-} + 6e^- + 14 H^+ \rightarrow 2 \text{Cr}^{3+} + 7 H_2O\]

\[\Rightarrow 1 \text{ mole of Cr}_2O_7^{2-} \text{ will accept 6 moles of } e^-\]

\[\Rightarrow 1 \text{ mole of FeC}_2O_4 \rightarrow \text{Fe}^{3+} + \text{CO}_2 + 3 e^-\]

\[\Rightarrow 1 \text{ moles of ferrous oxalate gives 3 moles of } e^-\]

\[\Rightarrow 0.2 \text{ moles of KMnO}_4 = 1/5 \text{ moles of KMnO}_4 \text{ oxidises 1 mole of } Fe^{2+} \text{ ion. (Tallies with statement A)}\]

\[0.6 \text{ moles of KMnO}_4 = 3/5 \text{ moles of KMnO}_4 \text{ will oxidise 1 mole of ferrous oxalate (Tallies with statement C)}\]

1 mole of \(K_2Cr_2O_7\), will oxidise 2 moles of ferrous oxalate. (Tallies with statement D)

Hence, (A), (C), (D) are correct while (B) is incorrect.

**D-12.**  \[5As_2S_3 + 28KMnO_4 + H^+ \rightarrow 10H_2AsO_4 + 28Mn^{2+} + SO_4^{2-}\]

m.moles of \(KMnO_4 = 50 \times 0.1 = 5\)

\[28 \text{ m.moles of } KMnO_4 \rightarrow 5 \text{ m.moles of As}_2S_3\]

\[\therefore 1 \text{ m.mole of } KMnO_4 \rightarrow 5/28 \text{ m.moles of } As_2S_3\]

\[\therefore 5 \text{ m.mole of } KMnO_4 \rightarrow \frac{5 \times 5}{28} \text{ m.moles of } As_2S_3\]

\[\text{Mass of } As_2S_3 = x = 246 \times \frac{5 \times 5}{28} \times 10^{-3} = 0.22 \text{ g}\]

**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.

\[\text{CaOCl}_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2\]

Max. % of available of \(Cl_2 = \frac{71}{127} \times 100 = 55.9\%\).
E-3. The weight % of available Cl₂ from the given sample of bleaching powder on reaction with dil acids or CO₂ is called available chlorine.

\[
\text{CaOCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2
\]

\[
\% \text{ of available Cl}_2 = \frac{3.55 \times 10 \times 0.125}{3.55 \times 25} \times 100 = 5\%.
\]

E-5. Excess of Mohr’s salt = \(30 \times 0.1 \times 5\) meq.

Mohr’s salt consumed = \([(35 \times 1.0 \times 1) – 15]\) meq

\[
\text{Now Cl}_2 + 2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{Cl}^{-} \quad \text{(balanced equation)}
\]

So moles of Cl₂ = \(\frac{1}{2}\) x moles of Fe²⁺ = \(\frac{1}{2}\) eq. of Fe²⁺ = \(\frac{1}{2}\) x 20 m moles = 10 mmoles

\[
= 10 \times 10^{-3} \times 71 \text{ gm} = 0.71 \text{ gm}
\]

So, required % = \(\frac{0.71 \times 100}{10} \times 100 \) = 7.1%

E-6. 

\[
\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{CO}_2 \quad \text{......(i)}
\]

\[
t = 0 \quad 0.1 \quad - \quad -
\]

\[
t = t \quad 0 \quad x \quad (0.1 – x)
\]

\[
5\text{CO} + \text{I}_2\text{O}_5 \rightarrow 5\text{CO}_2 + \text{I}_2 \quad \text{......(ii)}
\]

\[
t = 0 \quad x \quad -
\]

\[
t = t \quad 0 \quad x/5
\]

\[
\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}
\]

\[
.: \quad \text{moles of I}_2 \text{ liberated} = \frac{1}{2} \times \text{moles of hypo consumed} = \frac{1}{2} \times 120 \times 10^{-3} \times 0.1 = 0.1 \times 10^{-4}
\]

So, x = 5 × 60 × 10⁻⁴ = 0.03 moles (from reaction (ii) : 5 × mole of I₂ = mole of CO)

So, % of C forming CO = \(\frac{0.03 \times 12}{1.2} \times 100 = 30\%\)

E-7. From given reactions :

\[
\text{m.moles of hypo} = \text{m.moles of iodine} \times 2 = \text{m.moles of Cu}^{2+} \text{ ions} = 24.5 \times 0.1 \text{ m.moles}
\]

so, mass of copper = \(24.5 \times 0.1 \times 10^{-3} \times 63.5 \text{ g}\)

so, % of copper = \(\frac{24.5 \times 0.1 \times 10^{-3} \times 63.5}{0.305} \times 100 = 51\%\)

E-8. 2 moles of Cu²⁺ = 1 mole of I₂

\[
= 2 \times \text{moles of hypo}.
\]

so moles of hypo used = \(20 \times 10^{-3} \times 0.1 = 2 \times \text{moles of copper hence}\)

% of copper = \(\frac{2 \times 10^{-3} \times 63.5}{0.2} \times 10\% = 63.5\%\)

E-9. \(\text{Ni(CO)}_4 \rightarrow \text{Ni} + 4\text{CO}\)

\[
\text{5CO} + \text{I}_2\text{O}_5 \rightarrow \text{I}_2 + 5\text{CO}_2
\]

\[
\text{2S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow 2\text{I}^{+} + \text{S}_4\text{O}_6^{2-}
\]

so moles of I₂ produced = 4 moles

so moles of hypo used = 8 moles = (4 M) (2 litres).

F-3. \(\text{BrO}_3^{-} + 6\text{I}^{-} \rightarrow 3\text{I}_2 + \text{Br}^{-}\)

\[
\text{moles of I}_2 = 3 \times \text{moles of KBrO}_3
\]

\[
\text{moles of I}_2 = 0.02 \times 3 = 0.06
\]

\[
\text{Eq of I}_2 = \text{Eq of Hypo}
\]

\[
0.06 \times 2 = 0.1 \times V
\]

\[
V = 1.2 \text{ L} = 1200 \text{ mL}.
\]
F-4. 
\[ \text{Eq. of } \text{Hg}_5(\text{IO}_6)_2 = \text{Eq. of } I_2 = \text{Eq. of } \text{Na}_2\text{S}_2\text{O}_3 \]
\[ \therefore \text{moles of } \text{Hg}_5(\text{IO}_6)_2 \times 16 = 0.004 \times 1 \]
\[ \therefore \text{moles of } \text{Hg}_5(\text{IO}_6)_2 = 2.5 \times 10^{-4}. \]

F-5. 
\[ 6e^- + 10H^+ + V_2O_5 \rightarrow 2V^{2+} + 5 H_2O \]
\[ (Zn \rightarrow Zn^{2+} + 2e^-) \times 3 \]
\[ V_2O_5 + 3 Zn + 10 H^+ \rightarrow 3 Zn^{2+} + 2V^{2+} + 5H_2O \]

Now, 
\[ H_2O + V^{2+} \rightarrow VO^{2+} + 2H^+ + 2e^- \]
\[ 2e^- + I_2 \rightarrow 2I^- \]
\[ V^{2+} + I^- + H_2O \rightarrow 2I^- + VO^{2+} + 2H^+ \]
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 \( I_2 \)

F-7. 
\[ \text{m.eq of (NH}_4)\text{SO}_4 + \text{m.eq of } H_2SO_4 = \text{m.eq of } NaOH \]
\[ (\text{m.moles} \times 2) + (0.1 \times 10 \times \frac{250}{25}) = 0.2 \times 100 \]
\[ \therefore \text{m.mole of (NH}_4)\text{SO}_4 = 5 \]
\[ \text{wt. of (NH}_4)\text{SO}_4 = \frac{5}{1000} \times 132 = 0.66 \text{ g} \]
\[ \therefore \text{% of (NH}_4)\text{SO}_4 = \frac{0.66}{0.7} \times 100 = 94.28 \% \approx 94.3 \% \]

F-8. 
\[ \text{KOH} + \text{Na}_2\text{CO}_3 \]
\[ \text{a m.moles} \quad \text{b m.moles} \]
\[ \text{m.eq of KOH} + \text{m.eq of } \text{Na}_2\text{CO}_3 \text{ (v.f. = 1)} = \text{m.eq of } HCl \text{ (in presence of phenolphthalein)} \]
\[ a \times 1 + b \times 1 = 15 \times \frac{1}{20} \]
\[ \therefore a + b = 0.75 \quad \text{(i)} \] 
\[ \text{(in presence of phenolphthalein)} \]
\[ \text{m.eq of KOH} + \text{m.eq of } \text{Na}_2\text{CO}_3 \text{ (v.f. = 2)} = \text{m.eq of } HCl \text{ (in presence of methyl orange)} \]
\[ 1 \times a + 2 \times b = 25 \times \frac{1}{20} \]
\[ \therefore a + 2 \times b = 1.25 \quad \text{(ii)} \] 
\[ \text{(in presence of methyl orange)} \]
by solving (i) & (ii), \( a = 0.25 \) m.moles.
\[ \therefore \text{mass of KOH} = \frac{0.25}{1000} \times 56 = 0.014 \text{ g} \]

F-9. 
\[ \text{meq of } H_2SO_4 = \text{meq of } NaOH + \text{meq of } \text{Na}_2\text{CO}_3 \]
\[ N \times 25 = 0.5 \times 50 + \frac{0.265}{106/2} \times 10^3 \quad \text{or} \quad N = 1.2 \]

In original \( H_2SO_4 \) solution
\[ N_1V_1 = N_2V_2 \quad \text{or} \quad N_1 \times 10 = 1.2 \times 100 \quad \text{or} \quad N_1 = 12N \]

**PART - II**

2. 
(A) Eq of \( Sn^{2+} \) = Moles \times v.f. = 3.5 \times 2 = 7.
Eq of \( MnO_{4}^- \) = Moles \times 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 \( H_2C_2O_4 \) = Moles \times v.f. = 8.4 \times 2 = 16.8.
Eq of \( MnO_{4}^- \) = Moles \times v.f. = 3.6 \times 5 = 18.
Since \( H_2C_2O_4 \) (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 $\text{S}_2\text{O}_3^{2-}$: Moles × v.f. = $7.2 \times 1 = 7.2$.
Eq of $\text{I}_2$: Moles × v.f. = $3.6 \times 2 = 7.2$.
Since $\text{S}_2\text{O}_3^{2-}$ (RA) and $\text{I}_2$ (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 $\text{Fe}^{2+}$: Moles × v.f. = $9.2 \times 1 = 9.2$.
Eq of $\text{Cr}_2\text{O}_7^{2-}$: Moles × v.f. = $1.6 \times 6 = 9.6$.
Since $\text{Fe}^{2+}$ (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).

3. $10\, \text{e}^- + 2\text{MnO}_4^- \rightarrow 2\text{Mn}^{2+}; \text{v.f.} = 10$
   .
   
   Eq. mass of $\text{Ba(MnO}_4)_2 = \frac{M}{10}$

4. $\text{Fe}_{0.9}\text{O} + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{Fe}^{2+} + \text{Cr}^{3+}$
   
   n factor of $\text{Fe}_{0.9}\text{O} = 0.9\left(3 - \frac{2}{0.9}\right) = 0.7$
   
   $\therefore$ Eq mass = $\frac{M}{0.7} = \frac{10M}{7}$

5. n factor is 2
   
   Eq weight = $\frac{\frac{M}{2}}{2} = \frac{128}{2} = 64$.

**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 $\text{Cu}_2\text{S}$ is 2 + 6 = 8
   
   .
   
   Eq. wt. of $\text{Cu}_2\text{S} = \frac{M_2}{8}$
   
   v.f. of CuS is 6
   
   .
   
   Eq. wt. of CuS = $\frac{M_1}{6}$
   
   v.f. of $\text{KMnO}_4$ is 5
   
   .
   
   Eq. wt. of $\text{KMnO}_4 = \frac{M_3}{5}$

8. Metal sulphate (aq) $\overset{(0.98 \text{ g})}{\longrightarrow} + \text{BaCl}_2$ $\overset{(0.95 \text{ g})}{\longrightarrow} \text{BaSO}_4$
   
   Now, 233.34 g $\text{BaSO}_4 = 96 \text{ g} \text{ SO}_4^{2-}$
   
   $\therefore$ 0.95 g $\text{BaSO}_4 = \frac{96}{233.34} \times 0.95$ or 0.39 g $\text{SO}_4^{2-}$
   
   Mass of metal in metal sulphate = 0.98 – 0.39 = 0.59 g
   
   Now, $\text{eq}_{\text{metal}} = \text{eq}_{\text{SO}_4^{2-}}$
   
   $0.59 \text{ \, 0.39}$
   
   $E_{\text{metal}} = \frac{96}{2}$
   
   $E_{\text{metal}} = 72.61$
10. Final No. of eq. of H$_2$SO$_4$ = $0.2 \times 30 \times 10^{-3}$
    = $6 \times 10^{-3}$
Initial No. of eq. of H$_2$SO$_4$ = $1 \times 30 \times 10^{-3}$
    = $30 \times 10^{-3}$
No. of reacted Eq. of H$_2$SO$_4$ = $24 \times 10^{-3}$
So. No. of equivalent of NH$_3$ = $24 \times 10^{-3}$
No. of Mole of NH$_3$ = $24 \times 10^{-3}$ (v.f. = 1)
Volume at S.T.P = $24 \times 22400 \times 10^{-3}$
    = $24 \times 22.4$ mL
    = 537.6 mL

15. Fe$^{2+}$ + Cr$_2$O$_7^{2-}$
            \[ \text{v.f.} = 6 \]
            \[ \text{v.f.} = 1 \]
Fe$^{3+}$ + Cr$^{3+}$

No. of m.eq. of Fe$^{2+}$ = No. of m.eq. of Cr$_2$O$_7^{2-}$
\[ [M \times 25] \times 1 = [0.01 \times 50] \times 6 \]
M = \[ \frac{0.01 \times 50 \times 6}{25} \]
M = 0.02 \times 6 = 0.12

18. Let mole of FeSO$_4$ = x
Now, KMnO$_4$ oxidises only FeSO$_4$
equivalent of FeSO$_4$ = equivalent of KMnO$_4$
\[ x \times 1 = \frac{100}{1000} \times 2 \times 5 \]
\[ \Rightarrow \quad x = 1 \]
so, mole fraction of FeSO$_4$ = \[ \frac{n_{\text{FeSO}_4}}{n_{\text{mixture}}} = \frac{1}{3} \]

20. Excess of Mohr’s salt = $30 \times 0.1 \times 5$ meq. = 15 meq
Mohr’s salt consumed = $(35 \times 1 \times 1) - 15$ meq = 20 meq.
Now \[ \begin{align*}
\text{Cl}_2 + 2\text{Fe}^{2+} & \longrightarrow 2\text{Fe}^{3+} + 2\text{Cl}^- \quad \text{(balanced equation)} \\
\text{So moles of Cl}_2 & = \frac{1}{2} \times \text{moles of Fe}^{2+} = \frac{1}{2} \times 20 \times 10^{-3} \text{ moles} = 10 \times 10^{-3} \text{ moles} \\
\text{Mass of Cl}_2 & = 10 \times 10^{-3} \times 71 = 0.71 \text{ g} \\
\text{So, required % of available Cl}_2 & = \frac{0.71}{10} \times 100 = 7.1\% 
\end{align*} \]

22. Let moles of As$_2$O$_3$ and As$_2$O$_5$ are x and y respectively. In first step, only As$_2$O$_3$ react with I$_2$.
So,
\[ \text{eq. of As}_2\text{O}_3 = \text{eq. of I}_2 \]
\[ x \times 4 = 20 \times 0.05 \times 10^{-3} \]
\[ x = 0.25 \times 10^{-3} \]
wt. of As$_2$O$_3$ = $x \times $ Mol. mass
\[ = 0.25 \times 10^{-3} \times 198 \]
wt. of As$_2$O$_5$ = 0.0495 g
In second step, As$_2$O$_5$ react with I$^-$
So, total eq. of As$_2$O$_5$ = eq. of I$^-$ reacted = eq. of I$_2$ released = eq. of hypo used

Total moles of As$_2$O$_5$ x v.f. = \[ \frac{\text{wt. of Hypo} \times \text{v.f.}}{\text{Mol. Mass}} \]
(Total moles of As$_2$O$_5$ = moles of As$_2$O$_5$ formed in 1st stage + moles of As$_2$O$_5$ 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}
mass of $\text{As}_2\text{O}_5 = y \times \text{Mol. mass}$

$$= 0.875 \times 10^{-3} \times 230$$

$$= 0.20125 \text{ g}$$

Total mass of mixture $= 0.20125 + 0.0495 = 0.25075 \text{ g Ans.}$

23.

$$2\text{I}^- + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{OH}^- + \text{I}_2 + \text{O}_4$$

$I_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$

From the above reaction:

$2\text{Na}_2\text{S}_2\text{O}_3 = \text{I}_2 = \text{O}_3$

moles of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{40 \times 0.1}{1000} = 0.004$

moles of $\text{I}_2 = \text{moles of } \text{O}_3 = 0.002$

volume of $\text{O}_3$ at STP $= 0.002 \times 22.4 = 0.0448 \text{ L}$ (present in 1 L mixture)

Percentage of $\text{O}_3 = \frac{0.0448 \times 100}{1} = 4.48\% \text{ (by volume)}$

24.

$\text{MnO}_2 \xrightarrow{\text{HCl}} \text{Cl}_2 \xrightarrow{\text{KI}} \text{I}_2 \xrightarrow{\text{Na}_2\text{S}_2\text{O}_3} \text{Na} + \text{Na}_2\text{S}_4\text{O}_6$

Redox changes are:

$2\text{e}^- + \text{I}_2 \xrightarrow{\text{Na}_2\text{S}_2\text{O}_3} 2\text{I}^-$

$2\text{S}^{2-} \xrightarrow{\text{S}_4\text{O}_6^2^- + 2\text{e}}$

$2\text{e} + \text{Mn}^{4+} \xrightarrow{\text{Mn}^{2+}}$

The reactions suggest that:

$m.\text{eq. of } \text{MnO}_2 = m.\text{eq. of } \text{Cl}_2 \text{formed} = m.\text{eq. of } \text{I}_2 \text{liberated} = m.\text{eq. of } \text{Na}_2\text{S}_2\text{O}_3$ used

$= \frac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30 \quad \text{[v.f.: MnO}_2 = 2, \text{Na}_2\text{S}_2\text{O}_3 = 1]}$

or $w = \frac{0.1 \times 1 \times 30 \times M}{2000} = \frac{0.1 \times 1 \times 30 \times 87}{2000}$

$w_{\text{MnO}_2} = 0.1305 \text{ g} \quad \therefore \text{Purity of } \text{MnO}_2 \text{ sample} = \frac{0.1305}{0.5} \times 100 = 26.1\%$

25. At phenolphthalein end point

$\text{eq. of } \text{Na}_2\text{CO}_3 + \text{eq. of } \text{NaOH} = \text{eq. of HCl used}$

Let $x$ mole of $\text{Na}_2\text{CO}_3$ and $y$ mole of $\text{NaOH}$ present in 25 mL solution

$x \times 1 + y \times 1 = 19.5 \times 0.995 \times 10^{-3}$

$x + y = 19.4 \times 10^{-3}$ \quad \text{...(i)} \quad \text{(The v.f. of } \text{Na}_2\text{CO}_3 \text{ is 1 when phenolphthalein is used)}

At Methyl orange (MeOH) end point,

$\text{eq. of } \text{Na}_2\text{CO}_3 + \text{eq. of } \text{NaOH} = \text{eq. of HCl used}$

$x \times 2 + y \times 1 = 25 \times 0.995 \times 10^{-3}$

$2x + y = 24.875 \times 10^{-3}$ \quad \text{...(ii)} \quad \text{(The v.f. of } \text{Na}_2\text{CO}_3 \text{ is 2 when methyl orange (MeOH) is used)}

On solving eq. (1) and (2),

$x = 5.475 \times 10^{-3}$ and $y = 13.925 \times 10^{-3}$

or $\text{wt. of } \text{Na}_2\text{CO}_3$ in 25 mL $= 5.475 \times 10^{-3} \times 106$

$\text{wt. of } \text{Na}_2\text{CO}_3$ in 1 litre $= \frac{5.475 \times 10^{-3} \times 106}{25} \times 1000 = 23.2 \text{ g Ans.}$

$\text{wt. of } \text{NaOH}$ in 25 mL solution $= 13.925 \times 10^{-3} \times 40$

$\text{wt. of } \text{NaOH}$ in 1 litre $= \frac{13.925 \times 10^{-3} \times 40}{25} \times 1000 = 22.28 \text{ g Ans.}$

26. $\text{CH}_3(\text{CH}_2)_n\text{COOH} + \text{O}_2 \longrightarrow (n + 2)\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

excess

moles of $\text{CH}_3(\text{CH}_2)_n\text{COOH} = \frac{\text{moles of } \text{CO}_2}{(n + 2)}$ \quad \text{...... (1)}

When $\text{CO}_2(\text{g})$ is passed into excess of NaOH solution, then $\text{Na}_2\text{CO}_3$ will form according to reaction:

$2\text{NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$

$\therefore \text{moles of } \text{NaOH reacted} = 2 \times \text{moles of } \text{Na}_2\text{CO}_3$ \quad \text{...... (2)}

Now solution contain remaining NaOH and $\text{Na}_2\text{CO}_3$ formed.

Let moles of NaOH and $\text{Na}_2\text{CO}_3$ are $x$ and $y$ respectively and solution divided into two equal parts.
Part I: At pH end point,
Eq. of NaOH + eq. of Na$_2$CO$_3$ = Eq. of HCl used
\[ \frac{x}{2} \times 1 + \frac{y}{2} \times 1 = 50 \times 1 \times 10^{-3} \]
\[ x + y = 0.1 \] \hspace{1cm} \text{(1)}

Part II: At MeOH end point,
Eq. of NaOH + eq. of Na$_2$CO$_3$ = Eq. of HCl used
\[ \frac{x}{2} \times 1 + \frac{y}{2} \times 2 = 80 \times 1 \times 10^{-3} \]
\[ x + 2y = 0.16 \] \hspace{1cm} \text{(2)}

On solving equation (1) and (2),
\[ y = 0.06 \]
\[ x = 0.04 \]

Since moles of CO$_2$ = moles of Na$_2$CO$_3$ = 0.06
\[ \therefore \text{From equation (1),} \]
\[ \frac{1.16}{48 + 14n} = \frac{0.06}{n + 2} \]

On solving, we get \( n = 4 \) \text{ Ans.}

Amount of NaOH remaining = 0.04 mole
Amount of NaOH reacted = moles of Na$_2$CO$_3$ \times 2
\[ = 0.06 \times 2 = 0.12 \]

Total moles of NaOH taken = 0.04 + 0.12 = 0.16
wt. of NaOH taken = 0.16 \times 40 = 6.4 g.

28. millimoles of K$_2$Cr$_2$O$_7$ = 25 \times 0.002 = 0.050
meq or millimoles of Fe$^{3+}$ present in water sample = 25 \times 0.002 \times 6 - 7.5 \times 0.01 = 0.225
\[ \therefore \text{Mass of Fe}^{3+} \text{ in water sample} = 0.225 \times 56 \times 10^{-3} = 12.6 \times 10^{-3} \text{ grams} \]
assuming 100 mL water = 100 gram water
\[ \text{ppm} = \frac{12.6 \times 10^{-3}}{100} \times 10^6 = 126 \text{ ppm} \]

29. Each mole of K$_2$Cr$_2$O$_7$ releases 6 moles of electrons which is used by Fe for its reduction so assuming the sample contains x grams of CuFeS$_2$ originally.
\[ \text{(CuFeS}_2^{+3} \rightarrow \text{Fe}^{2+} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7^{2+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+}) \]
\[ 40 \times 0.01 \times 6 = (x / 183.5) \times 1000 \]
\[ x = 0.4404 \text{ g} \]

% of CuFeS$_2$ in sample = (0.4404/0.5) \times 100 = 88.08%

30. Let m.moles of Fe$_2$(SO$_4$)$_3$ and FeC$_2$O$_4$ are x and y. In first reaction, only FeC$_2$O$_4$ react with KMnO$_4$ as :
\[ \text{FeC}_2\text{O}_4 + \text{KMnO}_4 \rightarrow \text{Fe}^{3+} + \text{CO}_2 + \text{Mn}^{2+} \]
\[ \text{v.f.} = 3 \hspace{1cm} \text{v.f.} = 5 \]
\[ \text{m.eq. of FeC}_2\text{O}_4 = \text{m. eq. of KMnO}_4 \]
\[ y \times 3 = 40 \times \frac{1}{16} \]
\[ y = \frac{40}{48} \] \hspace{1cm} \text{(1)}

In II$^\text{nd}$ reaction, all Fe$^{3+}$ is convert into Fe$^{2+}$ :
\[ \text{Fe}^{3+} \text{ from FeC}_2\text{O}_4 + \text{Fe}^{3+} \text{ from Fe}_2\text{(SO}_4)_3 \rightarrow \text{Zn}/\text{H}^+ \rightarrow \text{Fe}^{2+} \]
\[ t = 0 \hspace{1cm} y \hspace{1cm} 2x \]
\[ t = t \hspace{1cm} 0 \hspace{1cm} 0 \hspace{1cm} (y + 2x) \]

In III$^\text{rd}$ reaction all Fe$^{2+}$ again react with KMnO$_4$ as :
\[ \text{Fe}^{2+} + \text{KMnO}_4 \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+} \]
\[ \text{v.f.} = 1 \hspace{1cm} \text{v.f.} = 5 \]
\[ \text{m.eq. of Fe}^{2+} = \text{m.eq. of KMnO}_4 \]
\[ y + 2x = 60 \times \frac{1}{16} \]
Putting the value of \( y \) from equation 1st,

\[
2x = \frac{60}{16} - \frac{40}{48}
\]

\[
2x = \frac{140}{48}
\]

\[
x = \frac{70}{48} \quad \ldots \ldots \quad (2)
\]

From eq. (1) and (2),

\[
\frac{x}{y} = \frac{7}{4} \quad \text{Ans.}
\]

31. Balanced reactions are :

- \( 5\text{SeO}_3^{2-} + 2\text{BrO}_3^- + 2\text{H}^+ \longrightarrow 5\text{SeO}_4^{2-} + \text{Br}_2 + \text{H}_2\text{O} \)
- \( \text{BrO}_3^- + 3\text{AsO}_2^- + 3\text{H}_2\text{O} \longrightarrow \text{Br}^- + 3\text{AsO}_4^{3-} + 6 \text{H}^+ \)

Total millimoles of \( \text{BrO}_3^- = 20 \times 1/60 = 1/3 \)

Millimoles of \( \text{BrO}_3^- \) backtitrated = \( 5 \times 1/25 \times 1/3 = 1/15 \)

Millimoles of \( \text{SeO}_3^{2-} \) for reaction = \( 4/3 - 1/15 = 4/15 \)

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 \( \text{NaOH} \)

   \[
   \left( \frac{6.3 \times 1000}{126/2} \right) \times \frac{10}{250} = 0.1 \times V \quad \text{(in litre)}
   \]

   \[ \therefore V = 0.04 \text{ L} = 40 \text{ mL.} \]

3. \( 2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2 \)

   \( 2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 \)

   \( \text{MnO}_2 + \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{MnSO}_4 + 2\text{CO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \)

   \[ \therefore \text{meq. of MnO}_2 = \text{meq of Na}_2\text{C}_2\text{O}_4 = 10 \times 0.2 \times 2 = 4 \]

   \[ \therefore \text{millimoles of MnO}_2 = \frac{4}{2} = 2 \quad \left[ \begin{array}{c} \text{Mn}^{4+} + 2\text{e}^- \rightarrow \text{Mn}^{2+} \\
\text{Valency factor of MnO}_2 = 2 \end{array} \right] \]

   Now, \( 2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \)

   Since \( \text{MnO}_2 \) is derived from \( \text{KMnO}_4 \) and \( \text{MnSO}_4 \) both, thus it is better to proceed by mole concept

   Millimoles of \( \text{KMnO}_4 = \text{millimoles of MnO}_2 \times (2/5) = 4/5 \)

   Also, \( 5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2 \)

   \[ \therefore \text{millimoles of H}_2\text{O}_2 = \text{millimoles of KMnO}_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2 \]

   \[ \therefore \text{M}_\text{H}_2\text{O}_2 = \text{M}_\text{H}_2\text{O}_2 = 0.1 \text{ M} \]

5. Dilute nitric acid converts chromate into dichromate and \( \text{H}_2\text{O} \).

   \( 2\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{HNO}_3 \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3 + \text{H}_2\text{O} \)

6. \( \text{2MnO}_2^- + \text{I}^- + \text{H}_2\text{O} \longrightarrow 2\text{MnO}_2^- + \text{IO}_3^- + 2\text{OH}^- \)

7. \( ^6\text{Cr}_3\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow ^3\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2 \)
8. \[ CrO_2^{2-} + Fe^{2+} \rightarrow 2Cr^{3+} + Fe^{3+} + 7H_2O \]
\[ n = 6 \quad n = 1 \]
1 mole of \( CrO_2^{2-} \) 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
\[ NH_3 + HCl \rightarrow NH_4Cl \]
HCl (remaining) + NaOH \( \rightarrow NaCl + H_2O \)
\[ (1.5 \text{ m mole}) \]
Total millimole of HCl = 2
mili mole of HCl used by \( NH_3 = 2 - 1.5 = 0.5 \)
mili mole of \( NH_3 = 0.5 \)
weight of \( NH_3 = 0.5 \times 17 \text{ mg} = 8.5 \text{ mg} \)
weight of nitrogen \( = \frac{14}{17} \times 8.5 \text{ mg} = 7 \text{ mg} \)
\[ \therefore \% \text{ of Nitrogen in compound} = \frac{7}{29.5} \times 100 = 23.7 \% . \]

11. mili mole of Hypo \[ = \frac{0.25 \times 48}{2} = 6 \text{ mili mole} \]
mili mole of \( Cl_2^- \) \[ = \frac{0.25 \times 48}{2} = 6 \text{ mili mole} \]
\[ = \text{ mili mole of } Cl_2^- = \text{ mili mole of } CaOCl_2 \]
So, molarity \[ = \frac{6}{25} \text{ M} = 0.24 \text{ M} \]

12. \( CaOCl_2 = Ca(OCl)ClOCl \)
Hypochlorite ion which is anion of \( HOCl \)
Anhydride of \( HOCl = Cl_2O \).

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**SOLUTION OF ADVANCED LEVEL PROBLEM**

1. \[ 85.5 = E_{\text{metal}} + E_{\text{Cl}} \]
\[ \text{or } 85.5 = E_{\text{metal}} + 17 \]
\[ \text{or } E_{\text{metal}} = 68.5 \]

2. (a) \( E_F = \frac{31}{3} = 10.33 \)
(b) \( E_{Al} = \frac{27}{3} = 9 \)
(c) \( E_{Fe} = \frac{56}{2} = 28 \)
(d) \( E_S = \frac{32}{6} = 5.33 \)

3. 40 g, O = 60 g metal
\[ \therefore \quad 8 \text{ g, O} = 12 \text{ g metal} (E) \]

4. v.f. of \( Na_2S_2O_3 = 2 (2.5 - 2) = 1 \)
\[ \therefore \quad \text{ Eq. wt.} = M/1 \]

5. v.f. of \( KBrO_3 = 1 (5 - (- 1)) = 6 \)
\[ \therefore \quad \text{ Eq. wt.} = \frac{M}{6} \]

6. v.f. of oxalic acid = 2 (4 - 3) = 2
\[ \therefore \quad \text{ Eq. wt.} = \frac{M}{2} \]

7. \( \text{ meq } H_2SO_4 = \text{ meq } NaOH \)
\[ 0.2 \times V = 0.02 \times 20 \]
\[ V = 2 \text{ mL} \]
8. m eq. of HCl reacted with alkalline earth metal carbonate = \((25 \times 1) - (50 \times 0.1) = 20\)

\[\therefore \text{Eq. wt. of metal carbonate} = 20\]

\[\therefore \text{Eq. wt. of Metal} = \text{Eq. wt. of metal carbonate} - \text{Eq. wt. of carbonate} = 20 - \frac{60}{2} = 20\]

\[\text{At wt. of Metal} = \frac{20}{2} = 10\]

9. \(2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4\)

\(2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}\)

\[\therefore \text{m.eq of H}_2\text{SO}_4 \text{ neutralized by NH}_3 = (50 \times 1) - (24.5 \times 1) = 25.5\]

\[\therefore \text{m.moles of NH}_3 \text{ present in double sulphate} = 25.5\]

\[\therefore \text{Mass of NH}_3 \text{ present in double sulphate} = \frac{25.5 \times 1000}{5.25} = 0.4335 \text{ g}\]

\[\therefore \% \text{ of NH}_3 \text{ in double sulphate} = \frac{54335}{100} = 8.67\%\]

10. \(\text{KMnO}_4 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+}\)

\[\text{milli equivalent of KMnO}_4 = \text{milli equivalent of Fe}^{2+}\]

\[1 \times 5 \times M = 1\times \frac{140}{56}\]

\[M = \frac{140 \times 1}{56 \times 5} = 0.5\]

\(\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 = 2\text{C}_2\text{O}_4^{2-} + \text{KMnO}_4 \rightarrow \text{Mn}^{2+} + \text{CO}_2\)

\[\text{milli eq. of KMnO}_4 = \text{milli eq. of KH}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4\]

\[100 \times 5 \times 0.5 = 1 \times 2 \times 2 \times M\]

\[M = 0.0625\]

\(\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 + 3\text{NaOH} \rightarrow 3\text{H}_2\text{O} + \text{Na}_2\text{C}_2\text{O}_4 + \text{KNaC}_2\text{O}_4\)

\[\text{meq of KHC}_2\text{O}_4 \cdot \text{KHC}_2\text{O}_4 = \text{meq of NaOH}\]

\[3 \times 1 \times 0.0625 = 0.20 \times V\]

\[V = \frac{3 \times 0.0625}{0.20} = 0.9375 \text{ mL} \quad \text{or} \quad \frac{15}{16} \text{ mL}.

11. \(\text{milli eq. of FeSO}_4 \text{ in 20 mL} = \text{milli eq. of KMnO}_4\)

\[N_1 \times V_1 = N_2 \times V_2\]

\[N_1 \times 25 = \frac{1}{10} \times 20\]

\[N_1 = \frac{20}{10 \times 25} = M_1 \text{ (V.f. = 1)}\]

\[\text{Weight of FeSO}_4 \cdot 7\text{H}_2\text{O}, W = \frac{20}{10 \times 25} \times 278 = 22.24 \text{ g}\]

\[\% \text{ of FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{22.24}{25} \times 100 = 88.96\%\]

12. Redox changes are:

\(\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(in H}_2\text{SO}_4)\)

\(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad \text{(with K}_2\text{Cr}_2\text{O}_7)\)

\(6e + \text{Cr}_2\text{O}_7^{6-} \rightarrow 2\text{Cr}^{3+}\)

\[\text{m.eq. of Fe}^{2+} \text{ in 20 mL} = \text{m.eq. of K}_2\text{Cr}_2\text{O}_7 = 30 \times \frac{1}{30} = 1\]

\[\therefore \text{m.eq. of Fe}^{2+} \text{ in 100 mL} = \frac{1 \times 100}{20} = 5\]
\[ \text{m.moles of Fe}^{2+} = \frac{\text{meq}}{\text{v.f.}} = \frac{5}{1} = 5 = \text{m.moles of Fe} \]

\[ \text{Mass of pure Fe in wire} = 5 \times 10^{-3} \times 56 = 0.28 \text{ g} \]

\[ \% \text{ of Fe in wire} = \frac{0.28}{0.2828} \times 100 = 99\% \]

13. On balancing the reaction,

\[ \text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+} \]

\[ \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]

or

\[ \text{KMnO}_4 + 5\text{FeCl}_2 + 8\text{HCl} \rightarrow \text{MnCl}_2 + 5\text{FeCl}_3 + 4\text{H}_2\text{O} + \text{KCl} \]

\[ \text{moles} \quad \frac{10}{158} \quad 1.07 \quad \frac{500}{1000} \quad \times 3 = 1.5 \]

So, KMnO\(_4\) is limiting reagent.

\[ \text{mole of } \text{KMnO}_4 = \frac{1}{5} \text{ Mole of FeCl}_3 \]

\[ \text{mole of FeCl}_3 = \frac{10}{158} \times 5 = 0.316 \]

14. Let V mL of reducing agent be used for KMnO\(_4\) in different medium which act as oxidant

Acid medium, Mn\(^{7+}\) + n\(_1\) e\(^-\) \rightarrow Mn\(^{n+}\)

\[ n_1 = 7 - a \]

Neutral medium, Mn\(^{7+}\) + n\(_2\) e\(^-\) \rightarrow Mn\(^{n+}\)

\[ n_2 = 7 - b \]

Alkaline medium, Mn\(^{7+}\) + n\(_3\) e\(^-\) \rightarrow Mn\(^{n+}\)

\[ n_3 = 7 - c \]

\[ \text{meq of reducing agent} = \text{meq. of KMnO}_4 \text{ in acid} \]

\[ = \text{meq. of KMnO}_4 \text{ in neutral} \]

\[ = \text{meq. of KMnO}_4 \text{ in alkali} \]

\[ = 1 \times n_1 \times 20 = 1 \times n_2 \times 33.3 = 1 \times n_3 \times 100 \]

\[ n_1, n_2, n_3 \text{ are integers and are } \leq 7, \]

\[ n_1 = 5, n_2 = 3 \text{ and } n_3 = 1 \]

Therefore, different oxidation state of Mn are:

Acid media, Mn\(^{7+}\) + 5e\(^-\) \rightarrow Mn\(^{n+}\)

\[ a = + 2 \]

Neutral media, Mn\(^{7+}\) + 3e\(^-\) \rightarrow Mn\(^{n+}\)

\[ b = + 4 \]

Alkaline media, Mn\(^{7+}\) + e\(^-\) \rightarrow Mn\(^{n+}\)

\[ c = + 6 \]

Now, same volume of reducing agent is treated with K\(_2\)Cr\(_2\)O\(_7\) and therefore,

\[ \text{m.eq. of reducing agent} = \text{m.eq. of K}_2\text{Cr}_2\text{O}_7 \]

But, m.eq. of reducing agent = m.eq. of KMnO\(_4\) in acid

\[ \text{m.eq. of KMnO}_4 \text{ in acid} = \text{m.eq. of K}_2\text{Cr}_2\text{O}_7 \]

\[ 20 \times 5 = 1 \times 6 \times V \quad \text{(v.f. for Cr}_2\text{O}_7^{2-} = 6) \]

\[ V = \frac{100}{6} = 16.67 \text{ mL} \]

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:

\[ \text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]  (Acidic medium)

\[ \text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^- \]  (Neutral medium)

\[ \text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-} \]  (Basic medium)
15. \[ \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e \]

\[ 6e + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]

Since \( \text{Sn}^{2+} \) is oxidized by \( \text{K}_2\text{Cr}_2\text{O}_7 \),

\[ \therefore \text{m.eq. of } \text{Sn}^{2+} = \text{m.eq. of } \text{K}_2\text{Cr}_2\text{O}_7 \] used for oxidation of tin = \( N \times V_{\text{m mL}} \)

\[ = \frac{2.5}{294} \times 0.5 \times 10 = 1.02 \]

\[ \therefore N = \frac{2.5}{294 \times 0.5} \]

\[ \therefore \text{m.eq. of } \text{Sn}^{2+} = 0.0607 \text{ g} \]

\[ \therefore \% \text{Sn} = \frac{0.0607}{0.4} \times 100 = 15.17 \% \]

16. \( \text{KIO}_3 + 5\text{KI} \xrightarrow{\text{HCl}} 3\text{I}_2 \)

\[ \frac{0.214}{214} \text{ mole (excess)} \quad 3 \times 10^{-3} \text{ mole} \]

\[ \frac{I_2}{\text{v.f.} = 2} + 2\text{Na}_2\text{S}_2\text{O}_3 \xrightarrow{\text{v.f.} = 1, \text{ 50 ml, M(say)}} \]

\[ 3 \times 10^{-3} \text{ mole} \quad 6 \times 10^{-3} = 50 \times M \times 10^{-3} \quad \Rightarrow M = 0.12 \text{ M.} \]

17. Used millimoles of \( I_2 = 0.05 - 0.002 \times 10/2 \)

\[ = 0.04 \text{ = millimoles of } \text{Sn}^{2+} \]

\[ \text{wt of tin} = 0.04 \times 119 = 4.76 \text{ mg.} \]

18. Moles of iodine = moles of chlorine = \( \frac{80 \times 0.2}{2} \times 10^{-3} = 8 \times 10^{-3} \)

so required % = \( \frac{8 \times 71 \times 10^{-3}}{7.1} \times 100 \% = 8 \% \)

19. Excess of \( \text{Sn}^{2+} = 30 \times 0.1 \times 5 \text{ meq.} = 15 \text{ meq} \)

\( \text{Sn}^{2+} \) consumed = \( [(35 \times 0.5 \times 2) - 15] \text{ meq} \)

\[ = 20 \text{ meq.} \]

Now \( \text{Cl}_2 + \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{Cl}^- \) (balanced equation)

So moles of \( \text{Cl}_2 \) = moles of \( \text{Sn}^{2+} \) = \( \frac{1}{2} \text{ eq. of } \text{Sn}^{2+} = \frac{1}{2} \times 20 \text{ m moles} = 10 \text{ mmoles} \)

\[ = 10 \times 10^{-3} \times 71 \text{ g} = 0.71 \text{ g.} \]

So, required % = \( \frac{0.71}{10} \times 100 = 7.1\% \)

20. Bleaching powder \( \xrightarrow{\text{KI + CH}_3\text{COOH}} \text{I}_2 \xrightarrow{\text{Na}_2\text{S}_2\text{O}_3} \text{I}^- + \text{Na}_2\text{S}_4\text{O}_6 \)

The redox changes are \( 2e^- + \text{I}_2 \rightarrow 2 \text{I}^- \)

\[ 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_{6}^{2-} + 2e^- \]

m.eq. of available \( \text{Cl}_2 \) = m.eq. of \( \text{I}_2 \) liberated = m.eq. of \( \text{Na}_2\text{S}_2\text{O}_3 \) used.

\[ \therefore \text{m.eq. of available } \text{Cl}_2 \text{ in } 20 \text{ mL bleaching powder solution} \]

\[ = \text{m.eq. of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} \]

\[ = 20 \times \frac{1}{10} \]

\[ \therefore \text{m.eq. of available } \text{Cl}_2 \text{ in } 500 \text{ mL bleaching powder solution} = 20 \times \frac{1}{10} \times \frac{500}{20} = 50 \]
.
\[
\frac{w}{71/2} \times 1000 = 50 \\
\therefore w = \frac{50}{1000} \times \frac{71}{2} = 1.775 \text{ g}
\]
.
\% \text{ of available Cl}_2 \text{ in bleaching powder} = \frac{1.775}{5} \times 100 = 35.5\%

21.  
\[ \text{H}^+ + \text{IO}_3^- + \text{I}^- \rightarrow \text{I}_2 \]
On balancing the reaction,
\[ 6\text{H}^+ + \text{IO}_3^- + 5\text{I}^- \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \]
Let normality of HCl is X.
\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-} \]
m.eq. of I$_2$ = m.eq. of Na$_2$S$_2$O$_3$
\[ \therefore \text{(millimoles of I}_2\text{)} \times 2 = M \times \text{v.f.} \times V \]
mill moles of I$_2$ = \[
\frac{0.021 \times 24 \times 1}{2} = 0.252
\]
Now,
\[ \frac{\text{m mole of HCl}}{6} = \frac{\text{m mole of I}_2}{3} \]
\[ \frac{25 \times X}{1} \times \frac{1}{6} = \frac{0.252}{3} \quad \text{(v.f. for HCl} = 1) \]
\[ \therefore X = 0.02 \text{ N} \]
\[ \text{m mole of IO}_3^- = \frac{\text{m mole of I}_2}{3} \]
\[ 0.2 \times V = \frac{0.252}{3} \]
\[ V = 0.42 \text{ mL} \]

22.  
Mole of KMnO$_4$ = \[20 \times 10^{-3} \times \frac{1}{50} = \frac{2}{5} \times 10^{-3}\]
so, mole of Fe$^{2+}$ = \[5 \times \frac{2}{5} \times 10^{-3} = 2 \times 10^{-3}\]
so, mole of N$_2$H$_4$ = \[\frac{1}{4} \times 2 \times 10^{-3} = \frac{1}{2} \times 10^{-3}\]
Now mole of N$_2$H$_6$SO$_4$ = mole of N$_2$H$_4$
so, mass of N$_2$H$_6$SO$_4$ = \[\frac{1}{2} \times 10^{-3} \times 130 = 65 \times 10^{-3} \text{ g}\]
so, in 10 mL solution, quantity of N$_2$H$_6$SO$_4$ = \[65 \times 10^{-3} \times 1000 = 6.5 \text{ g}\]
\[ \therefore \text{in 1 liter solution, quantity of N}_2\text{H}_6\text{SO}_4 = \frac{65 \times 10^{-3}}{10} \times 1000 \text{ g} = 6.5 \text{ g} \]

23.  
\[ \text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3, \text{Impurity} \]
\[ \downarrow \quad \downarrow \quad \downarrow \]
x mole y mole
In first reaction,
\[ \text{Fe}_3\text{O}_4 + \text{l}^- \rightarrow \text{Fe}^{2+} \]
v.f. = 2
\[ \downarrow \quad \downarrow \]
x mole 3x mole
\[ \text{Fe}_2\text{O}_3 + \text{l}^- \rightarrow \text{Fe}^{2+} \]
v.f. = 2
\[ \downarrow \quad \downarrow \]
y mole 2y mole
(Eq. of \( \text{Fe}_3\text{O}_4 \) + Eq. of \( \text{Fe}_2\text{O}_3 \)) in 10 mL solution = Eq. of Hypo

\[
2(x + y) \times \frac{10}{50} = 4.8 \times 1 \times 10^{-3}
\]

\[
2x + 2y = 4.8 \times 10^{-3} \times 5
\]

\[
x + y = 12 \times 10^{-3}
\]

.....(1)

In \( \text{II}^{\text{nd}} \) reaction,

\[\text{Fe}^{2+} + \text{KMnO}_4 \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+}\]

\[
\text{v.f.} = 1 \quad \text{v.f.} = 5
\]

\[
\text{moles} \quad 3x + 2y \quad 3.2 \times 10^{-3} \times 1
\]

eq. of \( \text{Fe}^{2+} \) in 25 mL solution = eq. of \( \text{KMnO}_4 \)

\[
(3x + 2y) \times \frac{10}{20} = 3.2 \times 1 \times 5 \times 10^{-3}
\]

\[
3x + 2y = 32 \times 10^{-3}
\]

.....(2)

On solving eq. (1) and (2),

\[
x = 8 \times 10^{-3}
\]

\[
y = 4 \times 10^{-3}
\]

wt. of \( \text{Fe}_3\text{O}_4 \) = 8 \times 10^{-3} \times 232 = 1.856 g

wt. of \( \text{Fe}_2\text{O}_3 \) = 160 \times 4 \times 10^{-3} = 0.64 g

\[
\% \text{Fe}_3\text{O}_4 = \frac{1.856}{6} \times 100 = 30.93 \% \text{ Ans.} ; \quad \% \text{Fe}_2\text{O}_3 = \frac{0.64}{6} \times 100 = 10.67 \% \text{ Ans.}
\]

24. Let , weight of \( \text{H}_2\text{C}_2\text{O}_4 \) = 'a' g and weight of \( \text{NaHC}_2\text{O}_4 \) = 'b' g

for acid base reaction

(meq. of \( \text{H}_2\text{C}_2\text{O}_4 \) + meq. of \( \text{NaHC}_2\text{O}_4 \)) in 10 mL = 3 \times 0.1

\[
\therefore \text{meq. of } \text{H}_2\text{C}_2\text{O}_4 \text{ + meq. of } \text{NaHC}_2\text{O}_4 \text{ in one litre} = 3 \times 0.1 \times 100 = 30
\]

\[
\therefore \frac{a}{90/2} \times 1000 + \frac{b}{112/1} \times 1000 = 30
\]

\[
\therefore \frac{1000a}{45} + \frac{1000b}{112} = 30
\]

.....(1)

For redox change :

\[
\text{C}_2^{3+} \rightarrow 2 \text{C}_4^{4+} + 2e^{-}
\]

\[
\text{Mn}^{7+} + 5e^{-} \rightarrow \text{Mn}^{2+}
\]

(meq. of \( \text{H}_2\text{C}_2\text{O}_4 \) + meq. of \( \text{NaHC}_2\text{O}_4 \)) in 10 mL = 4 \times 0.1

\[
\therefore \text{meq. of } \text{H}_2\text{C}_2\text{O}_4 \text{ + meq. of } \text{NaHC}_2\text{O}_4 \text{ in one litre} = 4 \times 0.1 \times 100 = 40
\]

\[
\therefore \frac{a}{90/2} \times 1000 + \frac{b}{112/2} \times 1000 = 40
\]

\[
\therefore \frac{1000a}{45} + \frac{2000b}{112} = 40
\]

.....(2)

Solving equation (1) and (2), we get :

\[
a = 0.9 \text{ g} \quad \text{and} \quad b = 1.12 \text{ g}
\]

(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 \( \text{Cu}^{2+} \) and 'b' mole of \( \text{C}_2\text{O}_4^{2-} \) be present in solution.

Case I : The solution is oxidized by \( \text{KMnO}_4 \) which reacts with only \( \text{C}_2\text{O}_4^{2-} \).

\[
5e^{-} + \text{Mn}^{7+} \rightarrow \text{Mn}^{2+}
\]

\[
\text{C}_2^{3+} \rightarrow 2\text{C}_4^{4+} + 2e^{-}
\]

\[
\therefore \text{m. eq. of } \text{C}_2\text{O}_4^{2-} = \text{m. eq. of } \text{KMnO}_4
\]

\[
\therefore b \times 2 \times 1000 = 0.02 \times 5 \times 22.6
\]

\[
\therefore b = 1.13 \times 10^{-3}
\]

Case II : After oxidation of \( \text{C}_2\text{O}_4^{2-} \), the resulting solution is neutralized by \( \text{Na}_2\text{CO}_3 \), acidified with dilute \( \text{CH}_3\text{COOH} \) and then treated with excess of \( \text{KI} \). The liberated \( \text{I}_2 \) required \( \text{Na}_2\text{S}_2\text{O}_3 \) for its titration :

\[
\text{Cu}^{2+} \rightarrow \text{Cu}^{-} \quad + \quad \text{I}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_2\text{O}_5 + \text{I}^{-}
\]
\[ \text{m. eq. of Cu}^{2+} = \text{m. eq. of I}_2 \text{ liberated} = \text{m. eq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \]
\[ \text{m. eq. of Cu}^{2+} = \text{m. eq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \]
\[ a \times 1 \times 1000 = 11.3 \times 0.05 \times 1 \]
\[ a = 5.65 \times 10^{-4} \]
\[ \text{Molar ratio} = \frac{\text{Cu}^{2+}}{\text{S}_2\text{O}_3^{2-}} = \frac{a}{b} = \frac{5.65 \times 10^{-4}}{1.13 \times 10^{-3}} = \frac{1}{2} \]

26. Number of millimoles of KIO\textsubscript{3} in 30 mL of solution = Molarity × Volume in mL

\[ = \frac{1}{10} \times 30 = 3 \]

Given equation: KIO\textsubscript{3} + 2KI + 6HCl → 3ICl + 3KCl + 3H\textsubscript{2}O

According to the equation of the reaction given, 1 mole of KIO\textsubscript{3} is equivalent to 2 moles of KI

\[ \Rightarrow \text{No. of millimoles of KI in 20 mL of stock solution} = 2 \times 3 = 6 \]

\[ \Rightarrow \text{No. of millimoles of KI in 50 mL of the same solution} = 6 \times \frac{50}{20} = 15 \]

No of millimoles of KIO\textsubscript{3} in 50 mL of solution = \[ \frac{1}{10} \times 50 = 5 \]

No. of millimoles of KI used with 50 mL of KIO\textsubscript{3} solution = 2 × 5 = 10 (from reaction)

No. of millimoles of KI used with AgNO\textsubscript{3} = 15 − 10 = 5

\[ \text{AgNO}_3 + \text{KI} \rightarrow \text{AgI} + \text{KNO}_3 \]

1 mole of AgNO\textsubscript{3} reacts with 1 mole of KI. Therefore,

No. of millimoles of AgNO\textsubscript{3} is equal to 5.

Weight of AgNO\textsubscript{3} = 5 × 10\textsuperscript{-3} × 170 g = 0.85 g

\[ \% \text{ of AgNO}_3 = \frac{0.85 \times 100}{1} = 85 \% \]

27. Assume 10 mL of titrant, so there is 0.1 × 10 = 1 m.mole NaOH or KMnO\textsubscript{4}. The acidity is due of KHC\textsubscript{2}O\textsubscript{4} + H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (KH\textsubscript{2}A\textsubscript{2})

\[ \text{m.eq. of KH}_2\text{A}_2 = \text{m.eq. of NaOH} \]
\[ 3 \times \text{m.mole of KH}_2\text{A}_2 = \text{m.mole of NaOH} \times 1 \]

\[ \Rightarrow \text{m.moles of KH}_2\text{A}_2 = 1 \times \frac{1}{3} = 0.33 \quad \ldots \quad (1) \]

m.eq. of KMnO\textsubscript{4} = m.eq. of NaA + m.eq. of KH\textsubscript{2}A\textsubscript{2}

\[ 5 \times \text{m.mole of KMnO}_4 = \text{m.mole of NaA} \times 2 + \text{m.mole of KH}_2\text{A}_2 \times 4 \quad \text{(C}_2\text{O}_4^{2-} \rightarrow \text{2CO}_2, \text{v.f.} = 2) \]

\[ 5 \times 1 = \text{m.mole of NaA} \times 2 + 0.33 \times 4 \quad \text{(from (1))} \]

\[ \Rightarrow \text{m.mole of NaA} = 1.83 \quad \ldots \quad (2) \]

From (1) and (2),

\[ \frac{\text{mNa}_2\text{A}}{\text{mKH}_2\text{A}_2} = \frac{1.83 \times 10^{-3} \times 134}{0.33 \times 10^{-3} \times 218} = 3.38 \]

\[ \Rightarrow \text{Mixing proportion by mass} = 3.38 : 1. \]

28. The redox changes are:

for reducing of Fe\textsubscript{2}O\textsubscript{3} by zinc dust

\[ \text{Fe}^{2+} + 2e^- \rightarrow 2\text{Fe}^{3+} \]

\[ \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + e^- \]

oxidant + ne\textsuperscript{-} → product

meq. of Fe\textsubscript{2}O\textsubscript{3} in 25 mL

\[ = \text{meq. of Fe}^{3+} \text{ in Fe}_2\text{O}_3 \]
\[ = \text{meq. of Fe}^{2+} \text{ formed} \]
\[ = \text{meq. of oxidant used to oxidize Fe}^{2+} \text{ again} \]

\[ \Rightarrow \text{meq. of Fe}_2\text{O}_3 \text{ in 25 mL} = \text{meq of oxidant} \]
\[ = 17 \times 0.0167 \times n \]

Where, \( n \) is the number of electron gained by 1 mole of oxidant

\[ \Rightarrow \text{meq. of Fe}_2\text{O}_3 \text{ in 100 mL} = 17 \times 0.0167 \times n \times \frac{100}{25} \]
\[
\frac{1 \times 55.2 \times 1000}{100 \times \frac{M}{2}} = 17 \times 0.0167 \times n \times 4
\]

\[
\therefore \text{molecular wt. of } \text{Fe}_2\text{O}_3 = 160
\]

\[
\therefore n = \frac{1 \times 55.2 \times 1000 \times 2}{100 \times 160 \times 17 \times 0.0167 \times 4} = 6
\]

Hence, number of moles of electrons gained by one mole of oxidant = 6.

29. Let total mole of Mg used for MgO and \(\text{Mg}_3\text{N}_2\) be 'a' and 'b' respectively.

\[
2\text{Mg} + \text{O}_2 \longrightarrow 2\text{MgO}
\]

Before reaction

\begin{align*}
\text{a} & \\
\text{b} & \\
\end{align*}

After reaction

\begin{align*}
\text{0} & \\
\text{a} & \\
\end{align*}

\[
3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2
\]

Before reaction

\begin{align*}
\text{0} & \\
\text{b} & \\
\end{align*}

After reaction

\begin{align*}
\text{0} & \\
\frac{b}{3} & \\
\end{align*}

Now \((a + \frac{b}{3})\) mole of MgO and \(\text{Mg}_3\text{N}_2\) are present in the mixture.

\[
\text{MgO} + 2\text{HCl} \longrightarrow \text{MgCl}_2 + \text{H}_2\text{O} ; \quad \text{Mg}_3\text{N}_2 + 8\text{HCl} \longrightarrow 3\text{MgCl}_2 + 2\text{NH}_4\text{Cl}
\]

or the solution contains 'a' mole of MgCl\(_2\) from MgO and 'b' mole of MgCl\(_2\) from \(\text{Mg}_3\text{N}_2\) and \(\frac{2b}{3}\) mole of \(\text{NH}_4\text{Cl}\).

Also mole of HCl used for this purpose = 2a + \(\frac{8b}{3}\)

\[
\text{(for MgO) (for } \text{Mg}_3\text{N}_2)\]

Now mole of HCl reacted with MgO and \(\text{Mg}_3\text{N}_2\) = \(\frac{60 - 12}{1000}\) = 0.048

\[
2a + \frac{8b}{3} = 0.048 \quad \ldots (1)
\]

Further, mole of \(\text{NH}_4\text{Cl}\) formed = mole of \(\text{NH}_3\) liberated

= mole of HCl used for absorbing \(\text{NH}_3\)

= Total equivalent of acid – equivalent of base used for back titration

= \(\frac{10 - 6}{1000}\) = 4 \times 10^{-3}

\[
\therefore \frac{2b}{3} = 4 \times 10^{-3} \quad \text{or} \quad b = 6 \times 10^{-3} \quad \ldots (2)
\]

From (1) \[2a + \frac{8 \times 6 \times 10^{-3}}{3} = 0.048 \quad \text{or} \quad a = 16 \times 10^{-3}\]

Thus, % of Mg burnt to \(\text{Mg}_3\text{N}_2\) = \(\frac{6}{6 + 16}\) \times 100 = 27.27 %

30. In presence of Hph indicator

m. eq. of HCl = m. eq. of \(\text{Na}_2\text{CO}_3\) + m. eq. of NaOH

\[
30 \times 0.1 = (a \times 1) + (a \times 1)
\]

\[
\therefore a = 1.5
\]

In presence of MeOH indicator

m. eq. of \(\text{H}_2\text{SO}_4\) = m. eq. of \(\text{Na}_2\text{CO}_3\) + 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-1. \[
\begin{array}{c}
\text{CH}_3 \text{CH}_2 \text{Cl} \\
\text{Li}
\end{array} + \begin{array}{c}
\text{H}_2 \text{Ni}
\end{array} \rightarrow \text{CH}_3 \text{CH} - \text{CH} \text{CH}_3
\]

A-2. Symmetrical alkane with even no. of carbon atoms can be prepared by Wurtz reaction.

A-5. \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{Li}} & \text{CH}_3\text{CH}_2\text{Li} \\
\text{CuLi} & \rightarrow 2\text{CH}_3\text{CH}_2\text{Li} + \text{CuI} \rightarrow (\text{CH}_3\text{CH}_2)_2\text{CuLi} \xrightarrow{\text{CuI}} \\
\text{CH}_3 & \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3
\end{align*}
\]

A-6. \[\beta\text{-keto acid decarboxylate readily.}\]

B-3. \[\begin{array}{c}
\text{H}_2\text{C} \\
\text{Br}_2 / \text{h} \end{array} \xrightarrow{\text{Br}_2 / \text{h}} \text{CH}_3 \xrightarrow{\text{C}} \text{CH}_{\text{Br}}
\]

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 \(-134 \text{ kJ/mol}\).

C-4. \[\text{CH}_3 - \text{CH} - \text{COOH} \xrightarrow{\text{Electrolysis}} \text{CH}_3 - \text{CH} + 2\text{CO}_2 + \text{H}_2 + 2\text{NaOH}
\]

C-5. \[\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \xrightarrow{\text{Zn dust}} \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3 \text{ (But -2- yne)}
\]

C-6. \[\text{H}_2\text{C} \xrightarrow{\text{I} + 6\text{Ag} + \text{I}} \text{CH} \xrightarrow{\text{CH}} \text{CH} + 6\text{AgI}
\]

C-7. \[\text{CH} - \text{COONa} \xrightarrow{\text{Electrolysis}} \text{CH} + 2\text{CO}_2 + 2\text{NaOH} + 2\text{H}_2\text{O}
\]

C-9. \[2\text{Mg}^{2+} (\text{C} = \text{C} - \text{C}^3) \xrightarrow{\text{H}_2\text{O}^+} \text{Mg} (\text{OH})_2 + \text{CH} = \text{C} - \text{CH}_3 \text{ (Propyne)}
\]

D-1. Electron releasing group and stability of carbocation will decide rate of reaction in electrophilic addition reaction.

D-3. \[\text{C} = \text{C} \text{ at position 1 is more reactive towards electrophile } \text{Br}^{\circ} \text{ as this is adjacent to O atom to provide } +\text{m}
\text{ effect. } \text{C} = \text{C} \text{ at position 3 is more substituted as compared to } \text{C} = \text{C} \text{ at position 2. Alkyne is less reactive}
\text{ towards } \text{Br}^{\circ} \text{ as compared to alkene.}\]
E-2.

E-3.

E-5.

E-8.

(A) Ph – C – CH = CH₂ → Ph – C – CH – CH₃ → Migration of CH₃ → Ph – C – CH – CH₃
  ↓
  Ph – C – CH – CH₃

(B) Ph – CH – C = CH₂ → Ph – C – CH₂ → H⁺ shift → Ph – C – CH – CH₃

(C) Ph = C – C = C – CH₂ → Ph = C – CH = CH₂ → Ph = C – CH₂ → Ph = C – CH₃

(D) Ph = C – C = CH₂ → Ph = C – CH = CH₂ → Ph = C – CH₂ → Ph = C – CH₃

E-9.

CH₃ – C = CH – O – CH₃ → H⁺ → CH₃ – C = CH – OCH₃ → CH₃ – C = CH – OCH₃ → CH₃ – C = CH – OCH₃ → - H⁺ → CH₃ – C = CH – OCH₃
E-10. \[ \text{H}_2\text{O}^+ \xrightarrow{1. \text{Ring exp.}} \text{H}_2\text{O} \]

E-14. \[ R - \text{CH} = \text{CH}_2 \xrightarrow{\text{BH}_3/\text{THF}} \left(R - \text{CH}_2 - \text{CH}_2\right) \xrightarrow{\text{H}_2\text{O}_2/\text{OH}^+} 3 \xrightarrow{\text{Red P + H}_2\text{O}} \]

E-16. \[ \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 \xrightarrow{\text{NBS}} \text{CH}_2 = \text{CH} = \text{CH} - \text{CH}_2 \]

F-4. \[ \begin{align*}
\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br} & \xleftarrow{\text{NBS}} \text{CH}_2 = \text{CH} = \text{CH} - \text{CH}_2 \\
\end{align*} \]

G-2. \[ \begin{align*}
\text{HOBr} & \xrightarrow{\text{H}_2\text{O})} \xrightarrow{\text{OH}^+} \text{HOBr} \\
\end{align*} \]

G-5.* \[ \begin{align*}
\text{(I)} \text{CH}_2 = \text{C} = \text{CH}_2 & \xrightarrow{\text{H}_2\text{O})} \text{CH}_2 = \text{C} = \text{CH}_2 - \text{H}^+ \\
\text{(II)} \text{CH}_3 - \text{C} = \text{CH} & \xrightarrow{\text{H}_2\text{SO}_4/\text{Hg}^+} \text{CH}_3 - \text{C} = \text{CH}_2 - \text{H}^+ \\
\text{(III)} \text{CH}_3 - \text{C} = \text{CH} & \xrightarrow{\text{BH}_3/\text{THF}} \text{CH}_3 - \text{CH} = \text{CH}_2 - \text{CHO} \\
\end{align*} \]

G-6. \[ \begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{C} = \text{CH} & \xrightarrow{(1)\text{BH}_3/\text{THF}} \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{C} \\
\end{align*} \]

H-2.* \[ \begin{align*}
\text{(A)} \text{when H}^+ \text{add to the Buta-1, 3-diene in the r.d.s., an allylic carbocation is formed, however from But-1-ene, an 2}^\circ \text{ carbocation will form which will be less stable.} \\
\text{(B)} \text{At room temperature, product will be TCP.} \\
\text{(C)} \text{CH}_2 = \text{CH} - \text{C} = \text{CH} & \xrightarrow{\text{H}^+} \text{CH}_2 - \text{CH} = \text{C} = \text{CH}_2 \\
\end{align*} \]
I-5. \[ \text{Resonance} \]

I-6. \[ \text{Syn addition with Baeyer's Reagent, So cis will form meso compound however peroxy acid in anti addition gives enantiomer.} \]

I-7. \[ \text{CH}_3 - \text{CH}_2 - \text{C} = \text{CH} \xrightarrow{\text{Kmno}_4} \text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2 + \text{H}_2\text{O} \]

I-8. \[ \text{CH}_3 - \text{CH}_2\text{COOH} \xrightarrow{(1)\text{O}_3, (2)\text{H}_2\text{O}} 2\text{CH}_2\text{COOH} \]

I-10. \[ \text{J-1.} \]

J-3. \[ \text{J-3.} \]

J-8. \[ \text{Primary monochloride can be which is chiral} \]

\[ \text{CH}_3\text{CH} = \text{CH}_2\text{CH}_3 \]

6 \([1^\circ \text{H}] \times 1 = 6 \text{ (Chiral)}\]

2 \([2^\circ \text{H}] \times 3 = 6\]

1 \([3^\circ \text{H}] \times 5 = 5\]

3 \([1^\circ \text{H}] \times 1 = 3\]

% yield = \[ \frac{6}{20} \times 100 = 30\% \]

J-10. \[ \text{OH} \xrightarrow{\text{H}^+} \text{But-2-ene} \text{But-1-ene} \]

H_{2}O \xrightarrow{-H^+} \text{Trans + Cis} \]
Trans + Br₂ → Meso
Cis + Br₂ → d + l (enantiomer)
But-1-ene + Br₂ → CH₃ – CH₂ – ⋅CH – CH₂Br
d/l Br

J-11. \[
\text{CH}_3\text{C}=\text{C} = \text{C} = \text{CH}_3 \xrightarrow{\text{HOBr}} \]

J-13. \[
\text{CH}_3 \text{C} = \text{C} = \text{CH}_3 \xrightarrow{\text{Br}_2} \xrightarrow{\text{H}_2/\text{Pd/CaCO}} \xrightarrow{\text{Br}_2} \xrightarrow{\text{H}_2/\text{Pd}} \]

J-14. \[
\text{CH}_3\text{C} = \text{C} = \text{CH}_3 \xrightarrow{\text{Birch reduction}} \xrightarrow{\text{Li/NH}_3} \xrightarrow{\text{Br}_2} \]

K-1. \[
\text{HO} \xrightarrow{\text{H}^+ (-\text{H}_2\text{O})} \xrightarrow{(\text{H}_2\text{SO}_4)} (\text{Aromatic carbocation})
\]

K-3. (I) \[
\text{PhMgBr} \rightarrow \xrightarrow{\text{aromatic}} \]

(II) \[
\text{PhMgBr} \rightarrow \xrightarrow{\text{Anti aromatic}} \]

L-4. Rate of electrophilic substitution ∝ Stability of arenium ion.

L-5. \[
\text{O} \xrightarrow{\text{Br}_2/\text{Fe}} \xrightarrow{\text{Conc. HBr}} \text{CH}_2 – \text{Br} + \text{HO} – \text{Br}
\]

L-7. \[
\text{OCH}_3 (+ \text{M}) \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{H}^+} \]

Resonance
Educating for better tomorrow
Hydrocarbon - 139
L-11. (1) Strong activity group (–NH₂ and –OH) and –M groups do not show Friedel-Craft reaction. 
(2) Vinyl halide and aryl halide do not give Friedel-Craft reaction.

L-13. \[ \text{CH}_3 + \text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{CH}_3\text{CH}_2\text{Cl} \]

L-15. \[ \text{CH}_2\text{C} \xrightarrow{\text{Br}_2/\text{Fe}} \text{Br} \xrightarrow{\text{Br}_2/\text{Fe}} \text{CH}_2\text{C} \]

L-18. \[ \text{CH}_2 + \text{CH}_2=\text{CHCH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{CH}_2=\text{CHCH}_2\text{Cl} \]

L-19. \[ \text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{CH}_2\text{Br} \xrightarrow{\text{HO}^-} \text{CH}_2\text{OH} \xrightarrow{\text{MnO}_2} \text{CH} = \text{O} \]

L-20. \[ \text{Cl} \xrightarrow{\text{AlCl}_3} \text{Cl} \xrightarrow{\text{Zn/Hg}} \text{Cl} \xrightarrow{\text{[I/AlCl}_3]} \text{Cl} \]

L-22. \[ \text{Br} \xrightarrow{\text{conc. HNO}_3/\text{conc. H}_2\text{SO}_4} \text{Br} + \text{Br} \xrightarrow{\text{Br} \text{Br}} \text{Br} \xrightarrow{\text{Br} \text{Br}} \text{Br} \]

PART - II

1. (A) \[ \text{COOH} \xrightarrow{\text{NaOH/CaO}} \text{O} \xrightarrow{\text{Zn/Hg}} \]
   (B) \[ \text{COOH} \xrightarrow{\text{NaOH/CaO}} \text{O} \xrightarrow{\text{Zn/Kg}} \]
   (C) \[ \text{COOH} \xrightarrow{\text{Electrolysis}} \text{H}_2/\text{Ni} \]
   (D) \[ \text{Cl–CH}_2–\text{CH}_2 \xrightarrow{\text{Na/ether}} \text{Cl–CH}_2–\text{CH}_2 + 2\text{NaCl} \]
2. (A) CaC₂ + H₂O → Ca(OH)₂ + CH = CH
(B) MgC₂ + H₂O → Mg(OH)₂ + CH₃ – C = CH
(C) HC – COOK \[\xrightarrow{\text{Kolbe’s Electrolysis}}\] HC
(D) HC – COOK \[\xrightarrow{\text{Kolbe’s Electrolysis}}\] HC
(E) 2HCl₃ + 6Ag → CH + 6AgI
(F) CH₃ – C – C – H \[\xrightarrow{\text{Zn powder}}\] CH₃ – C = CH + 2 Zn Br₂
(G) CH₃ – C – C – CH₃ \[\xrightarrow{\text{NaI Acetone}}\] CH₃ – C = C – CH₂ But -2-yne

3. (A) –CH=CHCOOH is deactivating due to –I of –COOH group, but o,p-directing due to stability of carbocation.
(B) –CCl₃ is electron withdrawing group due to –I nature.
(C) –OH is electron donating due to +m.
   –NO₂ is electron withdrawing due to –m.

4. (A) \[
\text{HOOC-} \xrightarrow{\text{Con.H₂PO₄}} \text{CH₃}
\]
\[\xrightarrow{\text{Zn–Hg/HCl}}\]
\[
\text{CH₃}
\]
(B) \[
\text{Cl-} \xrightarrow{\text{AlCl₃}} \text{CH₃}
\]
\[\xrightarrow{\text{Pd–C/Δ}}\]
\[
\text{CH₃}
\]
(C) \[
\text{CH₃} \xrightarrow{H^0} \text{CH₂}
\]
\[\xrightarrow{\text{Pd–C/Δ}}\]
\[
\text{CH₃}
\]
(D) \[
\text{O-} \xrightarrow{\text{HCl (dry)}} \text{CH₃}
\]
\[\xrightarrow{\text{–H^0}}\]
\[
\text{CH₃}
\]
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

$$\text{CH}_3 - \text{CH} = \text{CH} \xrightarrow{\text{NaNH}_2} \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{Br}_2} \text{CH}_3 - \text{CH} = \text{CH} + \text{Br}$$

8. alco. KOH

9. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br} \xrightarrow{\text{C}, \text{H}_2 \text{Br}} (X)$

10. (More stable $\sigma$ complex)

11. (More stable $\sigma$-Complex)

12. (More stable $\sigma$-Complex)

13. More stable $\sigma$-Complex

**EXERCISE # 2**

1. (i) $\text{Br} \xrightarrow{\text{Na/dry ether}} \text{Br}$

   (ii) $\text{Br} \xrightarrow{\text{Na/dry ether}}$ (Not a reaction shown)

   (iii) Ph−Br + CH$_3$−Br $\xrightarrow{\text{Na/dry ether}}$ Ph−Ph + CH$_3$−CH$_3$ + Ph−CH$_3$

These are wurtz reaction.
4. 

\[
\begin{align*}
\text{HOOC} & \quad \text{COOH} \\
\text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

\[
\text{NaOH} \quad \text{Electrolysis}
\]

6. 

\[
\text{HOOC} 
\]

\[
\text{Soda lime} 
\]

\[
\text{HI + Red (\text{I}_2\text{P})} 
\]

\[
\text{H}_2\text{C} 
\]

\[
\text{Br}_2/\text{hv} \quad \text{five products}
\]

8. Stability of alkene \( \propto \) 1 \( \text{heat of hydrogenation} \)

10. 

(i) \( R-\text{CH}_2-\text{C} \quad \text{or} \quad R-\text{CH}-\text{CH}-\text{R} \rightarrow R-\text{CH}=\text{C} \rightarrow R-\text{C}=\text{C}-\text{R} \)

(ii) \( \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \rightarrow \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3 \rightarrow \text{CH}_3-\text{CH}=\text{C}-\text{CH}_3 \rightarrow \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \)

11. \( \text{CaC}_2 + \text{H}_3\text{O}^+ \rightarrow \text{Ca(OH)}_2 + \text{CH}_3=\text{CH} \rightarrow \text{NH}_3\text{OH} + \text{AgNO}_3 \rightarrow \text{Ag}^+ \text{C}^- \rightarrow \text{Ag}^+ \) White ppt.

13. Since the reactivity towards ionic addition \( \propto \) stability of carbocation intermediate formed.

I \( \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \rightarrow \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \)

II \( \text{CH}_3-\text{C}=\text{CH}_3 \rightarrow \text{CH}_3-\text{C}=\text{CH}_3 \)

III \( \text{Ph}-\text{C}=\text{CH}-\text{CH}_3 \rightarrow \text{Ph}-\text{C}=\text{CH}_2-\text{CH}_3 \)

IV \( \text{Ph}-\text{C}=\text{CH}-\text{CH}_3 \rightarrow \text{Ph}-\text{C}=\text{CH}_2-\text{CH}_3 \)

Stability of carbocation intermediate: IV > III > II > I. Reactivity of alkene: IV > III > II > I.

16. 

(a) \( \text{C}_3\text{H}_7\text{CH}=\text{CH}_2 \rightarrow \text{Hg(OAc)}_2 \rightarrow \text{C}_3\text{H}_7\text{CHCH}_{\text{HgOAc}} \rightarrow \text{NaBH}_4/\text{NaOH} \rightarrow \text{C}_3\text{H}_7\text{CHCH}_{\text{3OH}} \)

(b) Self explanatory.

(c) Self explanatory.

(d) Self explanatory.
18. \[
\begin{align*}
&\text{CH}_3 \\
&\text{H}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 \\
&\text{CH}_3
\end{align*}
\]
\[\text{dil. aqueous H}_2\text{SO}_4\rightarrow \]
\[
\begin{align*}
&\text{H} \\
&\text{H}_3\text{C} - \text{C} - \text{CH}_3 \\
&\text{CH}_3 \text{OH}
\end{align*}
\] \[\Delta \rightarrow \]
\[
\begin{align*}
&\text{H}_3\text{C} - \text{C} - \text{CH}_3 \\
&\text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]
3,3 - dim ethyl - 1 - butene
2,3 - dim ethyl - 2 - butanol

23. \[
\begin{align*}
&\text{HBr} / (\text{CH}_3)_2\text{O} \\
&\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Br} \\
&\text{Br} \\
&(A)
\end{align*}
\]
\[
\begin{align*}
&\text{HBr} \\
&\text{CH} = \text{CH} - \text{CH}_3 \\
&\text{HBr} \\
&(B)
\end{align*}
\]

24. (a) \[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{C} = \text{CH} \\
&\text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2
\end{align*}
\]
(b) \[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{C} = \text{CH} \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{CH} \\
&\text{CH}_3\text{CH}_2\text{C} = \text{CH} \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2
\end{align*}
\]

26. This reaction proceeds through a carbocation. Since the alkyl carbocation from the alkene group is more stable than the vinyl carbocation from the alkyne group.

\[
\begin{align*}
&\text{H}_3\text{C} = \text{CHCH}_2\text{C} = \text{CH} \\
&\text{H}^+ \rightarrow \text{H}_3\text{C} - \text{CHCH}_2\text{C} = \text{CH} \\
&\text{Br}^- \rightarrow \text{H}_3\text{C} = \text{CHCH}_2\text{Br} = \text{CH} \rightarrow \text{H}_3\text{C} = \text{CHBrCH}_2\text{C} = \text{CH}
\end{align*}
\]
(no reaction)

31. \[
\begin{align*}
&\text{CH}_3\text{C} = \text{C(CH}_3)_2\text{C} = \text{CCH}_3 \\
&\rightarrow \text{CH}_3\text{COOH, HOOC(CH}_3)_2\text{COOH, HOOCCH}_3
\end{align*}
\]

32. \[
\begin{align*}
&\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{C} - \text{H} \\
&\text{and} \quad \text{CH}_3 - \text{CH} - \text{C} - \text{H}
\end{align*}
\]

34. \[
\begin{align*}
&\text{CuLi} + \text{CH}_3\text{CH}_2\text{Br} \\
&\rightarrow \text{[CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3]\text{Cl}_2 / \text{hv}
\end{align*}
\]

4 isomers (with one d-pair) \[\text{Fractional distillation} \rightarrow 3 \text{ fractions}\]

35. After addition of HBr, we get two chiral centres, so total isomers will be four.

36. \[
\begin{align*}
&\text{H}_2\text{C} = \text{CH} - \text{CH} - \text{CH}_3 \\
&\text{Br}
\end{align*}
\]
\[\text{d/e by 1, 2-addition}\]
\[
\begin{align*}
&\text{H}_2\text{C} = \text{CH} - \text{CH} - \text{CH}_3 \\
&\text{Br}
\end{align*}
\]
\[\text{E/Z by 1, 4-addition}\]
Thus total isomers is 4.
EXERCISE # 3

ALKANE

1. Clemmensen's reagent or Wolf kishner reagent are preferred for reduction of > C = O group into – CH₂. With Zn(Hg) /HCl OH group will also undergo SN reaction.

2. \[ \text{H}_2\text{C} - \text{H}_2\text{C} - \text{HC} = \text{CH}_2 \xrightarrow{\text{Pd}/\text{H}_2} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \]

3. \[ \text{CH}_3 - \text{C} - \text{CH}_3 \xrightarrow{\text{Cl}_2 / \text{hv}} \text{ClCH}_3 - \text{C} - \text{CH}_3 \]

   Neopentane only one monochloro product

4. \[ \text{CH}_3 - \text{CH} - \text{CH}_3 - \text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 + \text{ClCH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \]

5. \[ \text{H}_2\text{C} - \text{C} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{Zn}/\text{HCl}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \]

   Butane -2-one

6. \[ \text{Br} \quad + \ 2 \ \text{Na} \rightarrow \text{Cl} \quad \rightarrow \quad \text{Cl} \]

7. \[ \text{CH}_3 - \text{C} - \text{CH}_2 \text{CH}_3 + \text{Br}_2 \xrightarrow{\text{hv}} \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \]

   2-Bromo-2-methyl butane

8. \[ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{Cl}_2 / \text{hv}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \text{Cl} + \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \text{Cl} \]

   \[ (d + 1) \]

   \[ + \text{ClCH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 + \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \]

   \[ (d + 1) \]

   \[ N = 6 \ , \ P = 4 \]

9. \[ \text{CH}_3 \xrightarrow{\text{Cl}_2 / \text{hv}} \]

   \[ \text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_3 \]

   \[ \text{Cl} \quad 2' = 2 \quad \text{Cl} \quad 2' = 4 \]
11. \[ \text{H}_2\text{C} \quad \text{C} \quad \text{H}_3 \quad \text{Cu/\textit{hv}} \quad \text{monohalogenation} \quad \text{single product.} \]

Four monochloro derivatives are chiral.

**ALKENE & ALKYNE**

4. \[ \text{(A) } \text{CH}_3 \quad \text{CH}_2 \quad \text{C} = \text{CH} + \text{H}_2\text{O} \quad \text{HgSO}_4 \quad \text{Dil. H}_2\text{SO}_4 \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{C} = \text{CH} \quad \text{Tautomiser} \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{C} = \text{C} + \text{H}_2\text{O} \]

(Because keto form is more stable than enol)

5. Terminal alkyne gives white ppt with ammonical silver nitrate.

\[ \text{CH}_3 \quad \text{C} = \text{CH} + \text{NH}_3 + \text{AgNO}_3 \rightarrow \text{CH}_3 \quad \text{C} = \text{C} \quad \text{Ag} + \text{NH}_4\text{NO}_3 \quad \text{white ppt.} \]

while propene does not give any reaction with ammonical AgNO\textsubscript{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\textsuperscript{+} attacks therefore it is an electrophilic addition.

7. \[ \text{CH}_3 \quad \text{CH}_2 \quad \text{C} = \text{CH} \quad \text{CuCl}_2 \quad \text{NH}_3\text{OH} \rightarrow \text{CH}_3 \quad \text{CH}_2 \quad \text{C} = \text{C} \quad \text{Cu} \quad \text{NH}_4\text{Cl} \quad \text{H}_2\text{O} \quad \text{Blood red Colour} \]

8. \[ \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{Br} \quad \text{alco. NaOH} \quad \text{HBr} \rightarrow \text{CH}_3 \quad \text{CH} = \text{CH}_2 \quad \text{CH}_3 \quad \text{CH} = \text{CH}_2 \]

9. \[ \text{Ph} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{H}^+ \rightarrow \text{Ph} \quad \text{C} \quad \text{CH}_3 \quad \text{H}_2\text{O} \rightarrow \text{Ph} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{Ph} \quad \text{O} \quad \text{H} \]

\[ \text{Ph} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \leftrightarrow \text{Ph} \quad \text{O} \quad \text{H} \]

(Keto - form)
10. \[ \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 \xrightarrow{\text{Pd}/\text{H}_2} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \]

11. \[ \text{HC} = \text{CH} \xrightarrow{\text{2HOCI}} \text{OH} \quad \text{CH} - \text{CHCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{H} - \text{C} - \text{CHCl}_2 \]

12. \[ \text{H}_3\text{C} - \text{C} = \text{CH}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{OH} \quad \text{Ph} \rightarrow \text{CH}_3 - \text{C} - \text{CH}_3 \]

14. Boiling Point \( \propto \) surface area \( \propto \frac{1}{\text{Branching}} \)

Iso butene has smallest vander wall surface area of contact so its boiling point least.

15. \[ \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow{\text{HBr} / 40^\circ\text{C}} \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br} \]

(80%) (1,4) Thermodynamically product

16. \[ \text{C}_6 - \text{C} - \text{CH} = \text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{by Markownikoff's rule} \]

by 1, 2-hydride shift

17. \[ \text{CH}_2 = \text{CH} - \text{CH}_3 \xrightarrow{\text{O} = \text{N} - \text{Cl}} \text{CH}_2 - \text{O} = \text{N} - \text{CH}_3 \xrightarrow{\text{CF}^0} \text{CH}_2 - \text{CH} - \text{CH}_3 \]

18. \[ \text{Br} - \text{CH} = \text{CH}_2 \xrightarrow{\text{Ac. KOH}} \text{Br} - \text{CH} = \text{CH} \]

\[ \text{NaNH}_2 \xrightarrow{\text{NH}_2} \text{CH} = \text{CH} \]

19. \[ \text{CH}_3 - \text{C} - \text{CH}_3 \xrightarrow{\text{B}^+} \text{CH}_3 - \text{Br} \text{ (meso)} \]
21. \( \text{CH}_3\text{CH}_2\text{C} = \text{CH} \overset{\text{Na/LiqNH}_3}{\Delta} \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{CHNa} \)

22. \( \text{CH}_3\text{CH} = \text{CHCH}_3 \overset{\text{O}_3}{\rightarrow} \text{CH} = \text{CH} \overset{\text{Zn/H}_2\text{O}}{\rightarrow} 2\text{CH}_3\text{CH} = \text{O} \)

23. \( \text{C}_n\text{H}_{2n} = 44 \)
\( \text{C}_n\text{H}_{2n} = 44 - 16 \)
\( \text{C}_n\text{H}_{2n} = 28 \)
\( n = 2 \)

\( \text{CH}_3\text{CH} = \text{CH} - \text{CH}_3 \overset{\text{O}_3/Zn}{\rightarrow} \text{CH}_3\text{CH} = \text{O} \)

**Sol. (24 & 25)**

26. \( \text{CH}_2 = \text{C} \overset{\text{O}_3}{\rightarrow} \text{CH} = \text{O} + \text{O} = \text{C} \)

Presence of one vinyl group gives formaldehyde as one of the product in ozonolysis.

**BENZENE**

1. 'N' has lone pair, so it is activating and o/p directing % p > % O.

2. It is \( \text{ArSe}^2 \) reaction, N has lone pair so it is activating and substitutions occurs at most activated position.

3. Reaction involved are
   
   (1) \( A \rightarrow B \)
   \( 3\text{H}_2\text{SO}_4 + 2\text{NaBr} + \text{MnO}_2 \rightarrow \text{Br}_2 + \text{MnSO}_4 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} \)
   \( \text{(A)} \)
   
   (2) \( A \rightarrow C \)
   \( 2\text{H}_2\text{SO}_4 + \text{H} - \text{O} - \text{N} = \text{O} \rightarrow (\text{H} - \text{O} - \text{N} = \text{O} + \text{HSO}_4^- + \text{H}_2\text{SO}_4) \rightarrow \text{H}_2\text{O} + \text{NO}_2 + 2\text{HSO}_4^- \)
5. \[
\begin{align*}
\text{NO}_2 & \quad \text{NH} \\
\text{NO}_2 & \quad \text{NH}
\end{align*}
\]
\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{O}_2 & \quad \text{N}
\end{align*}
\]
\[
\text{Con. HNO}_3 \quad \text{Con. H}_2\text{SO}_4
\]
\[
\begin{align*}
\text{NO}_2 & \quad \text{NH} \\
\text{NO}_2 & \quad \text{NH}
\end{align*}
\]
\[
\begin{align*}
\text{O}_2 & \quad \text{N} \\
\text{O}_2 & \quad \text{N}
\end{align*}
\]
Note: (-NH– part is p-directing).

6. \[
\begin{align*}
\text{CH}_3 + \text{Cl}_2 & \xrightarrow{\text{FeCl}_3} \text{CH}_3\text{Cl} \\
& + \text{p-chlorotoluene}
\end{align*}
\]
The reaction proceeds by electrophilic substitution mechanism. The CH\textsubscript{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**

1. \[
\begin{align*}
\text{CH}_3 - \text{Cl} & \quad \text{CH}_3 - \text{Cl} \\
\text{Na} / (\text{Dry ether}) & \quad \text{CH}_3 - \text{CH}_3 + \text{CH}_3 - \text{CH}_3
\end{align*}
\]

2. \[
\begin{align*}
\text{Cl}_2 / \text{hv} & \quad \text{Cl}_2 / \text{hv} \\
\text{Cu} & \quad \text{Cu} \\
\text{Li} & \quad \text{Li}
\end{align*}
\]

3. \[
\begin{align*}
\text{Cl} & + 2\text{Na} + \text{Cl} \\
& \rightarrow \text{Cl} + \text{Cl}
\end{align*}
\]

4. \[
\begin{align*}
\text{CH}_3\text{CH}_2 - \text{Br} & \xrightarrow{\text{Li}} \text{CH}_3\text{CH}_2 - \text{Li} \\
& \xrightarrow{\text{CuI}} \text{CH}_3 - \text{CH}_3 - \text{CH}_3 - \text{CH}_3 - \text{CH}_3
\end{align*}
\]

5. \[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl} & \xrightarrow{2\text{Na} / \text{Et}_2\text{O}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3
\end{align*}
\]

6. Products are CH\textsubscript{3} – C – Cl and CHCl\textsubscript{3}

---

Resonance
Educating for better tomorrow

Hydrocarbon - 149
9.  
1° C – H = 12 \times 1 = 12  
2° C – H = 2 \times 3 = 6  
3° C – H = 2 \times 6 = 12  
Minimum yield = \frac{6}{30} \times 100 = 20\%  
Ans. 20\%  

10. 1° halides:  
BrCH_{2}CH_{2}CH_{3} \rightarrow CH_{3}=CHCH_{2}CH_{3}  
BrCH_{2}CH(CH_{3})_{2} \rightarrow CH_{3}=C(CH_{3})_{2}  
3° halides:  
(CH_{3})_{3}CB \rightarrow CH_{2} = C(CH_{3})_{2}  

11. C_{5}H_{11}X \xrightarrow{\text{alc. KOH}} CH_{3}–CH_{2}–CH=CH_{2} / CH_{3}–CH_{2}–CH=CH–CH_{3}  
Thus possible structure of halide may be  
(a) CH_{3}CH_{2}–CH_{2}–CH_{2}–CH_{2}–X  
(b) CH_{3}–CH_{2}–CH–CH_{2}–CH_{3}  

12.  
Pentene exist in the following isomeric forms:  
CH_{2}CH_{2}CH=CH_{2} : CH_{3}–CH_{2}–C–H  
H_{2}C=C–H  
Pent-1-ene  
Pent-2-ene (cis)  
CH_{2}–C=CHCH_{3} ; CH_{3}–CH=CH–CH_{2}  
2-Methylbut-2-ene  
3-Methylbut-1-ene  
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).  

13.  

16.  

17.  

18.  

H_{2}C=CH_{2} \xrightarrow{I^{-}} H_{2}C=CH_{2}I
20. (A) \[ \text{H}_2\text{C} = \text{CH}_2 \xrightarrow{\text{HBr}} \text{CH}_2\text{Br} \]  
\[ \text{B} \] \[ \text{HBr} \]  
\[ \text{HBr} / \text{R}_2 \text{O}_3 \]  
\[ \text{CH}_3 \text{Br} \]

21. \[ \text{CH}_3\text{C} = \text{CCH}_3 \xrightarrow{\text{D}_2 / \text{Lindlar’s catalyst}} \text{C} = \text{C} \text{C} = \text{C} \text{C} \text{H}_3 \xrightarrow{1. \text{BD}_3, \text{THF}} \text{C} = \text{C} \text{C} = \text{C} \text{C} \text{H}_3 \]

22. \[ \text{CH}_3\text{C} = \text{CCH}_3 \xrightarrow{1. \text{BD}_3, \text{THF}} \text{C} = \text{C} \text{C} = \text{C} \text{C} \text{H}_3 \xrightarrow{1. \text{BD}_3, \text{THF}} \text{C} = \text{C} \text{C} = \text{C} \text{C} \text{H}_3 \]

26. \[ \text{C} \xrightarrow{\text{Cl}_2 + \text{hv}} \text{Cl} \xrightarrow{\text{alc KOH} / \Delta} \text{Cl} \xrightarrow{\text{NBS}} \text{Cl} \xrightarrow{\text{alc KOH} / \Delta} \]

27. \[ \text{H}_2\text{C} = \text{CH} = \text{CH} = \text{CH} = \text{CH}_2 \xrightarrow{\text{Br}} \text{C} = \text{CH} = \text{CH} = \text{CH} = \text{CH}_2 \]
\[ \text{A} \]
\[ \text{B} \]
\[ \text{C} \]

(C) will be thermodynamically controlled.

28. \[ \text{H}_2\text{C} = \text{CH} = \text{CH} = \text{CH} = \text{CH}_2 \xrightarrow{\text{K}_2 \text{MnO}_4 / \text{H}^+} \text{O} = \text{C} = \text{O} + \text{HOOC} = \text{CH} = \text{CH}_2 \text{H}_3 \]

29. The products of ozonolysis are 2-pentanone and acetaldehyde. Writing the structure of both the carbonyl compounds.

![Pentan-2-one](image)

![Acetaldehyde](image)

Removing =O of the compounds and linking both through double bond, we get the alkene.

Thus, the alkene is 3-methylhex-2-ene.

**Reaction:**

\[ \text{C}_6\text{H}_7\text{C} = \text{C} = \text{C} = \text{C} \text{H}_3 \xrightarrow{\text{O}_2} \text{C}_6\text{H}_7\text{C} = \text{C} = \text{C} = \text{C} \text{H}_3 \xrightarrow{\text{Zn} / \text{H}_2 \text{O}_2} \text{C}_6\text{H}_7\text{C} = \text{C} = \text{C} = \text{C} \text{H}_3 \]

\[ \text{O} = \text{C} = \text{C} = \text{C} \text{H}_3 \]

\[ \text{O} = \text{C} = \text{C} = \text{C} \text{H}_3 \]

\[ \text{Acetaldehyde} \]

\[ \text{Pentan-2-one} \]
31.  
\[ \text{D} \quad \text{D} \quad \text{D} \quad \text{D} \quad \underset{\text{BH}_3, \text{THF}}{\longrightarrow} \quad \text{D} \quad \text{D} \quad \text{D} \quad \text{D} \quad \underset{\text{H}_2\text{O}, +\text{OH}}{\longrightarrow} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{Meso \ POS}(+) \quad \text{Opt. active \ d/L} \quad \text{Opt. active \ d/L} \quad \text{Meso \ COS}(+) \]

32.  
\[ \text{H}^+ \quad \text{H}^+ \quad \text{Ring} \quad \text{Expansion} \quad \text{OH} \quad \text{H}_2\text{O}^- \quad \text{Shift} \quad \text{OH} \quad 2^2 = 4; \quad (1) \]

33.  
(a)  
\[ \text{CH}_3 \quad \text{H} \quad \text{Br} \quad \text{CH} \quad \text{CH} \quad (\text{Trans}) \quad \underset{\text{Br}_2, \text{CCl}_4}{\longrightarrow} \quad \text{CH}_3 \quad \text{Br} \quad \text{Br} \quad \text{CH}_3 \quad \text{Br} \quad \text{Br} \quad \text{CH}_3 \quad \text{Meso}(\text{I}) \quad \text{Meso}(\text{II}) \]

(b)  
\[ \text{CH}_3 \quad \text{H} \quad \text{Br} \quad \text{CH} \quad \text{CH} \quad \text{cis} \quad \underset{\text{Br}_2, \text{CCl}_4}{\longrightarrow} \quad \text{CH}_3 \quad \text{Br} \quad \text{Br} \quad \text{H} \quad \text{CH}_3 \quad \text{Br} \quad \text{H} \quad \text{CH}_3 \quad \text{Optically active} \quad \text{Optically active} \]
34.  
(A) But-2-yne + Na / liq. NH₃ → trans But-2-ene + Br₂ → Meso-2,3-dibromobutane  
(B) But-2-yne + Lindlar → cis But-2-ene + HOCl/H⁺ → Racemic-3-chloro-2-butanol  
(C) But-2-yne + Lindlar → cis But-2-ene + Beyer’s reagent → Meso-2,3-butanediol  
(D) But-2-yne + Birch → trans But-2-ene + (i) HCOOOH / (ii) H₃O⁺ → Racemic-2,3-butanediol

36.  
(A) and its enantiomer - a case of syn addition. Mixture is optically inactive (racemic mix).  
(B) meso form by anti addition  
(C) and its enantiomer by anti addition.  
(D) meso by syn addition
38. ‘X’ will be:

H₃C - C - CH₂CH₃
OH

H₂SO₄

H

CH₂ = C - CH₂CH₃ + CH₂ - CH = CH - CH₃
(cis + trans)

3 alkenes

CH₃ - C - CH₂CH₃
OH

HCl / ZnCl₂

H

CH₃ - C - CH₂ - CH₃
Cl

Cl⁻

(R + S) 2 isomers

CH₃ - C - CH₂CH₃
OH

CrO₂ / H⁺

Oxidation

CH₃ - C - CH₂ - CH₃
(one oxygen atom)

42. o-HOOC - C₆H₄ - CH₂ - C₆H₅

SOCl₂

anhydrous

HCl

Zn - Hg

43. AlCl₃ + CH₂ - CH₂

AlCl₃

Ph

HO - CH - CH₂ - Cl

HCl / H⁺

44. (less activating) (more activating)

(NO₂)⁺

CH₃

(No directing)