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IIT JEE | MEDICAL | FOUNDATION

Solutions – JEE Advanced Revision Booklet | Chemistry

Stoichiometry-I & II

1.(D) $2CrO_5 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O + 7/2\ O_2$.

$$\begin{bmatrix} 2Cr^{+6} + 6e^- \longrightarrow 2Cr^{+3} \\ 7O^{-1} \longrightarrow 7\overset{0}{O} + 7e^- \\ O^{-1} + e^- \longrightarrow O^{-2} \end{bmatrix}$$

2.(B) $\underset{\text{mol (a)}}{Na_2C_2O_4} + \underset{\text{mol (b)}}{KHC_2O_4.H_2C_2O_4}$

With NaOH : $\text{eq of } Na_2C_2O_4 + \text{eq of } KHC_2O_4\ H_2C_2O_4 = \text{eq of } KMnO_4$

$2a + 4b = 5 \times 0.2 \times V$ **.......(i)**

With $KMnO_4$: $\text{gmeq of } KHC_2O_4.H_2C_2O_4\ (n = 3 \text{ as acid}) = \text{gmeq of NaOH}$

$3b = 1 \times 0.2 \times V$ **.........(ii)**

Divide (i)/(ii): $\dfrac{2a+4b}{3b} = 5 \quad \Rightarrow \quad \dfrac{a+2b}{3b} = \dfrac{5}{2} \quad \Rightarrow \quad \dfrac{a}{b} = \dfrac{11}{2}$

3.(C) $4Au + 16KCN + 6H_2O + 3O_2 \longrightarrow 4KAu(CN)_4 + 12KOH$.

$V(OH)_4Cl + FeCl_2 + 2HCl \longrightarrow VOCl_2 + 3H_2O + FeCl_3$.

$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + O_2 + 2H_2O$.

In above reaction out of 4 mol of $\overset{-2}{O}$ present in KOH (R.A) , two are oxidised to O_2 and other two moles remained as such and went to H_2O.

$2MnO + 5PbO_2 + 10HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 4H_2O$.

4.(C) $XeF_x + \dfrac{x}{2}H_2 \longrightarrow Xe + xHF$

$\text{m mol of Xe} = \dfrac{1000}{22400} \times 22.4 = 1$; m mol of HF (n = 1) = 6 ⇒ $x = 6$

5.(B) Ist Part meq of I_2(n= 2) = meq of $S_2O_3^{2-}$ (n = 1) = 15 × 0.4 ×1 = 6, m mol of I_2=3

IInd Part meq of I_2 reacted with NaOH = meq of NaOH initially – meq of H_2SO_4 = 100 × 0.3 – 2 × 10 × 0.3 = 24

m mol of I_2 (n = 2) reacted with NaOH = $\dfrac{24}{2} = 12$

Total m mol of I_2 = 3 +12 = 15 ; $[I_2] = \dfrac{15}{150} = 0.1$

6.(D) $\underset{n=1}{HCN}+\underset{n=1}{KOH}\longrightarrow KCN+H_2O$

m mol of HCN = meq of HCN = meq of KOH = 100

$\underset{n=10}{HCN}+\underset{\substack{n=5\\V=?}}{KMnO_4}\longrightarrow Mn^{2+}+NO_3^-+CO_2$

As HCN used in same for $KMnO_4$ as is used for KOH.

m mol of HCN (n = 1) = 100.

meq of HCN (n = 10) = 100 × 10 = 1000

meq of HCN = meq of $KMnO_4$ ⇒ $1000 = 5\times 5\times V$: ⇒ $V = 40\text{ mL}$

7.(A) $\overset{+6}{Mn}O_4^{2-}$ on disproportination gives $MnO_4^{\ominus}$ & MnO_2

$[MnO_4^{2-}\longrightarrow MnO_4^-+e^-]\times 2$

$MnO_4^{2-}+2H_2O+2e^-\longrightarrow MnO_2+4OH^-$

On addition, we get :

$$2MnO_4^-+MnO_4^-+2H_2O\longrightarrow 2MnO_4^-+MnO_2+4OH^-$$

$$3MnO_4^-+2H_2O\longrightarrow 2MnO_4^-+MnO_2+4OH^-$$

$$1\,MnO_4^-\longrightarrow \frac{2}{3}MnO_4^- \quad ; \quad 1\,MnO_4^-\longrightarrow \frac{1}{3}MnO_2$$

$RH_2+Ca^{2+}\longrightarrow RCa+2H^+$, $pH=2, [H^+]=10^{-2}M$

8.(A) $[Ca^{2+}]=5\times 10^{-3}$, mass of $Ca^{2+}=40\times 5\times 10^{-3}g$

Hardness in ppm of $Ca^{2+}=\dfrac{40\times 5\times 10^{-3}}{10^3}\times 10^6 = 200$

9.(D) Initial mmol of KOH = 500 × 0.1 = 50

$2KOH+CO_2\longrightarrow K_2CO_3+H_2O$

$K_2CO_3+BaCl_2\longrightarrow BaCO_3+2KCl$

$KOH+HCl\longrightarrow KCl+H_2O$

mmol of HCl = 30 × 0.1 = 3 ; mmol of KOH left unreacted in 50 mL solution = (50×0.1) –3 = 2

millimoles of KOH in 50 mL reacted with CO_2 = 2 ; millimoles of KOH in 500 mL reacted with CO_2 = 20

2 mol KOH = 1 mol CO_2 ; 20 mmol KOH = 10 mmol CO_2

Volume of CO_2 = $10\times 10^{-3}\times 22.4$ L

ppm of CO_2 = $\dfrac{10\times 10^{-3}\times 22.4}{224}\times 10^6 = 1000\text{ ppm}$

10.(C) mmol of $BaCO_3$ = mmol of K_2CO_3 = mmol of CO_2 = 1(considering in 50 mL)

$\dfrac{m_{BaCO_3}}{197}\times 1000=1,\quad m_{BaCO_3}=\dfrac{197}{1000}=0.197\text{ g}$

11.(A) $Fe + \underset{1\,mol}{Fe_2(SO_4)_3}\longrightarrow \underset{3\,mol}{3FeSO_4}$

$1\text{ mol }Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O\equiv 1\text{ mole }Fe_2(SO_4)_3$

$\dfrac{2.41}{964}\text{ mol }Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O\equiv\dfrac{2.41}{964}\text{ mole }Fe_2(SO_4)_3\equiv\dfrac{3\times 2.41}{964}\text{ mol }FeSO_4$

moles of $FeSO_4 = 0.0075$

12.(B) $Cu + \underset{1\,mol}{Fe_2(SO_4)_3} \longrightarrow \underset{2\,mol}{2FeSO_4} + CuSO_4$

[Note : – only $FeSO_4$ reacts with $K_2Cr_2O_7$ and not $CuSO_4$ as Cu is in its highest O.S].

$$\frac{2.41}{964}\,mol\,Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O \equiv \frac{2.41}{964}\,mole\;Fe_2(SO_4)_3 \equiv \frac{2\times 2.41}{964}\,mol\;FeSO_4$$

moles of $FeSO_4 = 0.005$

13.(C) meq of $FeSO_4$ = meq of $K_2Cr_2O_7$

$$1\times\left(\frac{3\times 2.41}{964}\right)\times 10^3 = 6\times\frac{1}{60}\times V \quad (\because \text{ n-factor of } FeSO_4 = 1 \text{ and } K_2Cr_2O_7 = +6\,)$$

$\Rightarrow \quad V = 75\ mL$

14.(AC) Cu^{2+} does not react with MnO_4^-. Only $C_2O_4^{2-}$ will react

meq of $MnO_4^- =$ meq of $C_2O_4^{2-}$

$20\times\frac{1}{4}\times 5 =$ meq of $C_2O_4^{2-} = 25$

m mol of $C_2O_4^{2-} = \frac{m\,eq}{n_f} = \frac{25}{2} = 12.5$

$$\underset{n_f=1}{2Cu^{2+}} + \underset{n_f=1/2}{4I^-} \longrightarrow Cu_2I_2 + I_2$$

$$\underset{n_f=2}{I_2} + \underset{n_f=1}{2S_2O_3^{2-}} \longrightarrow 2I^- + S_4O_6^{-2}$$

meq of Cu^{2+} = meq of KI = meq of I_2 = meq of $S_2O_3^{2-} = 25\times\frac{1}{10}\times 1 = 2.5$

m mol of $Cu^{2+}(n=1) = \frac{2.5}{1} = 2.5 \qquad \Rightarrow \qquad$ Difference in mmol of $C_2O_4^{2-}$ and Cu^{2+} = 12.5–2.5 = 10

15.(ABCD) $$Ca\left(\overset{+7}{Mn}O_4\right)_2 \longrightarrow Mn^{2+}$$

$n = 10$

meq of $Ca(MnO_4)_2$ = nMV = $10\times\frac{1}{10}\times 100 = 100$ meq

meq of $FeSO_4(n=1) = 1\times 1\times 100 = 100$ meq ; meq of $FeC_2O_4(n=3) = 3\times 1\times\frac{100}{3} = 100$ meq

meq of $K_2Cr_2O_7(n=6) = 6\times 1\times 16.6 = 100$ meq ; meq of $C_2O_4^{2-}(n=2) = 2\times 1\times 50 = 100$ meq

16.(ABC) $Na_2HPO_4 \rightleftharpoons 2Na^+ + HPO_4^{2-}$

$$\underset{\substack{Base\\ n=1}}{HPO_4^{2\ominus}} + \underset{acid}{H^+} \rightleftharpoons \underset{(n=1)}{H_2PO_4^{\ominus}} + H^+ \rightleftharpoons H_3PO_4$$

$$\underset{\substack{(n=2)\\ base}}{HPO_4^{2\ominus}} + 2H^+ \rightleftharpoons H_3PO_4 \quad ; \quad \underset{\substack{Acid\\ (n=1)}}{HPO_4^{2\ominus}} \rightleftharpoons H^+ + PO_4^{3\ominus}$$

17.(BCD) meq of H_2O_2 = meq of $KMnO_4$

$$\frac{w}{34/2}\times 1000 = 1\times 100\times\frac{1}{5} \quad\Rightarrow\quad w = 0.34\ g$$

In basic medium: $MnO_4^{\ominus} \longrightarrow MnO_4^{2-}$ (n = 1)

$H_2O_2 \longrightarrow O_2$ (n = 2)

18.(AB) $\underset{120\,\text{mmol}}{2HCl} + \underset{100\,\text{mmol}}{Ba(OH)_2} \longrightarrow BaCl_2 + 2H_2O$

L.R is HCl (Also 20 mL of water is also added)

mmol $Ba(OH)_2$ left = (100–60) = 40

mmol of OH^- in excess = 40 × 2 = 80

$[OH^-] = \frac{80}{100} = 0.8$; mmol of $BaCl_2$ = 60 ; mmol of Cl^- = 120

$[Cl^-] = \frac{120}{100} = 1.2M$; mmol of $Ba(OH)_2$ left + mmol of $BaCl_2$ = 40 + 60 = 100

$[Ba^{2+}] = \frac{100}{100} = 1$

19.(ABD)

$$\begin{array}{ccccc} H_2O & + & SO_3 & \longrightarrow & H_2SO_4 \\ 18 & & 80 & & 98 \\ 12 & & \frac{80}{18}\times 12 & & \frac{98}{18}\times 12 \\ & & = 53.3\text{ g} & & = 65.33\text{ g} \end{array}$$

(100 – 53.3) = 46.7 g of H_2SO_4 is initially present and 65.33 g of H_2SO_4 is newly formed on add of 12 g of water.

H_2SO_4 total = 65.33 + 46.7 = 112 g

But on addition of 9 g of water, moles of free $SO_3 = \frac{12}{18} - \frac{9}{18} = \frac{1}{6}$

Addition of 9 g of water will produce $\frac{98}{18} \times 9 = 49$ g of newly formed H_2SO_4.

Total H_2SO_4 = 49 + 46.7 = 95.7

20.(BD) 2 mol of HCO_3^- will make one mole each of $CaCO_3$, $CaCl_2$ and $MgCl_2$ to have equal hardness

ppm of $HCO_3^- = 61 \times 2 = 122$g in 10^6mL of H_2O

1 mol of $CaCO_3 = 100$ ppm; 1 mol of $CaCl_2 = 111$ ppm; 1 mol of $MgCl_2 = 95$ ppm

21.(AB) H_2O is L.R.

$$\begin{array}{ll} 6H_2O \longrightarrow & 4Fe(OH)_3 \\ 2\text{ mole} & \frac{4}{6}\times 2 = 1.33 \end{array}$$

22.(AB) Volume strength = 5.6 × N

$N_fV_f = N_1V_1 + N_2V_2 + N_3V_3$

0.5 L of each solution and 1.5 L of water makes final solution 3L

$N_{final} \times 3 = \frac{10}{5.6}\times 0.5 + \frac{15}{5.6}\times 0.5 + \frac{20}{5.6}\times 0.5$

$N_f = 1.34$

Volume strength of final solution = 1.34 ×5.6 = 7.5

23.(AD) $8MnO_4^- + 5S_2O_3^{2-} \longrightarrow 8Mn^{2+} + 10SO_4^{2-}$ (Acidic medium)

$\therefore$ 1 mole MnO_4^- oxidises $\frac{5}{8}$ mole $S_2O_3^{2-}$

Also, oxidation number of S changes from $+2$ to $+6$

In basic medium,

$$8MnO_4^- + S_2O_3^{2-} \longrightarrow 8MnO_4^{2-} + 2SO_4^{2-}$$

Change in medium from acidic to basic will change the nature of product & stoichiometry of reaction.

24.(AB) In Al_2O_3 – Al is in highest oxidation state of $+3$

$CrO_3 - Cr$ is in highest oxidation state of $+6$

25.(ABC) Oxidation reaction is $A_2O_n \longrightarrow 2AO_3^-$

$$1.34(10-2n) = 32.2\times0.05\times5$$

$$n = 2$$

$\therefore$ Molecular formula $\rightarrow$ A_2O_2

Empirical formula $\rightarrow$ AO

Since oxidation state of A changes from $+2$ to $+5$,

$\therefore$ It cannot be a Group-II metal

26.(AC) Number of equivalents of acid = Number of equivalents of base

$\therefore$ $\frac{1.25}{E_{acid}}\times1000 = 25\times0.25\times2 \Rightarrow E_{acid} = 100\,g$

If n-factor $= 2$, $M_0 = 200\,g$

n-factor $= 1$, $M_0 = 100\,g$

27.(AC) The hydrolysis reaction is

$$\underset{5\,mmol}{SO_2Cl_2} + 2H_2O \longrightarrow \underset{5\,mmol}{H_2SO_4} + \underset{10\,mmol}{2HCl}$$

$$M_{H_2SO_4} = \frac{5\,mmol}{100\,mL} = 0.05\,M$$

$$M_{HCl} = \frac{10\,mmol}{100\,mL} = 0.10\,M$$

10 mL stock solution has

$$= \underset{H_2SO_4}{\underline{10\times0.05\times2}} + \underset{HCl}{\underline{10\times0.10}} = 2\,\text{meq of acid}$$

$\therefore$ Volume of NaOH req. $= \frac{2}{0.2} = $ mL

28.(C) Let 100 mL mix (A) has R and S millimoles of NaOH and Na_2CO_3

At Phenolpthalein end pt: $a = R + S$

At Methyl orange end pt: $b = R + 2S$

Therefore $b - a = S$

$2a - b = R$

Let 100 mL of (B) has L & M millimoles of $NaHCO_3$ & Na_2CO_3

At Pthenolphtalein end point: $x = M$

At Methyl orange end point : $y = 2M + L$

Therefore $L = y - 2x$

29.(B) **(P) – 3** eq of $Fe_2(C_2O_4)_3$ + eq of FeC_2O_4 = eq of $KMnO_4$

$2.5 \times 6 + 2.5 \times 3 = 5 \times x$

$x = 4.5$

(Q)–4 eq of $Fe_2(C_2O_4)_3$ + eq of FeC_2O_4 = eq of $K_2Cr_2O_7$

$2.5 \times 6 + 2.5 \times 3 = 6 \times x$

$x = 3.75$

(R)–2 eq of CuS + eq of Cu_2S = eq of $KMnO_4$

$2.5 \times 6 + 8 \times 2.5 = 5 \times x$

$x = 7$

(S)–1 eq of $KMnO_4$ + eq of $K_2Cr_2O_7$ = eq of H_2O_2

$2 \times 5 + 2 \times 6 = x \times 2$

$x = 11$

30.(C) Reciprocal of n-factor is the molar ratio.

(P)–2 $\underset{n=3}{FeC_2O_4} + \underset{n=6}{Cr_2O_7^{2-}} \longrightarrow$

Molar Ratio of RA to OA is 2:1

(Q) –4 $\underset{n=2}{H_2O_2} + \underset{n=3}{Cr(OH)_3} \longrightarrow$

Molar Ratio of RA to OA is 2:3

(R) –3 $\underset{n=6}{N_2H_4} + \underset{n=2}{Cu(OH)_2} \longrightarrow$

Molar Ratio of RA to OA is 1:3

(S) –1 $\underset{n=2}{C_2O_4^{2-}} + \underset{n=3}{MnO_4^-} \longrightarrow MnO_2 + CO_2$

Molar Ratio of RA to OA is 3:2

31.(D) **(P) –3** $\underset{5\text{ mol}}{N_2} + \underset{9\text{ mol}}{3H_2} \longrightarrow \underset{6\text{ mol}}{2NH_3}$

L.R is H_2, % yield is 80. Therefore, moles of NH_3 produced, $\frac{x}{6} \times 100 = 80, \quad x = 4.8$

(Q) –1 $\underset{12\text{ mol}}{2C} + \underset{5\text{ mol}}{H_2} \longrightarrow \underset{5\text{ mol}}{C_2H_2}$

L.R is H_2, % yield is 70. Therefore, moles of NH_3 produced, $\frac{x}{5} \times 100 = 70, \quad x = 3.5$

(R)–2 $\underset{5\text{ mol}}{P_4} + \underset{20\text{ mol}}{5O_2} \longrightarrow \underset{8\text{ mol}}{2P_2O_5}$

L.R is O_2, % yield is 50. Therefore, moles of P_2O_5 produced, $\frac{x}{8} \times 100 = 50, \; x = 4$

(S)–4 $\underset{4\text{ mol}}{2SO_2} + \underset{3\text{ mol}}{O_2} \longrightarrow \underset{4\text{ mol}}{2SO_3}$

L.R is SO_2, % yield is 75.

Therefore, moles of SO_3 produced, $\frac{x}{4} \times 100 = 75, \; x = 3$

32.(5) $2\,K\overset{+7}{Mn}O_4 + 16H\overset{-1}{Cl} \longrightarrow 2KCl + 2MnCl_2 + 5\overset{0}{Cl_2} + 8H_2O$

2 mole of $KMnO_4$ gained $10e^-$.

Therefore 10 mol of HCl has lost $10e^-$ .For this to happen 10 mole of HCl is acting as reducing agent. So for per mole of $KMnO_4$ 5 mole of HCl as RA is required.

33.(4) $CH_3(CH_2)_nCOOH + \left(\frac{3n+4}{2}\right)O_2 \longrightarrow (n+2)CO_2 + \left(\frac{2n+4}{2}\right)H_2O$

1 mole of acid = (n + 2) mol of CO_2.

$$\frac{0.58}{60+14n} \text{ mol of acid} = \frac{n+2}{(60+14n)} \times 0.58 \text{ mol of } CO_2$$

This CO_2 is passed through excess of NaOH where CO_2 is converted to Na_2CO_3 and some NaOH is left.

With Phenolpthalin $\underset{\text{meq=a}}{Na_2CO_3} + HCl \longrightarrow NaCl + NaHCO_3$

$\underset{\text{meq=b}}{NaOH} + HCl \longrightarrow NaCl + H_2O$

$\frac{a}{2} + b = 50 \times 1$ .... (i)

With methyl orange $\underset{\text{meq= a}}{Na_2CO_3} + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

$\underset{\text{meq= b}}{NaOH} + HCl \longrightarrow NaCl + H_2O$

$a + b = 80$ .... (ii)

From (i) to (ii)

a(Mg of Na_2CO_3) = 60, b(meq of NaOH left) =20

meq of Na_2CO_3 = meq of CO_2

$$60 = \frac{(n+2)0.58}{60+14n} \times 2 \times 10^3 = n = 4$$

34.(9) $2IO_3^{\ominus} + 10I^{\ominus} + 12H^+ \longrightarrow 6I_2 + 6H_2O$

$2\text{mol } IO_3^- \longrightarrow 6 \text{ mol } I_2$; $1 \text{ mol } IO_3^- \longrightarrow 3 \text{ mol } I_2$

$$\% \text{ yield } = \frac{0.27}{3} \times 100 = 9$$

35.(1) $4\overset{0}{Mg} + 10H\overset{+5}{N}O_3 \longrightarrow 4\overset{+2}{Mg}(NO_3)_2 + \overset{+1}{N_2}O + 5H_2O$

4 mole of Mg required = 2 mole of HNO_3 as RA

2 mole of Mg required = 1 mole of HNO_3

36.(0.82)

Reaction	**Change in ON**
$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$	2 units
$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1 unit
$Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$	6 units

Thus, $0.04\,M\,Sn^{2+} = 0.08\,N\,Sn^{2+}$

$x\,M\,Fe^{2+} = x\,N\,Fe^{2+}$

$0.125\,M\,Cr_2O_7^{2-} = 0.125 \times 6 = 0.750\,N\,Cr_2O_7^{2-}$

Equivalent of Fe^{2+} + Equivalent of Sn^{2+} = Equivalent of $Cr_2O_7^{2-}$

$$\frac{15 \times 0.08}{1000} + \frac{15x}{1000} = \frac{18 \times 0.750}{1000}$$

$1.2 + 15x = 13.5 \Rightarrow 15x = 12.3 \Rightarrow x = 0.82\,M$

37.(1.75) Fe^{2+} is 1.0 ppm

Thus, 10^6 g solution has $Fe^{2+} = 1\,g$

$250\,mL (= 250\,g)$ solution has $Fe^{2+} = \frac{250}{10^6}\,g$ (Note $d = 1\,g/mL$)

$56\,g$ of Fe^{2+} is in $= 392\,g$ salt

$\therefore \quad \frac{250}{10^6}$ g of Fe^{2+} is in $= \frac{392}{56} \times \frac{250}{10^6}$ g $= 1.75 \times 10^{-3}$ g

38.(200) $RH_2 \; + \; Ca^{2+} \; \rightarrow \; RCa \; + \; 2H^+$

1 mol $\qquad$ 2 mol

? $\qquad$ 0.01 mol L^{-1}

When $[H^+]$ is 2 mol then, $[Ca^{2+}]$ is $= 1$ mol

When $[H^+]$ is 0.01 mol then $[Ca^+]$ is $= \frac{0.01}{2}$ mol L^{-1}

$\therefore \quad [Ca^{2+}] = 0.005\,M = 0.005 \times 40\,g\,L^{-1} = 0.2\,g\,L^{-1}$

1000 mL of water has $[Ca^{2+}] = 0.2\,g$

10^6 mL (parts per million) has $[Ca^{2+}] = \frac{0.2 \times 10^6}{10^3} = 200$

39.(3.12) Given reaction is not balanced

Based on stoichiometry

1 mol Na_2CO_3 is from 2 mol $NaHCO_3$

2 mol $NaHCO_3$ is from 2 mol NH_4HCO_3

2 mol NH_4HCO_3 is from 2 mol NH_3

Thus, 1 mol Na_2CO_3 is form $= 2$ mol NH_3

106 g Na_2CO_3 is from $= 2 \times 17$ g NH_3

34 g NH_3 gives $= 106$ g Na_2CO_3

Thus, 1000 g NH_3 gives $= \frac{106 \times 1000}{34}$ g $Na_2CO_3 = 3118$ g $Na_2CO_3 = 3.118$ kg Na_2CO_3

40.(44.25) 2 moles Na_2CO_3 give $= 4$ moles $NaNO_2$

0.3375 mole Na_2CO_3 gives

$= 2 \times 0.3375 = 0.6750$ mol $NaNO_2$

$= 0.6750 \times 69$ g $NaNO_2$

$= 46.575$ g $NaNO_2$ with 100% yield

$= 46.575 \times 0.95$ g $NaNO_2$ with 95% yield $= 44.2462$ g

41.(1.104)

$Na_2SO_4 \rightleftharpoons 2Na^+ \; + \; SO_4^{2-}$

1 mole $\qquad$ 2 moles $\qquad$ 1 mole

$Na_2SO_4 = 6.0$ micromoles $= 6.0 \times 10^{-6}$ mole

$\therefore \quad Na^+$ ions $= 2 \times 6.0 \times 10^{-6}$ mole $= 2 \times 6.0 \times 10^{-6} \times 23$ g

In 250 mL solution (250 g H_2O being dilute solution)

250 g H_2O has Na^+ ions $= 2 \times 6.0 \times 10^{-6} \times 23$ g

10^6 g (per million) H_2O has Na^+ ions $= \frac{2 \times 6.0 \times 10^{-6} \times 23 \times 10^6}{250} = 1.104$ g $= 1.104$ ppm

Atomic Structure

1.(B) As we know at radial nodes

$$\psi_{2s}^2 = 0 \quad \Rightarrow \quad 2 - \frac{r}{a_0} = 0 \quad \Rightarrow \quad r = 2a_0$$

2.(C)

$n_1 \to n_2$;	$n_2 \to 2$
$10 \cdot 2eV$	$17 \cdot 0eV$
$n_1 \to n_3$;	$n_3 \to 3$
$4 \cdot 25eV$	$5.95eV$

For $n_1 \to 2$ $\underset{n_1 \to 2}{\Delta E_1} = 13 \cdot 6 \times Z^2 \times \left(\frac{1}{2^2} - \frac{2}{n_1^2} \right) = 10 \cdot 2 + 17$

For $n_1 \to 3$ $\underset{n_1 \to 3}{\Delta E_2} = 13 \cdot 6 \times Z^2 \times \left(\frac{1}{3^2} - \frac{2}{n_1^2} \right) = 4 \cdot 25 + 5 \cdot 95$

Use subtraction to eliminate $\frac{1}{n_1^2}$ & get $Z = 3$

3.(B) First line is $3 \to 2$.

$$\Rightarrow \quad h\upsilon_0 = 13.6 \ .(1)^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

For He^+

$h\upsilon = 13.6 \times 2^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$ Hence $\upsilon = 4\upsilon_0$

4.(A) Angular Momentum: $mvr = \frac{nh}{2\pi}$

$$3.1652 \times 10^{-34} = \frac{n \times 6.6 \times 10^{-34}}{2\pi}$$

$n = 3$

$$\therefore \quad \bar{v} = R.\ Z^2. \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\bar{v} = R \cdot 1^2 \left(\frac{1}{1^2} - \frac{1}{3^2} \right) \Rightarrow R \left(\frac{8}{9} \right)$$

5.(A) For H : $\Delta E_{3 \to 1} = E_3 - E_1 = 13.6 \left[\frac{1}{1} - \frac{1}{9} \right]$ eV **...(1)**

For He^+ : $\Delta E = 13.6 \times 4 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ eV $= 13.6 \times 4 \left[\frac{1}{4} - \frac{1}{36} \right]$ eV **...(2)**

On comparison : $n_1 = 2,\ n_2 = 6$

6.(D) Check by option. Only $4 \to 1$ overall transition satisfies all the three condition $4 \to 1$ can be broken into

(i) $\underbrace{4 \to 2}_{\text{Balmer}};\ \underbrace{2 \to 1}_{\text{Lyman}}$ (ii) $\underbrace{4 \to 3}_{\text{Paschen}};\ \underbrace{3 \to 2}_{\text{Balmer}};\ \underbrace{2 \to 1}_{\text{Lyman}}$ (iii) $\underbrace{4 \to 3}_{\text{Paschen}};\ \underbrace{3 \to 1}_{\text{Lyman}}$

7.(A) $E_n = -\frac{13.6}{n^2}\text{eV}; E_2 = -\frac{13.6}{2^2}; E_4 = -\frac{13.6}{4^2}\text{ eV/atom}$

$\Delta E = E_4 - E_2 = 2.55\text{ eV}$

Absorbed energy = work function of metal + KE_{max}

$2.55 = 2 + KE_{max}$

$KE_{max} = 0.55\text{ eV}$

8.(C) $O_2 \xrightarrow{h\nu} O_{Normal} + O_{Excited}$

$O_2 \longrightarrow O_{Normal} + O_{Normal}$

Energy required for simple dissociation of O_2 into the normal atoms $498 \times 10^3\text{ J/mol}$

$$= \frac{498 \times 10^3}{6.023 \times 10^{23}}\text{ J/mol} = 82.68 \times 10^{-20}\text{ J/mol}$$

If one atom in excited state has more energy i.e. 2.5eV

$$= 2.5 \times 1.602 \times 10^{-19} = 4 \times 10^{-19} = 40 \times 10^{-20}\text{ J}$$

Total energy $= \left(82.68 \times 10^{-20}\right) + \left(40 \times 10^{-20}\right)\text{J} = 122.68 \times 10^{-20}\text{ J}$

$\therefore \quad E = \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{122.68 \times 10^{-20}} = 163\text{nm}$

9.(B) $\frac{1}{\lambda} = R(z)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \Rightarrow \quad \frac{1}{x} = R(2)^2(1-0)$

$\frac{1}{y} = R(3)^2\left(\frac{1}{4} - 0\right) \quad \Rightarrow \quad y = \frac{16}{9}x\text{ A°}$

10.(B) Using formula $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$ = number of spectral lines

$\lambda_{min} = \Delta E_{max} \Rightarrow 4 \to 1$ transition

$\frac{1}{\lambda} = RZ^2\left(\frac{1}{1^2} - \frac{1}{4^2}\right)$

$\lambda_{min} = \frac{4}{15R}$

11.(D) $\underset{4\to2}{\Delta E}(He^+) = 13 \cdot 6 \times 2^2 \times \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 13 \cdot 6 \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \underset{2\to1}{\Delta E}(H)$

12.(C) M shell $\Rightarrow n = 3$

Transitions possible are $3 \to 2; 2 \to 1; 3 \to 1$

13.(D) Lyman lines can still be observed if e^- falls to 2nd and 3rd orbit

14.(C) Range for Brackett series for H-atom is 1500 – 4000 nm

Similar range for Li^{2+} would be 166 to 450 nm

15.(D) Range for Brackett series for H-atom is 1500 – 4000 nm

Similar range for He^+ would be 375 to 1000 nm

16.(B) For H atom,

$$\Delta E = 13 \cdot 6 \times 1^2 \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 13 \cdot 6 \times 3^2 \times \left(\frac{1}{(3n_1)^2} - \frac{1}{(3n_2)^2}\right)$$

For corresponding transition in H is atom transition state should be divisible by 3.

17.(D) Energy of photon incident = $\dfrac{1242}{12.42}$ = 100 eV

18.(B) $\lambda = \dfrac{h}{\sqrt{2mKE}} = \dfrac{6.6\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times75\times1.6\times10^{-19}}} = 1.4\text{ Å}$

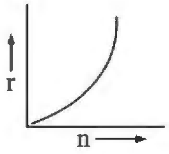
19.(A) $\lambda = \dfrac{h}{p} \Rightarrow d\lambda = -\dfrac{hd\rho}{p^2} \Rightarrow |\Delta\lambda| = \dfrac{h\lambda^2}{h^2}\Delta p = \dfrac{\left(1.4\times10^{-10}\right)^2\times6.62\times10^{-28}}{6.62\times10^{-34}} \Rightarrow |\Delta\lambda| = 1.96\times10^{-14}\text{m}$

20.(AB) Radius $= 0.529\dfrac{n^2}{z}$

$r \propto n^2$

$r \propto \dfrac{1}{z}$

So, r v/s n is

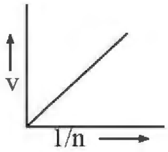


$\Rightarrow$ velocity $= 2.18\times10^6\dfrac{z}{n}$ m/s

$V \propto z$

$V \propto \dfrac{1}{n}$

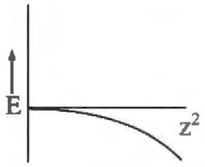
So, v v/s 1/n is



$\Rightarrow$ $E = -13.6\dfrac{z^2}{n^2}$ ev/atom

$E \propto z^2$

$E \propto \dfrac{1}{n^2}$



So, E v/s z^2

21.(ABD) Since six different wavelengths are emitted highest state is 4.
Since three wavelengths are shorter
$\Rightarrow$ Three transitions are releasing more energy that what was absorbed
Hence initial orbity may be 2.

Initially e^- were in n = 2 and were excited to n = 4. Six possible lines

$$\begin{matrix}4\to3\\4\to2\\3\to2\end{matrix}\quad\left\{\begin{matrix}3\to1\\4\to1\\2\to1\end{matrix}\right\}\to\lambda<\lambda_0$$

22.(ABD) BE for (n = 3) = $1.51Z^2 = 12\text{eV}$ (given)

$\therefore\quad Z^2 = 12/1.51$

I Excitation potential $= 10.2Z^2 = 10.2\times(12/1.51) = 81\text{V}$

II Excitation potential $= 12.09Z^2 = 12.09\times(12/1.51) = 96\text{eV}$

Ionisation potential $= 13.6Z^2 = 13.6\times(12/1.51) = 108\text{V}$

BE of (n = 2) = $3.4Z^2 = 3.4\times(12\times1.51) = 27\text{eV}$

23.(ABC) $4.25 = (W_0)_A + (\text{K.E.})_A$

$4.70 = (W_0)_B + (\text{K.E.})_A - 1.5$

So $(W_0)_B - (W_0)_A = 0.45 + 1.5 = 1.95$

Now, $\lambda_B = 2\lambda_A$

$$\frac{h}{\sqrt{2m(K.E)_B}} = \frac{2h}{\sqrt{2m(K.E)_A}}$$

So $(K.E)_A = 4(K.E)_B$

$4.25-(W_0)_A = 4[4.7-(W_0)_B]$

$4(W_0)_B-(W_0)_A = 14.55$

So $(W_0)_B = 4.2\,eV$

So $(W_0)_A = 2.25\,eV$

$(K.E.)_A = 2\,eV$

$(K.E.)_B = 0.5\,eV$

24.(AB) **(A)** Only first four spectral lines belonging to Balmer series in hydrogen spectrum lie in visible region.

(B) If a light of frequency ν falls on a metal surface having work functional $h\nu$, photoelectric effect will take place only if $\nu \geq \nu_0$, since ν_0 is the minimum frequency required for photoelectric effect.

25.(ABCD) Refer to Theory.

26.(AB) Refer to Theory

27.(6) $\frac{\lambda_1}{\lambda_2} = \frac{n_1}{n_2} \Rightarrow \frac{3}{1} = \frac{n}{2} \Rightarrow n = 6$

28.(4) Radial node $= n-\ell-1$

Angular node $= \ell$

Total node = $n-1$

5f orbital $= n=5,\ \ell=3$

Total node $5-1=4$

29.(4) Radius $= 0.529\frac{n^2}{z}$

$r_{(n+1)} - r_n = r_{(n-1)}$

$$0.529\frac{(n+1)^2}{z} - 0.529\frac{n^2}{z} = 0.529\frac{(n-1)^2}{z}$$

For hydrogen atom $z=1$

$(n+1)^2 - n^2 = (n-1)^2$

$n^2+1+2n-n^2 = n^2+1-2n$

$4n = n^2$

$n = 4$

30.(4) $2\pi r_n = n\lambda$

$2n\pi r_1 = \lambda$

$$n = \frac{\lambda}{2\pi r_1} = \frac{1340}{(2)(3.14)(53)} = 4$$

31.(199.26)

Photoelectric effect is represented by

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$h\nu = W_0 + \frac{1}{2}mv^2 = (\text{work function}) + \text{KE}$$

$$\therefore \qquad \nu = \frac{\text{work function}}{h} + \frac{\text{KE}}{h}$$

Graph between ν (y-axis) and $\frac{\text{KE}}{h}$ (x-axis) is a straight line with

$$OA = 5 \times 10^{14}\,\text{s}^{-1}$$

Thus, $\frac{W_0}{h} = 5 \times 10^{14}\,\text{s}^{-1}\,\text{atom}^{-1}$

$$W_0 = h \times 5 \times 10^{14}\,\text{s}^{-1}\,\text{atom}^{-1}$$

$$W_0 = 6.62 \times 10^{-34}\,\text{Js} \times 5 \times 10^{14}\,\text{s}^{-1} \times 6.02 \times 10^{23}\,\text{J mol}^{-1} = 199262\,\text{J mol}^{-1} = 199.262\,\text{kJ mol}^{-1}$$

32.(-1.22)

Binding energy is the minimum energy to which electron is bound to nucleus or which is required to eject the electron. Thus, binding energy $= -$threshold energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34}\,\text{Js} \times 3.0 \times 10^{8}\,\text{ms}^{-1}}{150 \times 10^{-12}\,\text{m}} = 1.324 \times 10^{-16}\,\text{J}$$

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2} \times 9.11 \times 10^{-31}\,\text{kg} \times (1.5 \times 10^{7})^2\,\text{m}^2\text{s}^{-2} = 1.025 \times 10^{-16}\,\text{J}$$

Thus, $E = h\nu_0 + \frac{1}{2}mv^2 = W_0 + \frac{1}{2}mv^2 = W_0 + \text{KE}$

$$\therefore \qquad W_0 = (E - \text{KE}) = 1.324 \times 10^{-15}\,\text{J} - 0.102 \times 10^{-16}\,\text{J} = 1.222 \times 10^{-15}\,\text{J}$$

$$\therefore \qquad \text{Binding energy} = -1.222 \times 10^{-15}\,\text{J}$$

33.(5) For He atom $(\Delta x \cdot \Delta p)_{He} \ge \frac{h}{4\pi}$ and for electron $(\Delta x \cdot \Delta p)_{electron} \ge \frac{h}{4\pi}$

$$(\Delta x)_{helium} = (\Delta x)_{electron} = \pm 1.00\,\text{mm} = \pm 100 \times 1.00 \times 10^{-3}\,\text{m}$$

Hence, $(\Delta p)_{helium} = (\Delta p)_{electron} = 5.0 \times 10^{-26}\,\text{kg ms}^{-1}$

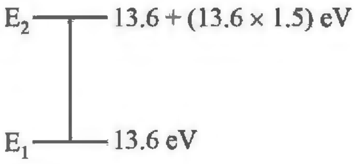
34.(20.4)

$E_1 =$ Energy of H-atom in the ground state $= 13.6\,\text{eV}$

Energy absorbed $= (13.6 \times 1.5) = 20.4\,\text{eV}$

$E_2 =$ Energy of the excited state $= 13.6 + 20.4 = 34.0\,\text{eV}$

$\Delta E = \text{KE} = (E_2 - E_1) = 34.0 - 13.6 = 20.4\,\text{eV}$



35.(173.9) $O_2 \longrightarrow O + O^*$

$$\Delta H^\circ = 498\,\text{kJ mol}^{-1} = \frac{498 \times 10^3\,\text{J}}{6.02 \times 10^{23}}\,\text{J molecule}^{-1} = 8.27 \times 10^{-19}\,\text{J molecule}^{-1}$$

Energy required to convert normal (O) into (O*) $= 1.967\,\text{eV}$

$$= 1.967 \times 1.6 \times 10^{-19}\,\text{J} = 3.147 \times 10^{-19}\,\text{J}$$

Total Energy $= (8.27 \times 10^{-19} + 3.15 \times 10^{-19}) = 1.142 \times 10^{-18}\,\text{J}$

Thus, $\lambda = \frac{hc}{E} = \frac{6.62 \times 10^{-34}\,\text{Js} \times 3 \times 10^{8}\,\text{ms}^{-1}}{1.142 \times 10^{-18}\,\text{J}} = 1.739 \times 10^{7} = 173.9 \times 10^{-9} \simeq 174\,\text{nm}$

Gaseous State

1.(C) $\underset{x}{CO_{(g)}} + \underset{x/2}{\frac{1}{2}O_{2(g)}} \rightarrow CO_{2(g)};$

$\underset{y}{N_{2(g)}} + \underset{y}{O_{2(g)}} \rightarrow 2NO_{(g)}$

$x + y = 10$ **...(i)**

$\frac{x}{2} + y = 7$ **...(ii)**

Solving equation (i) and (ii) $x = 6 \,\&\, y = 4$

2.(B) P.L = w *air displaced* – (weight of balloon + weight of gas)

$W_{\text{air displaced}} = v \times d = \frac{4}{3} \times \frac{22}{7} \times (10)^3 \times 1.2 = 5028.6\text{kg}$

$PL = 5028.6 - \left(100 + \frac{PVM}{RT}\right) \quad \left[PV = \frac{wRT}{M} \text{ for He}\right]$

$= 5028.6 - (100 + 1117.5) = 3811.1 \text{ kg}$

3.(C) KE per mole = $\frac{3}{2}RT$

KE per molecule = $\frac{3}{2}\frac{RT}{N} = \frac{3}{2}KT \qquad \left[K = \frac{R}{N}\right]$

4.(D) K.E. $\propto$ T in K.

5.(B) At critical point pressure applied is minimum and below this point gas can be liquified easily.

6.(C) Vapour pressure is pressure corresponding to the liquifaction curve.

7.(B) At temperature above critical temperature gas can't be liquefied whatever pressure is applied.

8.(D) For liquifaction 'a' should be greater and 'b' should be smaller.

9.(C) $PV = nRT$ If V constant $P \propto T \therefore T_1 > T_2 > T_3$

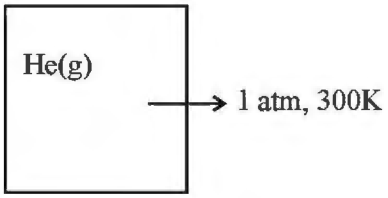
10.(C) $PM = dRT,$

$\frac{P_A}{P_B} = \frac{d_A}{M_A} \times \frac{M_B}{d_B}; \ \frac{P_A}{P_B} = \frac{3}{1.5} \times \frac{M_B}{\frac{M_B}{2}} = 4$

11.(C) $E_K = \frac{3}{2}KTN$

$\frac{E_1}{E_2} = \frac{T_1N_1}{T_2N_2}; \ \frac{E_k}{2E_k} = \frac{150N}{300N_2}; \ N_2 = N$

12.(D) $P_{(g)} \rightarrow Q_{(g)} + R_{(g)}$



$$n_{He} = \frac{V \times 1}{R \times 300}$$

$$n_{He} + \eta_p = \frac{2 \times V}{R \times 400}.$$

$$n_p = \frac{2V}{400R} - \frac{V}{300R} = \frac{600V - 400V}{120000R} = \frac{200V}{120000R} = \frac{1V}{600R}$$

After heating moles $= \frac{2V}{600R} \quad \therefore \quad n_T = \frac{2V}{600R} + \frac{V}{300R} = \frac{600V + 600V}{180000R} = \frac{1200V}{180000R}$

$$P = \left(\frac{12V}{1800R}\right) \times \frac{R \times 600}{V} = 4$$

13.(D) $\frac{P_1V_1}{P_2V_2} = \frac{Z_1nRT_1}{Z_2nRT_2}; \ V_2 = 4$

14.(B) $PM = dRT$

15.(C)

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

t = 0 11 12 –

t = eq 9 6 4

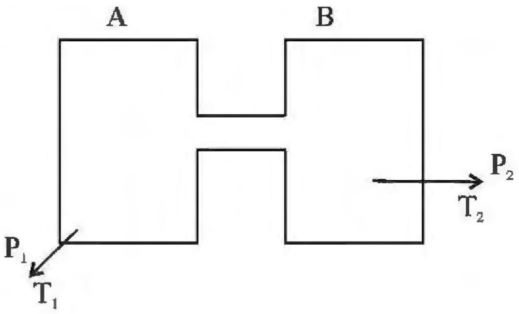
$NH_{3(g)} + H_2O_{(l)} \rightarrow NH_4OH_{(l)}$

3.58 L

Free volume for gases 20 – 3.58 = 16.42

Gaseous moles = $n_{N_2} + n_{H_2}$ at t_{eq}

$PV = nRT \rightarrow 22.5\text{atm}$



16.(B) $T_1 > T_2$

$\therefore$ x moles will move to B

$$P_A V = (n-x)RT_1$$

$$P_A V = (n+x)RT_2$$

$$x = \frac{n(T_1 - T_2)}{T_1 + T_2}$$

Finally $P_1 \times 2V = 2nRT_1$

$V = \frac{nRT_1}{P_1}$ substitute in above and calculate P_A

17.(ABC) $V \propto T$ (constant n and P)

18.(ABD) As temperature increased number of collision increases, hence presence of gas molecules increases. The energy of gas molecules also increases due to increase of T.

19.(BD) $U = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}}$, U will be doubled when P or T is made 4 times at constant volume

20.(ABC) Refer to theory

21.(BCD) With increase in T molecules with less speed will becomes less and with more speed will increase and with near about mps will also increase.

22.(BC) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT,\ T_b = \frac{a}{Rb}$

$T_b = \frac{a}{Rb}$ and $T_C = \frac{8a}{27Rb}$ $\quad\therefore\quad T_b > T_c$

23.(AC) For negligible size, $V_m >> b$

For negligible intermolecular forces, $P >> \frac{a}{V_m^2}$

$\therefore$ when $V_m >> b, \left(P + \frac{a}{V_m^2}\right)(V_m) = RT$

When $V_m >> b$ & $P >> \frac{a}{V_m^2}$, then $(P)(V_m) = RT$

$\Rightarrow \frac{PV_m}{RT} = 1 \quad \Rightarrow \quad Z = 1$

When $P >> \frac{a}{V_m^2}$, then $(P)(V_m - b) = RT$

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

$\Rightarrow Z = 1 + \frac{Pb}{RT}$

24.(BC) $\lambda = \frac{U_{av}}{Z_1},\ Z_1 = \sqrt{2}\pi\sigma^2 V_{av} N^*;\ \left[N^* = \frac{N}{V}\right]$

25.(CD) $n_f + \frac{2}{3}n_f = \frac{3n_f + 2n_f}{3} = \frac{5}{3}n_f$

$$\frac{5}{3}n_f \times 300 = n_f T$$

$$T = 500 \text{ K}$$

26.(AD) At very law pressure, $V_m >> b$

$\therefore \quad z = 1 - \frac{a}{RTV_m}$

At high pressures, $P >> \frac{a}{V_m^2}$

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

27.(ABD) $15 \times 1.24 = Z \times 0.0821 \times 250$

$PV = nRT$

$15V = 1 \times 0.0821 \times 250$

$V = 1.366$

$V = 1.368 - 0.12 = 1.24$

28.(B) Refer to theory

29.(AC) Equal no. of moles of both He & Ne shall exert equal pressure.

Average molecular speed, $C_{avg} = \sqrt{\dfrac{8RT}{\pi M}}$

$\therefore$ Helium has higher C_{avg} than Neon

30.(CD) At constant V & n,

$$P \propto T$$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \Rightarrow \frac{P_2}{1\,\text{atm}} = \frac{273}{546} \Rightarrow \boxed{P_2 = \frac{1}{2}\text{ atm}}$$

31.(AD) $Z = \dfrac{(V_m)_{real}}{(V_m)_{ideal}} > 1$

At STP, $(V_m)_{ideal} = 22.4L$

$\therefore$ $(V_m)_{real} > 22.4L$

As Z > 1, the gas will become less liquefiable.

32.(ABC) At critical temperature, T_C, densities of liquid and gas become same.

33.(AC) For H & He, Z is always greater than 1

For all other real gases,

Z < 1 at low pressure

34. **[A-s] → [B-p] → [C-r] → [D-q]**

$A \rightarrow T = \dfrac{PV}{nR}$

On moving along the line from i to f, P × V will increase or decrease depending upon the equation of straight line.

B → At constant temperature, $P \propto 1/V$

C → At constant volume, $P \propto T$

D → At constant pressure, $V \propto T$

35. **[A-p, q, r] → [B-s] → [C-s] → [D-s]**

Molecular speed of gas molecules is dependent on temperature and molecular mass of molecules.

$\therefore$ At constant temperature, speed of gas molecules will not change Also, $PM = dRT$

If density S is lowered, pressure also decreases in same proportion hence speed remains constant $\left[C \propto \sqrt{\dfrac{P}{\text{density}}}\right]$

36.(6) Volume of CH_4; x mL

Volume of CO; y mL

Volume of Ne: z mL

Final reduction of volume when passed through alkaline pyrogallol indicates there was residual oxygen.

Pyrogallol in alkaline medium absorbs oxygen. Thus, O_2 was not the limiting reagent.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$x \qquad 2x \qquad x$$

$$CO + 1/2\,O_2 \rightarrow CO_2$$
$$y \qquad y/2 \qquad y$$

Reduction of volume when passed through KOH means:

$x + y = 9$ mL (must be CO_2) …….(i)

Total volume initially used 40 + 10 = 50 mL

On cooling 36.5 mL means (H_2O gets condensed)

$$\underbrace{2x+\frac{y}{2}}_{\text{Oxygen consumed}} = 50-36.5=13.5\,\text{mL}$$

Thus solving (i) and (ii) equations x = 6 mL, y = 3 mL

37.(3) $C_xH_y + O_2 \rightarrow CO_2 + H_2O$

$16\,\text{mol} \quad 48\,\text{mol} \quad 48\,\text{mol}$

Applying POAC for 'C'

$$x \times 16 = 1 \times 48$$

$$x = 3$$

Applying POAC for 'H'

$$y \times 16 = 2 \times 48$$

$$y = 6$$

So, the formula of hydrocarbon is C_3H_6.

38.(2) $\frac{P_1V_1}{P_2V_2} = \frac{n_1T_1}{n_2T_2}$

$$\frac{n_1}{n_2} = \frac{P_1V_1T_2}{P_2V_2T_1}$$

$$\frac{n_1}{n_2} = \frac{1.5 \times 16.4 \times 500}{4.1 \times 5 \times 300} = \frac{2}{1}$$

39.(4) Volume of molecule in motion = 4×volume of molecule in rest

40.(7) Let m be the mass of SO_3 and O_2 enclosed in the vessel.

Number of moles of $SO_3 = \frac{m}{80}$

Number of moles of $O_2 = \frac{m}{32}$

Partial pressure of SO_3, $P_A = \frac{m}{80} \times \frac{R \times T}{V}$

Partial pressure of O_2, $P_A = \frac{m}{32} \times \frac{R \times T}{V}$

Now $\frac{P_A}{P_B} = \frac{m}{80} \times \frac{32}{m} = \frac{2}{5}$

Hence, the sum of the ratio of partial pressures of SO_3 and O_2 is 2 + 5 = 7

41.(4) Under identical conditions of T and P, volumes are in the ratio of their number of moles. Moles of CH_4 = 1.2/16.

Moles of hydrocarbon, $C_nH_{2n-2} = 8.1/M$

$$\therefore \quad \frac{1.2/16}{8.1/M} = \frac{1L}{2L} \text{ or } M = 54$$

Molecular mass of $C_nH_{2n-2} = 12n + 2n - 2 = 54$

$$14n = 56$$

$$n = 4.$$

42.(7) $P_1V_1 = n_1RT$, for the first bulb

$P_2V_2 = n_2RT$, for the second bulb

or $\quad P_1V_1 + P_2V_2 = (n_1+n_2)RT, \quad$ **...(i)**

When stopcock is opened; the total volume is (V_1 + V_2) and total no. of moles is (n_1+n_2). Suppose the equilibrium pressure at each bulb is P atm. Then,

$$P(V_1+V_2)=(n_1+n_2)RT \qquad \textbf{...(ii)}$$

From equations (i) and (ii), we have, $P_1V_1+P_2V_2=P(V_1+V_2)$

or $\quad 9\times5+6\times10=P\times15$

$P=7$ atm

43.(4) Given, $T_1=400K,\ T_2=60K$

Molecular weight of X, $M_1=40$

Molecular weight of Y, $M_2=?$

$$U_{rms(x)}=\sqrt{\frac{3RT_1}{M_1}},U_{mp(y)}=\sqrt{\frac{2RT_2}{M_2}}$$

Given, $v_{rms(x)}=v_{mp(y)}\quad\therefore\quad \sqrt{\frac{3R\times400}{40}}=\sqrt{\frac{2R\times60}{M_2}}$

$$30=\frac{120}{M_2}\quad\Rightarrow\quad M_2=4$$

44(5.26) $CO+H_2O\longrightarrow CO_2+H_2$

1 mol of CO will produce 1 mol H_2

$\Rightarrow$ 22.4 L of CO at STP will produce 22.4 L of H_2

$\Rightarrow$ Water gas sample contains 50% H_2, 45% CO and 5% CO_2

1 L of sample contains 0.45 L CO that will produce 0.45 L H_2 on reaction with steam. +0.5L of H_2 already present.

$\Rightarrow$ 1 L of sample will give 0.95 L H_2 $\Rightarrow$ 5 L of H_2 will be produced by $=\frac{1}{0.95}\times5=5.263L$

45(8.25) $r_{sample}=0.98r_{O_2}$

$$\Rightarrow\quad \frac{r_{sample}}{r_{O_2}}=0.98=\sqrt{\frac{M_{O_2}}{M_{sample}}}\quad\Rightarrow\quad M_{sample}=33.33\,g\,mol^{-1}$$

Sample contains O_2 and O_3

$$x_{O_2}\cdot M_{O_2}+x_{O_3}\cdot M_{O_3}=33.33$$

$\Rightarrow\quad (1-x_{O_3})32+x_{O_2}48=33.33 \qquad$ Total 1 mole $\Rightarrow$ 0.33 mol

$$\Rightarrow\quad x_{O_3}=\frac{33.33-32}{16}=0.0825\quad\Rightarrow\quad \%O_3=\frac{0.0825}{1}\times100=8.25\%$$

46(1.64) $2X(g)\ +\ 3Y(g)\ \longrightarrow\ Z(g)$

Initial	3	3	–	500 K	15 L
Final	1	0	1	300 K	15 L

After adding water, Z(g) will dissolve to from a solution and 1 mol of X is left in 15L flask at 300K.

$$PV=nRT$$

$P\times15L=1mol\times0.0821\ L\ atm K^{-1}mol^{-1}\times300K;\qquad P=1.642\,atm$

47(0.29) Density of mixture $(CO+CO_2)=1.7\,g\,L^{-1}$ at STP.

$$PM=\rho RT$$

$$1atm\times M=1.76gL^{-1}\times0.0821\ L atm K^{-1}mol^{-1}\times273K$$

$M=39.44\,g\,mol^{-1};\qquad x_{CO}\cdot28+(1-x_{CO})44=39.45;\quad 16x_{CO}=4.55\quad\Rightarrow\quad x_{CO}=0.285$

Chemical Bonding

1.(B) Bond angle : $ClO_3^- > BrO_3^- > IO_3^-$ **2.(A)** % s-character $BeCl_2 > BeCl_3^- > BeCl_4^{2-}$

3.(C) $NH_3 = 106.6°$ (VSEPR)

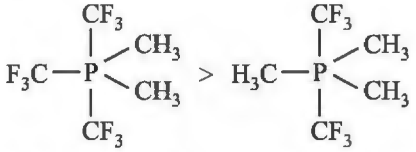
$(CH_3)_3N = 110.9°$ (size of $-CH_3$ group)

$(SiH_3)_3N = 120°$ (due to back bonding)

4.(B) O_2^+ = paramagnetic O_2^{2-} = diamagnetic

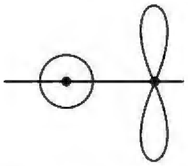
O_2^- = paramagnetic O^{2-} = diamagnetic

5.(ABC)



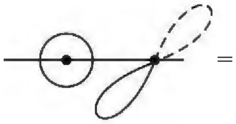
6.(AB) In sp^3-and sp^3d-hybridisation, there is no scope for opp. position of lone pair.

7.(BD) **(B)**



= Zero overlapping

(D)

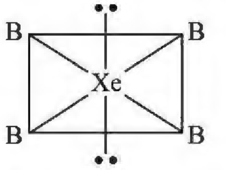


= Zero overlapping

8.(BD) π - bonding and π - antibonding molecular orbitals are not affected by s-p mixing.

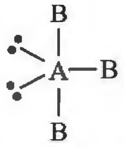
9.(AC)

(A) When n = 4;



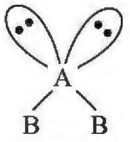
Square planar, non-polar

(B) When n = 3;



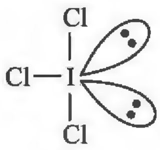
T-shape planar, non-polar

(C) When n = 2;

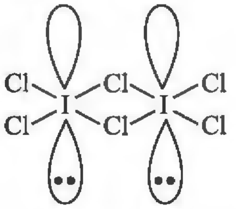


Planar, polar

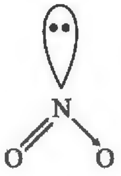
10.(AC)



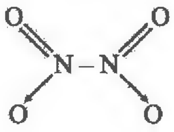
(Planar)



(Planar)



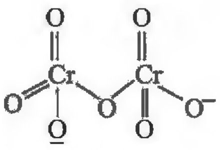
(Planar)



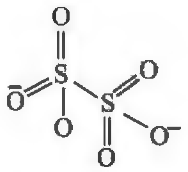
(Planar)

11.(AC) B.E. = $Cl_2 > Br_2 > F_2 > I_2$; B.E. = $N_2 > O_2 > C_2 > F_2$

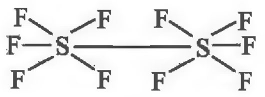
12.(ABCD)



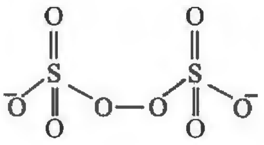
(A)



(B)



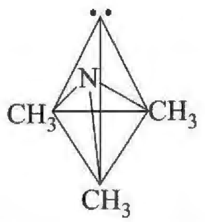
(C)



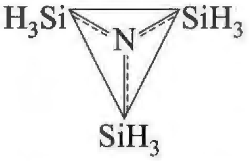
(D)

13.(D)

(A)

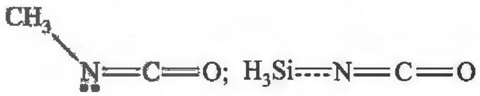


Structure of $(CH_3)_3\ddot{N}$, Hybridisation of N ⟶ sp^3



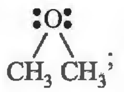
Structure of $(SiH_3)_3N$, Hybridisation of N ⟶ sp^2

(B)



H_3CNCO H_3SiNCO

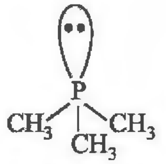
(C)



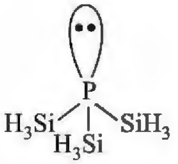
Bent
CH_3OCH_3

Bent
SiH_3OSiH_3

(D)



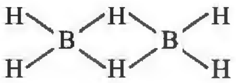
$(CH_3)_3P$

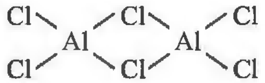


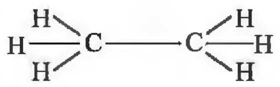
$(SiH_3)_3P$

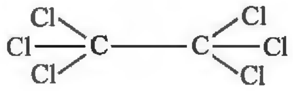
14.(ABC) All are isoelectronic.

15.(CD)









16.(C) Be_2 does not exist because B. O. = 0

17.(A) B.O. of $N_2^+ = 2.5$; B.O. of $O_2^+ = 2.5$

18.(C) C_2, N_2 and F_2 are diamagnetic.

19.(A)

	B.O.
O_2	2
O_2^{2+}	3
O_2^+	2.5
O_2^{2-}	1

20.(C) O_2^{2-} peroxide ion is diamagnetic ion

21.(CD) **(A)** $\bar{C}\equiv\bar{C}$ (One σ and Two π - bonds)

(B) O_2^- (One σ and 0.5 π - bonds)

(C) O_2^{2-} (One σ - bond)

(D) $F-F$ (One σ - bond)

22.(A) $N_2 \longrightarrow N_2^+$

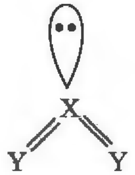
(B.O. = 3) (B.O. = 2.5)

$O_2 \longrightarrow O_2^+$

(B.O. = 2) (B.O. = 2.5)

23.(BC) SF_4, PF_5 have sp^3 d-hybridised central atom.

24.(C) $Y=\overset{\bullet\bullet}{X}=Y$

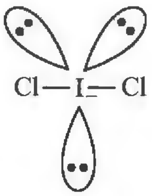


25.(C) XeF_4 and ICl_4^- both are square planar.

26.(ABD)

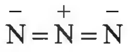
27.(ABC) $Cl-Be-Cl$

$S=C=S$

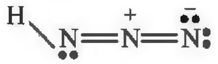


28.(AB) $BrF_3 + BrF_3 \longrightarrow BrF_2^+ \; BrF_4^-$

29.(ABCD)



$\overset{-}{N}=\overset{+}{N}=\overset{-}{N}$

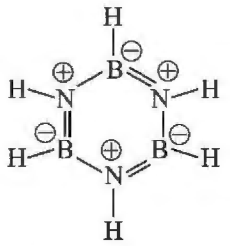


30.(D) σ bond overlapping is greater for p-orbital because p-orbital having good directional character as compared to the s-orbital that is oriented toward internuclear axis.

31.(C)

Molecule	Bond angle
PCl_3	less than 109°
$PCl_4^{\oplus}$	109°
PCl_5	90°, 120°
PCl_6^-	90°, 180°

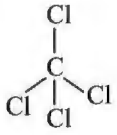
32.(C)

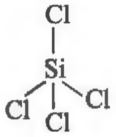


Inorganic Benzene ($B_3N_3H_6$)

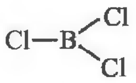
Hybridization of central atom B = sp^2, N = sp^2 planar.

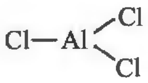
33.(C)



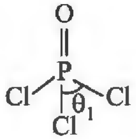


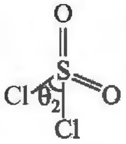
$\left.\begin{array}{l}Cl-C-Cl\\ Cl-Si-Cl\end{array}\right]$ Bond angle = 109° 28'



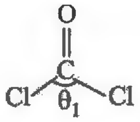


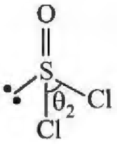
[Bond angle = 120°]





$(\theta_1 \neq \theta_2)$





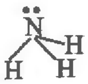
$(\theta_1 \neq \theta_2)$

34.(B) $ICl_4^- - sp^3d^2$ - hybridised no effect of lone pair on bond pair. Lone pairs are on axial position.

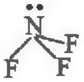
$XeF_2 - sp^3d$ - hybridised no effect of lone pair on bond pair. Lone pairs are on equatorial.

35.(B)

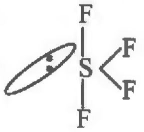
36.(C) $NH_3 \longrightarrow$



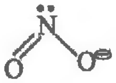
$NF_3 \longrightarrow$



$SF_4 \longrightarrow$

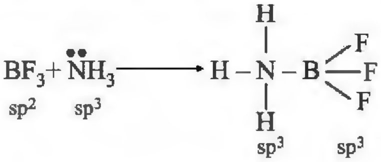


$NO_2^- \longrightarrow$



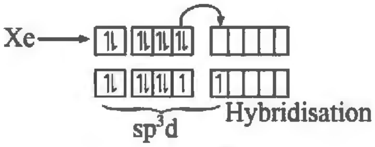
Among all, SF_4 having maximum bond pair – lone pair repulsion because of least bond angle between them.

37.(B)

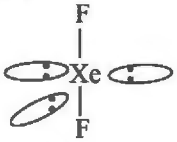


$\underset{sp^2}{BF_3} + \underset{sp^3}{\ddot{N}H_3} \longrightarrow H_3\underset{sp^3}{N}-\underset{sp^3}{B}F_3$

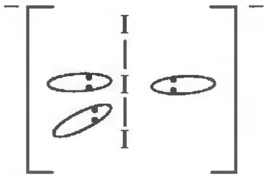
38. (C) XeF_2



Shape $\longrightarrow$

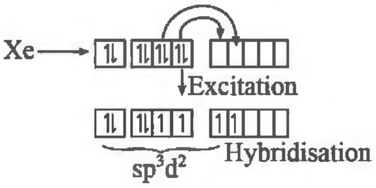


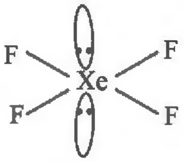
Structure of I_3^-



$\Rightarrow$ XeF_2 is linear and also isostructural with I_3^-

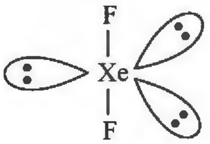
39.(D) XeF_4

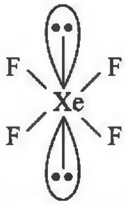


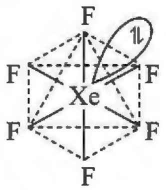


$\longrightarrow$ Shape of XeF_4
↓
Square planar

40.(B) $XeF_2 = sp^3d$ linear
$XeF_4 = sp^3d^2$ square planar
$XeF_6 = sp^3d^3$ caped octahedral

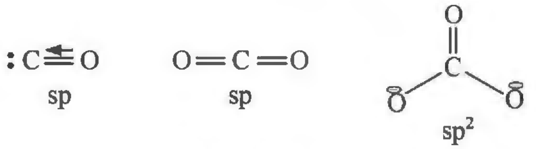






41.(A) Extent of back bonding in B–F bond is decreased if – NH_2 or – OH groups are bonded with boron

42.(B) **(I)**



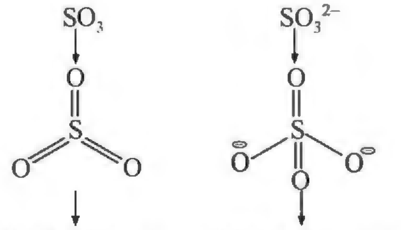
Molecule	**Bond order**	**No. of sigma bond**	**% σ bonding**
CO	3	1	33.3%
CO_2	4	2	50%
CO_3^{2-}	1.33	1	75%

Order of % σ bonding

$CO < CO_2 < CO_3^{2-}$

(II) Back bonding decreases down the group $BF_3 > BCl_3 > BBr_3 > BI_3$

(III)

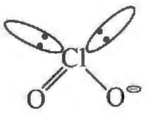
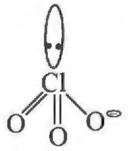
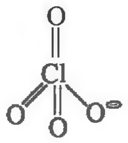


bond order = 2 bond order = 1.5

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

⇒ Order of bond length is $SO_4^{2-} > SO_3$

(IV)

Molecule	**Structure**	**Bond order**
ClO_2^-		1.5
ClO_3^-		1.6
ClO_4^-		1.75

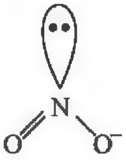
Order of π -bond order

$$ClO_4^- > ClO_3^- > ClO_2^-$$

43.(A) $\overset{-}{N} \underset{x\text{Å}}{=} \overset{+}{N} \underset{y\text{Å}}{=} O$ (Two type of bond)

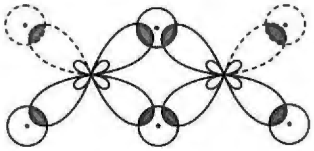
$\overset{-}{N} = C = \overset{-}{N}$ (Both bonds are identical)

$\overset{-}{N} = \overset{+}{N} = \overset{-}{N}$ (Both bonds are identical)

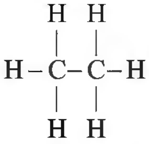


(Both bonds are identical)

44.(C) B_2H_6; $3 \times 2 + 6 = 12$

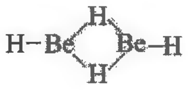


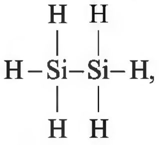
C_2H_6; $4 \times 2 + 6 = 14$



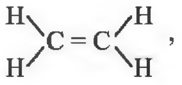
$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$$

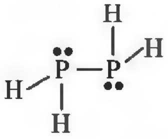
45.(C)



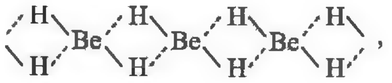


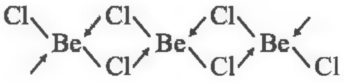
$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{Si}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{Si}}}}-H,$$





46.(A)

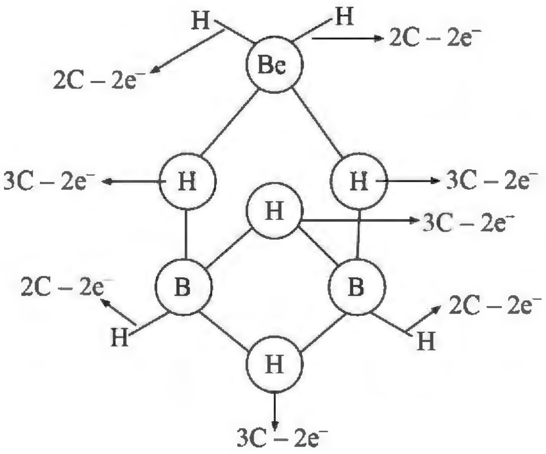




47.(D) $AlH_4^- = sp^3$ Tetrahedral $BH_4^- = sp^3$ Tetrahedral $AlCl_4^- = sp^3$ Tetrahedral

48.(A) In Al $(BH_4)_3$ each form 2-hydrogen bridges.

49.(C)



50.(C) **(A)** $N_2^+ \Rightarrow \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \pi p_x^2 = \pi 2p_z^2, \sigma 2p_z^1$

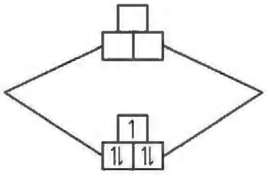
(B) $O_2^+ \Rightarrow \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_x^2, \pi 2\pi_y^2 = \pi 2\pi_z^2, \pi 2\pi_y^1 = \pi 2\pi_z$

(C) $O_2^- \Rightarrow \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2, \overset{*}{\pi}2p_y^2 = \overset{*}{\pi}2p_z^1$

(D) $CN^- \Rightarrow \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \pi 2p_y^2 = \pi 2p_z^2, \sigma 2p_x^2$

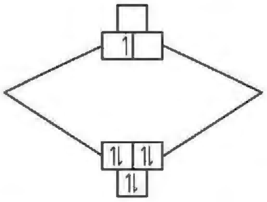
n n : No. of unpaired electron.

51.(A) N_2^+



Bond order $= \frac{5-0}{2} = 2.5$

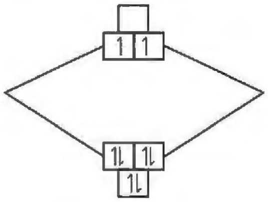
O_2^+



Bond order $= \frac{6-1}{2} = 2.5$

52.(D) Mot diagram of O_2

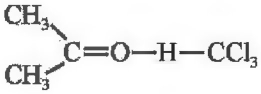
Having 2 unpaired electron



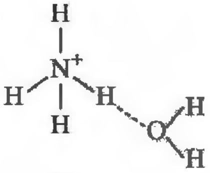
So, magnetic moment $= \sqrt{n(n+2)} = \sqrt{2(4)} = \sqrt{8}$

53.(D) **(I)** $K^+[F^- --- H — F]$

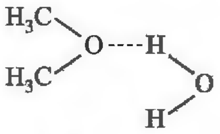
(II)



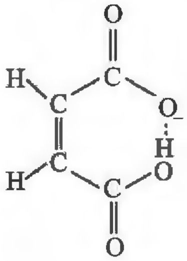
(III)



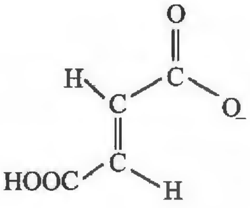
(IV)



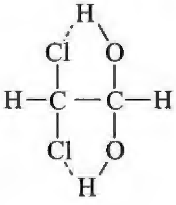
54.(B)



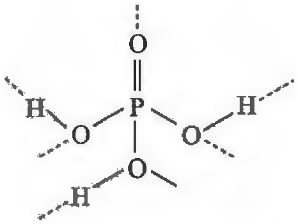
(Maleate ion)



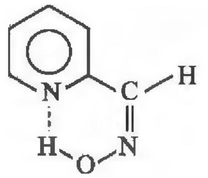
(Furnarate ion)



(Chloral hydrate)



(Intermolecular H-bonding responsible for more viscosity of H_3PO_4)



55.(D) Correct order of basic strength in (D) is reversed because L.P. of N in given molecule is involved in hydrogen bonding.

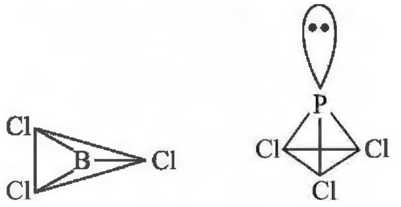
56.(B) Strength of hydrogen bond depends on EN of atom.

57.(D) Liquidation of Xe is explained by London forces which arise as a result of momentary imbalance in electronic distribution.

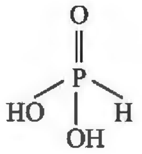
58.(D) AlF_3 has highest B.P. in option (D) because it is ionic but other are covalent.

59. **[A-p, q, r] → [B-p, s] → [C-s, t] → [D-q, t]**

(A)



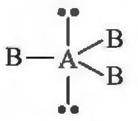
(B)



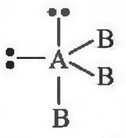
$B(OH)_3$

$$B(OH)_3 + H_2O \longrightarrow \left[B(OH)_4\right]^- + H^+$$

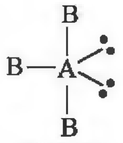
(C)



(Incorrect)

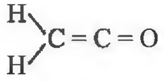


(Incorrect)

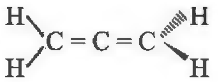


(Correct)

(D)



(Planar)



(Non-planar)

60. **[A-p, q, r] → [B-r, s, t] → [C-s, t] → [D-s, t]**

.(A) CsCl, CsBr, CsI

⇒ According to Fazan's rule larger size of anion → larger covalent character

⇒ Order of covalent character $CsCl < CsBr < CsI$

⇒ Covalent character $\propto \dfrac{1}{\text{Thermal}}$ stability

Order of thermal stability $CsCl > CSBr > CsI$

⇒ Order of taller energy → bond between more electron positive and more electron negative

$CsCl > CsBr > CsI$

(B) LiOH, NaOH, KOH

According to Fazan's rule

Smaller size of cation → larger covalent character.

Order of covalent character $LiOH > NaOH > KOH$

⇒ Covalent character $\propto \dfrac{1}{\text{Ionic character}} \propto \dfrac{1}{\text{Thermal stability}}$

⇒ Order of thermal stability and ionic character $LiOH < NaOH < KOH$

⇒ More lattice energy → Bond between electropositive and electronegative atom

$LiOH > NaOH > KOH$

(C) LiH, NaH, KH

(D) $Mg_3N_2, Ca_3N_2, Sr_3N_2$

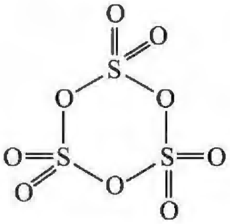
Lesser size of cation → More covalent character.

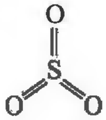
⇒ Order of covalent character $LiH > NaH > KH$ and $Mg_3N_2 > Ca_3N_2 > Sr_3N_2$

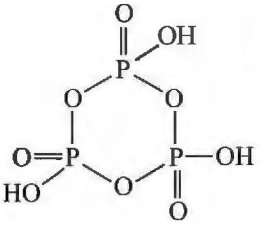
$\Rightarrow$ Covalent character $\propto \dfrac{1}{\text{Ionic character}} \propto \dfrac{1}{\text{Thermal stability}}$ order of Thermal stability and Ionic character

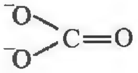
$LiH < NaH < KH$ and $Mg_3N_2 < Ca_3N_2 < Sr_3N_2$

61. **[A-s] → [B-p, q, t] → [C-r] → [D-p, q, t]**









62. **[A-p] → [B-p, r, s] → [C-p, q, r, s] → [D-p, q, r]**

CN (B.O. = 2.5) → CN^- (B.O. = 3) (Diamagnetic)
CN (B.O. = 2.5) → CN^+ (B.O. = 2) (Diamagnetic)

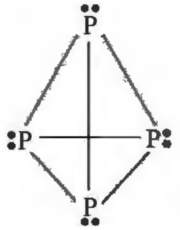
N_2 (B.O. = 3) → N_2^- (B.O. = 2.5) (Paramagnetic)
N_2 (B.O. = 3) → N_2^+ (B.O. = 2.5) (Paramagnetic)

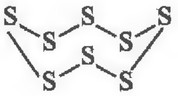
O_2 (B.O. = 2) → O_2^- (B.O. = 1.5) (Paramagnetic)
O_2 (B.O. = 2) → O_2^+ (B.O. = 2.5) (Paramagnetic)

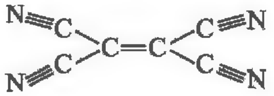
NO (B.O. = 2.5) → NO^+ (B.O. = 3) (Diamagnetic)
NO (B.O. = 2.5) → NO^- (B.O. = 2) (Paramagnetic)

63.(5) Five molecules have zero dipole moment

$O=C=O$







$N\equiv C—C\equiv N$

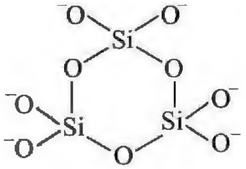
64.(5) B.P. depends molecular weight or hydrogen bonding.

65.(6) Non-existing molecule/ion BF_6^{3-}, BiCl, SI_6, ClF_7, NF_6^-, KH_3

66.(6) Six statements are correct which are II, III, IV, VI, VII, IX.

67.(6) $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

68.(3) $Si_3O_x^{6-}$ $x = 9$



69.(5) $PCl_4^+(sp^3)$, $ICl_2^+(sp^3)$

SF_2 (sp^3), SiF_4 (sp^3),

70.(4) NH_2^- (Bent) OH_2 (Bent) SO_2 (Bent) SF_2 (Bent)

71.(3) PF_3, CF_4 and BeF_2 have all the possible B.A. identical.

72.(4) Correct: Li > Be (size)
C > O (size)
F > Cl (IE)
N > O (IE)

73.(84.4) Percentage ionic character $= \dfrac{\text{Observed value of dipole moment} \times 100}{\text{Calculated value of dipole moment}}$

Observed dipole moment $= 6.32\,\text{D}$

$$0.156\,\text{nm} = 0.156 \times 10^{-9}\,\text{m} = 0.156 \times 10^{-7}\,\text{cm}$$

Calculated value of dipole moment $=$ charge $\times$ distance

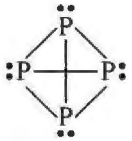
$$= 4.8 \times 10^{-10}\,\text{esu} \times 0.156 \times 10^{-7}\,\text{cm}$$

$$= 7.488 \times 10^{-18}\,\text{esu cm} = 7.488\,\text{D}$$

Thus, percentage ionic character $= \dfrac{6.32}{7.48} \times 100 = 84.4\%$

74.(75) $P(15) = 1s^2 2s^2 2p^6 3s^2 3p^3$

Valence electron $= 5$



Each P-atom has three $(P-P)$ bonds and one lone pair and is sp^3-hybridised.

Thus, p-character is $\dfrac{3}{4} \times 100 = 75\%$

75.(4) $p = \dfrac{n}{V}RT = \dfrac{w}{mV}RT$

Since $\dfrac{w}{V} = gL^{-1} = \text{density}$

Hence $p = \dfrac{d}{m}RT$

m (HF-associated) $= \dfrac{dRT}{p} = \dfrac{3.17 \times 0.0821 \times 300}{100} = 78.08\,gL^{-1}$

m (HF) of single unit $= 20\,gL^{-1}$

HF molecules associated by H-bonding $= \dfrac{78}{20} \simeq 4$

76.(7) $Na(11) : 1s^2 2s^2 2p^6 3s^1$

Electron in (3s) orbital is a conduction band. Each orbital has one electron, thus one energy level.

$$26.8\,\text{mg Na} = 26.8 \times 10^{-3}\,\text{g Na-atoms} = \frac{26.8 \times 10^{-3}}{23}\,\text{g mol Na}$$

$$= \frac{26.8 \times 10^{-3} \times 6.02 \times 10^{23}}{23}\,\text{Na-atoms}$$

$$= 7.0 \times 10^{20}\,\text{atoms} = 7.0 \times 10^{20}\,\text{conduction bands}$$

Thus, $n = 7$

Chemical Equilibrium

1.(B) $Q = \frac{1\times1}{1\times1} \Rightarrow 1$ ($Q > K_c$ so reaction will proceed in backward direction)

$$\begin{array}{lcccccccc} & A_2(g) & + & B_2(g) & \rightleftharpoons & C_2(g) & + & D_2(g) \\ \text{Concentration at equilibrium} & \frac{1.0+x}{10} & & \frac{1.0+x}{10} & & \frac{1.0-x}{10} & & \frac{1.0-x}{10} \end{array}$$

$$0.25 = \frac{\left(\frac{1-x}{10}\right)^2}{\left(\frac{1+x}{10}\right)^2}$$

$$0.5 = \frac{1-x}{1+x} \quad \Rightarrow \quad 0.5 + 0.5\,x = 1-x, \quad 1.5\,x = 0.5\,, \quad x = 0.333$$

$$\left[A_2(g)\right] = \frac{1+x}{10} \Rightarrow \frac{1.333}{10} \Rightarrow 0.13$$

2.(B) After t = 3 min reaction is going forward which should be due to increase in temperature

3.(A) $2AB(s) \rightleftharpoons A_2(g) + B_2(g)$

$$\begin{array}{cc} 0.5+x & x \end{array}$$

$K_p = P_{A_2}.P_{B_2} \Rightarrow 0.06 = (0.5 + x)\,x$

$x^2 + 0.5\,x - 0.06 = 0$

$$x = \frac{-0.5 \pm \sqrt{(0.5)^2 + 4(0.06)}}{2} \Rightarrow \frac{-0.5+0.7}{2}$$

$\Rightarrow \quad 0.1$

$P_{total} = P_{A_2} + P_{B_2} \Rightarrow 0.6 + 0.1 \quad \Rightarrow \quad 0.70$ atm

4.(A) $2A_2B(g) \rightleftharpoons 2A_2(g) + B_2(g)$

$$\begin{array}{cccc} t = t_{eq} & 1-\alpha & \alpha & \alpha/2 \end{array}$$

$$K_P = \frac{\left(\frac{\alpha}{1+\alpha/2}\cdot P_T\right)^2 \left(\frac{\alpha/2}{1+\alpha/2}\cdot P_T\right)}{\left(\frac{1-\alpha}{1+\alpha/2}\cdot P_T\right)^2} = P_T$$

$\Rightarrow \quad \alpha = \frac{2}{3}$

Initial moles = 4 has no use in calculation of α.

5.(D) $2HI \rightleftharpoons H_2 + I_2$

$$\begin{array}{lccc} \text{At equilibrium} & a(1-\alpha) & \frac{a\alpha}{2} & \frac{a\alpha}{2} \end{array}$$

$$a = \frac{0.96}{128} = 0.0075 \quad \Rightarrow$$

$$n_{I_2} = \frac{a\alpha}{2} = \frac{0.0075\times0.21}{2}$$

Meq of hypo required = Meq of I_2

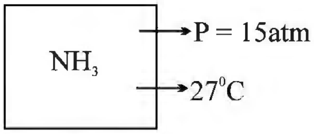
$$N_{I_2} \times n_f = 2\times 1000 = \left(\frac{0.0075\times0.21}{2}\right)\times 2\times 1000 = 1.575 \text{ Meq}$$

6.(A)

$$\begin{array}{lccc} & X_2 & + \; Y_2 & \rightleftharpoons \; 2XY \\ \text{At initial} & 1 & 2 & 0 \\ \text{At equilibrium} & 1-x & 2-x & 2x \\ \text{Equilibrium conc.} & \frac{1-x}{3} & \frac{2-x}{3} & \frac{2x}{3} \end{array}$$

$$\frac{2x}{3} = 0.6, \ \frac{x}{3} = 0.3$$

7.(A)



$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$\frac{15}{P_2} = \frac{300}{620}$, $\quad P_2 = 15 \times \frac{620}{300} = 31$ atm

	$2NH_3(g)$ $\rightleftharpoons$	N_2 +	$3H_2$
Initial Pressure	31	0	0
Equil. Pressure	31–2x	x	3x

$$31 - 2x + x + 3x = 50$$
$$31 + 2x = 50$$
$$2x = 19$$

P_{NH_3} decomposed = 2x = 19 $\qquad$ P_{NH_3} taken = 31

% of NH_3 decomposed = $\frac{19}{31} \times 100 = 61.29\%$

8.(A) $\Delta G = \Delta_r G^\circ + RT \ln Q$

$Q = \frac{2 \cdot 4}{(1 \cdot 5)^2}$

9.(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

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

$P = \left(\frac{\omega}{V}\right)\frac{RT}{M}$

$P = \rho \frac{RT}{M}$

$\frac{P}{\rho} = \frac{RT}{M_0} = \frac{0.082 \times 503}{(2 \times 62)}$

$\frac{P}{\rho} = 0.3326$

10.(C) $Q = \frac{p_{COCl_2}}{p_{CO} \times p_{Cl_2}} = \frac{0 \cdot 25}{0 \cdot 1 \times 0 \cdot 2} = 12 \cdot 5 > K$

$\Rightarrow$ reaction goes forward.

11.(A) $\Delta G^\circ = \Delta H^\circ - (298)\Delta S^\circ = -RT \ln K_{eq}$

Take $K_{eq} = K_1$ and $T_1 = 298K$

Find K_2 at $T_2 = 400K$ using

$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

12.(C) $k = A . e^{-\frac{\Delta H}{RT}}$

13.(D) $K_c = \frac{(0 \cdot 4)^1 (0 \cdot 4)^1}{(0 \cdot 2)^1 (0 \cdot 2)^1} = 4$

Use $K_c = 4$ to define equilibrium conditions

14.(A) As reaction goes forward molecular mass of mixture decreases. Hence vapour density also decreases

15.(A) Refer module OWS in chemical equilibrium

16.(C) $K_p = \frac{4\alpha^2}{1 - \alpha^2} \cdot P_T = 640$

17.(A) Let initial moles of N_2O_4 are 1

$N_2O_4 \rightarrow 2NO_2$

$1 - 0.4 \quad 0.8$

$= 0.6$

$K_P = \frac{0.8 \times 0.8}{0.6} \times \frac{1}{1.4} \quad \Rightarrow \quad \frac{1}{1.4} \times \frac{0.8 \times 0.8}{0.6} = \frac{8 \times 8}{1} \times \frac{P}{9} \quad \Rightarrow \quad P = 0.107$ atm

18.(C) $N_2O_3(g) \rightarrow NO(g) + NO_2(g)$

$1 - \alpha \qquad \alpha \qquad \alpha$

$\therefore \alpha = \frac{D - d}{d(n-1)} = \frac{38 - 23.75}{23.75(2-1)} = 0.6$

Mass % of N_2O_3 in the equilibrium mixture $= \frac{\text{wt. of } N_2O_3}{\text{Total wt.}} \times 100 = \frac{(0.4 \times 76)}{(0.6 \times 30) + (0.6 \times 46) + (0.4 \times 76)} \times 100 = 40\ \%$

19.(D) $H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$. If CO_2 is increased, $[H^+]$ will increase $\Rightarrow$ pH will decrease. Body very minutely maintains pH of the blood. The lungs will work faster so as to exhale the excess of CO_2 & maintain its at pH 7.4 again.

20.(B) Slope $= -\dfrac{\Delta H}{2\cdot 3R} = 230$ (use $R = 2 \text{cal/mol/K}$) **21.(B)** y-intercept $= \dfrac{\Delta S^\circ}{2\cdot 3R} < 0$

22.(B) T increases $\Rightarrow K_c$ increases $\Rightarrow$ On increasing temperature the reaction is going forwards $\Rightarrow$ $\Delta H > 0$

23 - 25 Pressure of $H_2O = 20$ torr

pressure due to CO, Cl_2 and $COCl_2$ in final state = 80 torr

$$\begin{array}{cccc} COCl_2(g) & \rightleftharpoons & CO(g) & + \quad Cl_2(g) \\ 100 - x & & x & x \end{array}$$

Total pressure $= (100 + x) \times \dfrac{2}{3} = 80$

$x = 20$ torr.

23.(C) $P_{COCl_2}(\text{final}) = 80 \times \dfrac{2}{3} = \dfrac{160}{3}$ torr

24.(D) $P_{CO}(\text{final}) = P_{Cl_2}(\text{final}) = \dfrac{20 \times 2}{3} = \dfrac{40}{3}$ torr

$P_{H_2O(g)} = 20$ torr ; $x_{CO} = \dfrac{\frac{40}{3}}{100} = \dfrac{4}{30} = \dfrac{2}{15}$

25.(C) $\dfrac{P_{CO}}{P_{COCl_2}} = \dfrac{40/3}{160/3} = 1:4$

26.(ABC) **27.(ABC)** As reaction is endothermic on increasing temperature reaction goes forward.

28.(ABC) Use $\Delta_r G^\circ = -RT \ln K$

$K_p = 1\cdot 8 \times 10^5$

Compare Q_P and K_P

29.(AB)

$$\begin{array}{cccc} N_2 & + \quad 3H_2 & \rightarrow & 2NH_3 \\ W_1 \text{ gm} & W_2 \text{ gm} & & 0 \\ \left(W_1 - \frac{3.4}{17} \times \frac{1}{2} \times 28\right) & \left(W_2 - \frac{3.4}{17} \times \frac{3}{2} \times 2\right) & & 3.4 \text{ gm} \\ = 3.4 \text{ gm} & = 3.4 \text{ gm} & & \\ W_1 = 6.2 \text{ gm} & W_2 = 4 \text{ gm} & & \end{array}$$

Limiting reagent is N_2, $\therefore$ Maximum possible mass of $NH_3 = \dfrac{6.2}{28} \times \dfrac{2}{1} \times 17 = 7.528$ gm

30.(AC) $K_p = K_c$ when Δn_g is zero

31.(BD) Indicator should have a small transition range. pH at equivalence point $\approx pK_{In}$ of the indicator

pH at equivalence point & at end point may be different.

32.(CD) Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as Δn_g is +ve.

33.(ABCD)

$$N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$$

(A) For changing pressure volume has to be changed, though number of moles of $NO(g)$ do not get changed but its concentration will get changed

(B) Temperature change will change K_P and hence concentration

(C) Volume change will change concentration, not the number of moles

(D) Catalyst does not change equilibrium concentrations

34.(AB) Number of moles will remain unchanged but due to decreased volume pressure will get increased and also the concentrations.

35.(ABC) Positive catalyst only alters the equilibrium time. The amount of product, heat of reaction and equilibrium constant remain unaffected by the catalyst.

36.(A) Rate constant of a reaction and ionic product of water both increase with increase in temperature. Equilibrium constant of exothermic reaction will decrease with rise in temperature

$$k = Ae^{-Ea/RT} \qquad .....(i)$$

$$\log_{10}\left(\frac{K^2}{K_1}\right)=\frac{\Delta H}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \qquad .....(ii)$$

Equation (i) shows the relation between temperature and rate constant, while equation (ii) shows relation between temperature and equilibrium constant.

37. **[A- r] → [B-r] → [C-q s] → [D-p]**

38.(4)

$$\begin{array}{lccc} & NO(g) + NO_3(g) & \rightleftharpoons & 2NO_2 \\ t = t_{eq} & 1 - x/2 \quad 3 - x/2 & & x \\ t = t_{eq} & 3 - x \quad 3 - x & & 2x \end{array}$$

$$K_P = \frac{x^2}{(1-x/2)(3-x/2)} = \frac{(2x)^2}{(3-x)^2}$$

$$x = 3/2$$

$$K_P = 4$$

39.(3) $A+B \rightleftharpoons P, \quad K'_c = 6$

$$2B+C \rightleftharpoons 2D, \quad K'_c = 4$$

So, $A+D \rightleftharpoons P+\frac{C}{2}, \quad K'_c = ?$

$$K'_c \times \frac{1}{\sqrt{K'_c}} = K'_c$$

$$6\times\frac{1}{\sqrt{4}} = K'_c$$

$$K'_c = 3$$

40.(9) For the reversible reaction,

$$A \rightleftharpoons P, \ \log K = 0.47 - \frac{2000}{T}$$

$$\Delta G^\circ = -2.303\ RT\log K$$

$$T\Delta S^\circ - \Delta H^\circ = 2.303\ RT\log K$$

$$\log K = \frac{T\Delta S^\circ - \Delta H^\circ}{RT\times 2.303}$$

$$\frac{\Delta S^\circ}{R\times 2.303} = 0.47$$

$$\Delta S^\circ = 0.47\times 8.314\times 2.303 = 9$$

41.(2) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_P = \frac{2^2}{2} = 2$$

At new equilibrium if $p_{N_2O_4} = 0.85$ atm

$$\frac{\left(p_{NO_2}\right)^2}{0.85} = 2 \Rightarrow p_{NO_2} = 1\cdot 3 \text{ atm}$$

$$P_T = 1\cdot 3 + 0\cdot 85 = 2\cdot 15 \text{ atm}$$

Ratio of P_T before and after expansion is $\frac{4}{2\cdot 15} \approx 2$

42.(2)

$$\begin{array}{lcccc} & PCl_3(g) \ + & Cl_2(g) & \rightleftharpoons & PCl_5(g) \\ \text{Given} & n \text{ moles} & n \text{ moles} & & n \text{ moles} \\ \text{At equilibrium} & n-\alpha & n+\frac{20}{3}-\alpha & & n+\alpha \end{array}$$

According to Gay Lussac's law, at constant temperature & pressure $v \propto n$

So, $$\frac{n-\alpha+n+\frac{20}{3}-\alpha+n+\alpha}{3n}=2 \qquad \text{...........}\ (1)$$

Also, as the temperature is constant, K_c does not change $\frac{1}{n}=\frac{n+\alpha}{(n-\alpha)\left(n+\frac{20}{3}-\alpha\right)}$ .... (2)

Solve equation (1) and (2) $n=\frac{50}{21}\approx 2$

43.(12) $A(g)+2B(g) \rightleftharpoons AB_2(g),\ K_c=\frac{1}{2}$

$$\begin{array}{lccc} \text{Given} & 2\text{ M} & 2\text{M} & ? \end{array}$$

$$K_c=\frac{(AB_2)}{[A][B]^2}$$

$$\frac{1}{2}=\frac{[AB_2]}{2\times(2)^2}$$

So, $[AB_2]=4$

On further addition of two moles of B, AB_2 should be 16M

44.(1) For equilibrium $A \rightleftharpoons P$

$\Delta G^\circ=-2.303RT\log K_c$

$0=-2.303RT\log K_c$

$\log K_c=0$

$K_c=1$

45.(4)

$$\begin{array}{lcccc} & A(g)+ & 2B(g) \rightleftharpoons & 2C(g) & +\ D(g) \\ \text{Initial conc.} & x & 1.5x & 0 & 0 \\ \text{At equilibrium} & x-\alpha & 1.5x-2\alpha & 2\alpha & \alpha \end{array}$$

$x-\alpha=1.5x-2\alpha$

$-0.5x=-\alpha$

$\alpha=0.5x$

$K_p=K_c$ as $\Delta n_g=0$

$$K_p=\frac{(2\alpha)^2\times\alpha}{(x-\alpha)(0.5x)^2}=\frac{1}{0.25}=4$$

46.(4) $P_T=P_1+P_2$

$$\begin{array}{lcc} NH_2COONH_4(s) \rightleftharpoons & 2NH_3(g) & +\ CO_2(g) \\ 2x+x=3 & 2x & x \end{array}$$

$x=1$

$K_p=(p_1)^2(p_2)=(2)^2(1)=4$

47.(6) $A(\ell)+B(g) \rightleftharpoons C(g)+D(g)$

$$K_p=\frac{p_c \cdot p_d}{p_B}=\frac{2\times 3}{1}=6$$

48(0.05) $CH_3Cl(aq)\ +\ OH^- \rightleftharpoons CH_3OH\ +\ Cl^-$

$$\begin{array}{lcccc} t=0 & 0.1\text{ M, V} & 0.2\text{ M, V} & & \\ \text{moles} & 0.1\text{ V} & 0.2\text{ V} & 0.1 & 0.1 \\ & 0 & \frac{(0.2-0.1)V}{2V} & & \end{array}$$

$$K_C=\frac{[CH_3OH][Cl^-]}{[CH_3Cl][OH^-]}=1\times10^{16}$$

Due to very large value of K_C, the reaction will go to completion $[OH^-]_{\text{left}}=\frac{(0.2V-0.1V)}{2V}$

49(22.62) $\Delta G^\circ = -RT\ln K_{eq}$

$$-534.52\times10^3 J = -8.314 JK^{-1}mol^{-1}\times 2000 K \ln K_{eq}$$

$$K_{eq} = 1.03\times10^{14}$$

Since the value of K_{eq} is very high, reaction will go to completion

$$2O_3 \rightleftharpoons 3O_2 \quad \therefore \quad P_{O_2} = 8 atm$$

$$K_P = \frac{P^3_{O_2}}{P^2_{O_3}} \qquad V_T = 10 L; \qquad P_T = 8 atm; \qquad T = 2000 K$$

$$1.03\times10^{14} = \frac{(8)^3}{(P_{O_3})^2} \Rightarrow P_{O_3} = 22.62\times10^{-7} atm$$

50(0.66)

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

$NH_4HS(s)$	$NH_3(g)$	$H_2S(g)$
C	–	–
C – P	P	P

$K_P = 0.109$ at 300K.

$$K_P = P_{NH_3}\cdot P_{H_2S} = P^2 \Rightarrow P = 0.33 atm$$

Total pressure $= 2P = 0.66 atm$

51.(0.0036)

Initial concentration of $Fe^{3+} = \frac{10^{-3} g}{10^3 L} = \frac{10^{-3}}{56} mol\ L^{-1}$

Let initial concentration of SCN^- be 'x'

	$[Fe(SCN)]^{2+}$	$\rightleftharpoons$ Fe^{3+}	+ SCN^-
$t = 0$	0	1.78×10^{-5}	x
$t = t_{eq}$	y	$(1.78\times10^{-5} - y)$	$(x - y)$

$$y = 6\times10^{-6} M$$

$$\Rightarrow \quad K = \frac{[Fe^{3+}][SCN^-]}{[Fe(SCN)]^{2+}} = \frac{(1.78\times10^{-5} - y)(x - y)}{y}$$

$$7.142\times10^{-3} = \frac{(1.78\times10^{-5} - 6\times10^{-6})(x - 6\times10^{-6})}{6\times10^{-6}} \Rightarrow x = 0.0036$$

52.(1.5) $3A_2(g) \rightleftharpoons A_6(g) \qquad K_p = 1.6$

$$A_2(g) + C(g) \rightleftharpoons A_2(g) \qquad K'_p = ?$$

At equilibrium,
Total $p = 1.4 atm$

$p_{A_6} = 0.2 atm$

Initially, $2:1$ molar ratio of A_2 and C are mixed

$$\begin{array}{llll} & 3A_2(g) & \rightleftharpoons & A_6(g) \\ t=0 & 2p & & \\ t=t_{eq} & (2p-3p'-p'') & & p' \end{array}$$

$$\begin{array}{llllll} & A_2(g) & + & C(g) & \rightleftharpoons & A_2C(g) \\ t=0 & 2p & & 1p & & \\ t=t_{eq} & (2p-p''-3p') & & (p-p'') & & p'' \end{array}$$

$$K_p=\frac{p_{A_6}}{p_{A_2}} \quad \Rightarrow \quad 1.6=\frac{0.2}{(p_{A_2})^3}$$

$\Rightarrow \quad p_{A_2}=0.5\,\text{atm} \quad \Rightarrow \quad 2p-3p'-p''=0.5\,\text{atm} \qquad (p''=0.2)$

$\Rightarrow \quad 2p-0.6-p''=0.5 \qquad \text{........ (i)}$

Total pressure $=p_{A_2}+p_{A_6}+p_{A_2C}+p_C \quad \Rightarrow \quad 1.4=0.5+0.2+p''+p-p'' \quad \Rightarrow \quad p=0.7\,\text{atm}$

Subs in (i)

$\Rightarrow \quad 2(0.7)-0.6-p''=0.5 \quad \Rightarrow \quad 1.4-0.6-p''=0.8 \quad \Rightarrow \quad p''=0.3$

$p_{A_2C}=0.3\,\text{atm}$

$p_C=p-p''=0.7-0.3=0.4\,\text{atm}$

$$K'_p=\frac{p_{A_2C}}{p_{A_2}\cdot p_C}=\frac{0.3}{0.5\times 0.4}$$

$K'_p=1.5$

53.(9)

$$\begin{array}{llllllllll} & AgNO_3 & + & 2KCN & \longrightarrow & [Ag(CN)_2]^- & + & 2K^+ & + & NO_3^- \\ t=0 & 0.1 & & 0.5 & & - & & & & \\ t=t_{eq} & 10^{-6} & & 0.5-2(0.1-10^{-6}) & & (0.1-10^{-6}) & & & & \end{array}$$

$$K_{eq}=\frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2}=\frac{0.1}{10^{-6}\times 0.3}$$

$K_1=0.33\times 10^6$

$$\begin{array}{llllll} & Zn^{2+} & + & 4CN^- & \rightleftharpoons & [Zn(CN)_4]^{2-} \\ t=0 & 0.1 & & 0.5 & & - \\ t=t_{eq} & 10^{-12} & & 0.5-4(0.1-10^{-12}) & & (0.1\times 10^{-12}) \\ & 10^{-12} & & 0.1 & & 0.1 \end{array}$$

$$K_2=\frac{[Zn(CN)_4]^{2-}}{[Zn^{2+}][CN^-]^4}=\frac{0.1}{10^{-12}\times(0.1)^4}=1\times 10^9$$

Multiply equation (1) by 2 and subtract from equation (2)

$$2[Ag(CN)_2]^- \rightleftharpoons 2Ag^+ + 4CN^- \qquad K_1=9\times 10^{12}$$

$$Zn^{2+}+4CN^- \rightleftharpoons [Zn(CN)_4]^{2-} \qquad K_2=10^9$$

$$Zn^{2+}+2[Ag(CN)_2]^- \rightleftharpoons [Zn(CN)_4]^{2-}+2Ag^+$$

$$K_{eq}=K_1K_2=(9\times 10^{12})(10^9) \quad \Rightarrow \quad K_{eq}=9\times 10^{21}$$

Ionic Equilibrium

1.(C) At pH = 3, $[H^+] = 10^{-3}$ M

At pH = 4, $[H^+] = 10^{-4}$ M

When equal volume of the two solutions are mixed, the $[H^+] = \frac{10^{-3}+10^{-4}}{2} = \frac{10^{-3}[1+0.1]}{2} = \frac{1.1}{2}\times10^{-3}$

$[H^+] = 5.5 \times 10^{-4}$

$-\log [H^+] = -\log (5.5) - \log 10^{-4}$

pH = – 0.7404 + 4 = **3.26**

2.(C)

		CH_3COOH +	$NaOH \longrightarrow$	CH_3COONa +	H_2O
Millimoles	t = 0	5	2.5	0	0
Millimoles	t = t′	2.5	0	2.5	

Here, millimoles of CH_3COOH and CH_3COONa are same. Together they constitute acidic buffer and for acidic buffer:

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

Because [salt] = [acid], so pH = pKa

$pH = -\log 2 \times 10^{-5}$

pH = **4.7**

3.(B) CH_3COO^- when hydrolysed generates OH^- ions making the solution basic. CH_3COONH_4 results in a neutral solution since $K_a(CH_3COOH) = K_b(NH_4OH)$

4.(C) $pH = \frac{1}{2}\left[pK_{a_1} + pK_{a_2}\right] = \frac{1}{2}[7+11] = 9$.

5.(B) $\alpha_1^2 = \frac{Ka_1}{C_1}$ $[HA \rightleftharpoons H^+ + A^-]$ where α_1 is degree of dissociation of HA.

$\alpha_2^2 = \frac{Ka_2}{C_2}$ $[HB \rightleftharpoons H^+ + B^-]$ where α_2 is degree of dissociation of HB.

or, $\frac{C_2}{C_1} = \left(\frac{\alpha_1}{\alpha_2}\right)^2 \times \frac{Ka_2}{Ka_1} = \left(\frac{1}{10}\right)^2 \times 50 = \frac{1}{2}$ $\therefore$ $C_1 : C_2 =$ **2 : 1**

6.(D) K_{sp} of $PbCl_2 = 4s^3 = 4 \times (0.01)^3 = 4 \times 10^{-6}$

$\therefore$ Concentration of Pb^{2+} in NaCl solution $= \frac{Ksp}{\left[Cl^-\right]^2} = \frac{4\times10^{-6}}{10^{-2}} = \mathbf{4 \times 10^{-4}\ M}$

7.(D) $CaF_2(g) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

s 2s

$K_{sp} = (s)(2s)^2 = 4s^3 = 4 \times (2 \times 10^{-4})^3$

$K_{sp} = 4 \times 8 \times 10^{-12} = 32 \times 10^{-12}$.

8.(D) $[H^+] = \sqrt{K_a C}$

$\sqrt{K_1 \times C_1} = \sqrt{K_2 \times C_2}$

$\sqrt{\frac{C_1}{C_2}} = \sqrt{\frac{K_2}{K_1}} = \sqrt{\frac{1}{4}}$ $\therefore$ $\frac{C_1}{C_2} = \frac{1}{4} =$ **0.25**

9.(D)

$$\begin{array}{lccccccc} & NaOH & + & HCl & \longrightarrow & NaCl & + & H_2O \\ \text{initial} & 4.5\text{ m mol} & & 4\text{ m mol} & & 0 & & 0 \\ \text{final} & 0.5\text{ m mol} & & 0 & & 4\text{ m mol} & & 4\text{ m mol} \end{array}$$

So solution is basic hence $[OH^-] = \dfrac{0.5}{50} = 10^{-2}\,M$

pOH = 2 ; so pH = **12**.

10.(D)

$$\begin{array}{lccccccc} & CH_3NH_2 & + & HCl & \rightleftharpoons & CH_3\overset{(+)}{N}H_3 & + & Cl^- \\ \text{Initial} & 0.22 & & 0.02 & & 0 & & 0 \\ \text{Final} & 0.20 & & 0 & & 0.02 & & 0.02 \end{array}$$

It's a basic buffer

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} = 6 + \log\frac{[.02]}{[.20]}$$

pOH = 6 – 1 = 5; So pH = 9 or $[H^+] = 10^{-9}$ M.

11.(A) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$Ksp = [Ag^+]^2\,[CrO_4^{2-}]$

12.(C) $CH_3COOH + CH_3COONa$ is an acidic Buffer.

13.(B) $pH = pK_a + \log\dfrac{[Salt]}{[Acid]} = 4.76 + \log\left(\dfrac{20\times0.5}{10}\right) = \mathbf{4.76}$

14.(A) When half of the ammonium hydroxide is neutralised a basic buffer is formed.

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} = 4.75 + \log(1)$$

pH = 9.25

15.(A) $AgI \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{I^-}$

In presence of 10^{-4} N KI, solubility of AgI decreases due to common ion effect. Let it be S.

$$\begin{array}{ccccc} AgI & \rightleftharpoons & Ag^+ & + & I^- \\ s'(10^{-4}) = 10^{-16} & & s' & & s' + 10^{-4} \\ & & & & \approx 10^{-4} \end{array}$$

$s' = 1 \times 10^{-12}$ M.

16.(B) $2NH_3(l) \rightleftharpoons NH_4^+ + NH_2^-$

$K_{NH_3} = [NH_4^+]\,[NH_2^-] = [NH_2^-]^2 = 10^{-30}\,M^2$

$[NH_2^-] = 10^{-15}$ M

NH_2^- ions per cm³ of liquid $NH_3 = \dfrac{10^{-15}}{1000}\times 6\times10^{23} = 6\times10^{5}$ ions/cm³.

17.(D) For preparing a buffer solution of given pH, we prefer to choose an acid/base having pK_a/pK_b value as close as the pH value.

These are all acidic buffers, so pH is given by $pH = pK_a + \log\dfrac{[Salt]}{[Acid]}$

In (d), $pK_a = -\log K_a = -\log(8\times10^{-8}) = 8 - 3\log 2 = 8 - 0.9 = 7.1$.

18.(D) $pH_{CH_3COOH} = 3$

$\therefore \quad [H_3O^+] = \sqrt{c \times K_a} = 10^{-3}$

$\sqrt{c \times 10^{-5}} = 10^{-3}$

$c = 10^{-1}$ M

pH of 10^{-1} M solution of NH_4OH

$[OH^-] = \sqrt{10^{-1} \times 10^{-5}} = 10^{-3}$

$pOH = 3$

$\therefore \quad pH = 11.$

19.(C) $HIn \Leftrightarrow H^+ + In^-; pH = pK_{in} + \log\dfrac{[In^-]}{[HIn]}$

$(pH)_1 = pK_{in} + \log\dfrac{20}{80} = pK_{in} - 2\log 2$

$(pH)_2 = pK_{in} + \log\dfrac{80}{20} = pK_{in} + 2\log 2$

Hence, $(pH)_2 - (pH)_1 = pK_{in} + 2\log 2 - (pK_{in} - 2\log 2)$ = 4 log 2 = 1.20

20.(D) $SrF_2 \rightleftharpoons Sr^{2+} + 2F^-$

$S' \qquad 2S' + 0.1$

$NaF \longrightarrow Na^+ + F^-$

0.1 M 0.1 M

Let the solubility of SrF_2 in 0.1 M NaF solution be S′

$K_{sp} = [Sr^{2+}][F^-]^2$

$8 \times 10^{-10} = S'(2S' + 0.1)^2$

$(2S' + 0.1) \simeq 0.1$

$S' = \dfrac{8 \times 10^{-10}}{10^{-2}}$

$S' = 8 \times 10^{-8}.$

21.(D) For precipitation, Ionic product > Solubility product.

24.(A) $pH = -\log[H^+] = -\log[C\alpha] = -\log(0.5 \times 6 \times 10^{-3})$

$= 2.52$

25.(C) We want to double the pH i.e. = 5.04

$pH = 5.04 = -\log[H^+] = -\log[c_1\alpha_1]$

$10^{-6} = c_1\alpha_1$

$K_a = \dfrac{[H^+]\ [CH_3COO^-]}{[CH_3COOH]}$

$K_a = \dfrac{c_1\alpha_1 \times c_1\alpha_1}{c_1(1-\alpha_1)} = \dfrac{c_1\alpha_1 \times \alpha_1}{1-\alpha_1}$

$1.8 \times 10^{-5} = \dfrac{9.12 \times 10^{-6} \times \alpha_1}{1-\alpha_1}$

22.(C) $K_{sp} = [Mg^{2+}][OH^-]^2$

$1 \times 10^{-11} = S \times (2S)^2$

$S = \sqrt[3]{\dfrac{1 \times 10^{-11}}{4}}$

$S = 1.35 \times 10^{-4}$

$[OH^-] = 2S = 2.7 \times 10^{-4}$

$pOH = -\log[OH^-] = -\log 2.7 \times 10^{-4}$

$= 4 - 0.43 = 3.7$

$pH = 14 - 3.7 = 10.43$

23.(B) $K_a = C\alpha^2$

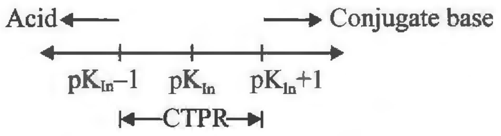
$\alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{1.8 \times 10^{-5}}{0.5}} = \sqrt{3.6 \times 10^{-5}}$

$= 6 \times 10^{-3}$

26.(B) $pK_{In} = \dfrac{4+6}{2} = 5$

$\Rightarrow \quad K_{In} = 10^{-5}$

27.(A) As per pH scale:



$\therefore$ In mid way $pH = pK_{in}$

$$1.8\times10^{-5}-1.8\times10^{-5}\alpha_1=9.12\times10^{-6}\alpha_1$$

$$1.8\times10^{-5}=9.12\times10^{-6}\alpha_1+1.8\times10^{-5}\alpha_1=\alpha_1\times2.712\times10^{-5}$$

$$\alpha_1=\frac{1.8\times10^{-5}}{2.712\times10^{-5}}=0.6637$$

$$c_1\alpha_1=9.12\times10^{-6}$$

$$c_1=\frac{9.12\times10^{-6}}{0.6637}=1.37\times10^{-5}\,\text{M}$$

28.(C) When acid is half neutralized pH = pK_a

$\therefore$ $pK_a = 5$

29.(A) $K_{eq}=\dfrac{K_a(\text{HB})}{K_a(\text{HA})}=\dfrac{10^{-5}}{10^{-6}}=10$

30.(B) When $V_{NaOH} = 0$ mL; pH = 3 or $\left[H^+\right]=0.001$

$$K_{a(\text{HB})}=\frac{C\alpha^2}{(1-\alpha)}=\frac{(0.001)\alpha}{1-\alpha}=10^{-5}$$

$$\alpha=0.01$$

$$C=\frac{0.001}{0.01}=0.1$$

$$C=\frac{n_{HB}}{V}$$

$$0.1=\frac{5}{V};\ V=50\,\text{mL} \qquad \therefore \qquad [\text{NaB}]=\frac{\text{milli-moles of acid}}{\text{total volume}}=\frac{5}{50+50}=0.05$$

$$pH=\frac{1}{2}\left[pK_w+pK_a+\log C\right]=\frac{1}{2}\left[14+5+\log(0.05)\right]=8.85$$

31.(A) For best indicator, pH = pK_{In} of an indicator as well as pH transition range of the indicator must coincide with the steep portion of the titration curve.

32.(A) $\left[S^{2-}\right]_{min}$ for SnS $=\dfrac{K_{SP}(\text{SnS})}{\left[Sn^{2+}\right]}$; $\left[S^{2-}\right]_{min}$ for CdS $=\dfrac{K_{SP}(\text{CdS})}{\left[Cd^{2+}\right]}$; $\left[S^{2-}\right]_{min}$ for NiS $=\dfrac{K_{SP}(\text{NiS})}{\left[Ni^{2+}\right]}$

and K_{sp} (NiS) > K_{sp}(CdS) > K_{sp}(SnS) $\therefore$ SnS will precipitate first

33.(C) $H_2S \rightleftharpoons 2H^+ + S^{2-} \Rightarrow K_1K_2=\dfrac{\left[H^+\right]^2\left[S^{2-}\right]}{[H_2S]}=10^{-21}$

$\left[S^{2-}\right]_{min}(\text{NiS})=3\times10^{-20}\,\text{M}$, $\left[H^+\right]=\sqrt{\dfrac{10^{-22}}{3\times10^{-20}}}=5.77\times10^{-2}$, pH $=2-\log5.77=2-0.76=1.24$

34.(B) Solubility of either CdS, NiS, SnS = $\sqrt{K_{SP}}$ $\Rightarrow$ look for highest K_{SP}.

35.(A) $K_1K_2=\dfrac{\left[H^+\right]^2\left[S^{2-}\right]}{[H_2S]} \Rightarrow \left[S^{2-}\right]_{sat.}=10^{-20}\,\text{M} \Rightarrow \left[Cd^{2+}\right]_{allowed}=\dfrac{K_{SP}(\text{CdS})}{\left[S^{2-}\right]_{sat.}}=10^{-8}\,\text{M}$

36.(ACD) NH_3/NH_2^-, HCO_3^-/CO_3^{2-}, H_2S/HS^- are conjugate acid-base pairs.

37.(ABC)

(A) $C=10^{-3}, \alpha=10^{-1}$

$[H^+]=C\alpha=10^{-4}$ $\Rightarrow$ pH = 4

(B) $[H^+]=\sqrt{K_a.c}=\sqrt{10^{-2}\times10^{-6}}=10^{-4}$ $\Rightarrow$ pH = 4

(C) $[H^+]=[A^-]=10^{-4}$ $\Rightarrow$ pH = 4

38.(BC) $H_2PO_4^- / HPO_4^{2-}$ is conjugate acid base pair.

pH = 7, salt of strong acid and strong base

39.(BC) $$\underset{\text{base}}{\underset{(A)}{Cu[(H_2O)_3(OH)]^+}} + \underset{\text{acid}}{[Al(H_2O)_6]^+}$$

$$\Rightarrow \underset{\text{acid}}{[Cu(H_2O)_4]^{2+}} + \underset{\text{base}}{[Al(H_2O)_5OH]^+}$$

40.(AB) Option (A) is a basic buffer while option (B) is an acidic buffer. The pH of a buffer solution does not change on dilution.

41.(ABC) (A) $0.1\text{mol NaOH} + 0.15\text{mol of } CH_3COOH$

$\downarrow$

$0.1\text{mol } CH_3COONa + 0.05\text{mol of } CH_3COOH$

$\downarrow$

Buffer solution

(B) Salt of WA & WB acts as a mixed buffer solution.

(C) Conjugate acid – base pair

42.(A) Concentration of Cl^- is solution when pure AgCl(s) is added to 0.01 M $AgNO_3$ is given by $[Cl^-] = \dfrac{K_{sp}}{[Ag^+]} = \dfrac{K_{sp}}{0.01}$

Similarly, concentration of Ag^+ in the second solution when pure AgCl(s) is added to 0.025 M KCl is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{K_{sp}}{0.025}$$

The ratio of $[Cl^-]$ in the first solution to $[Ag^+]$ in the second solution is given by $\dfrac{[Cl^-]_1}{[Ag^+]_2} = \dfrac{0.025}{0.01} = 2.5$.

43.(ACD) $$\frac{[H^+]_1}{[H^+]_2} = \frac{C\alpha_1}{C\alpha_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}$$

44.(ABCD) **(A)** $[CH_3COOH] > [NaOH]$: Final solution $[CH_3COOH] + [CH_3COONa]$

(B) $[CH_3COONa] > [HCl]$: Final solution $[CH_3COOH] + [CH_3COONa]$

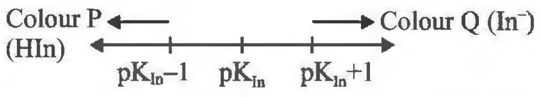
(C) (weak acid + weak base) salt

(D) Acid + conjugate base pair

45.(CD) Bronsted acid is H^+ donor. Lewis acid is e^- pair accept D stronger the acid, weaker is conjugate base

46.(ABCD) Refer theory

47.(AB)



48.(BC) $$pH = pK_{In} + \log\frac{[In]}{[HIn]}$$

75% red $\Rightarrow \dfrac{[HIn]}{[In^-]} = \dfrac{3}{1}$

$$pH = (5 - \log 3) + \log\left(\frac{1}{3}\right)$$

$$pH = 4.05$$

75% blue $\Rightarrow \dfrac{[HIn]}{[In^-]} = \dfrac{1}{3}$

$$pH = (5 - \log 3) + \log 3$$

$$pH = 5$$

49.(ABCD) All statements are correct.

50.(ACD) Two weak acids HA, & HA_2,

$$HA_1 \rightleftharpoons H^+ + A_1^- \qquad HA_2 \rightleftharpoons H^+ + A_2^-$$

$$[H^+]_1 = C_0\alpha_1 = \sqrt{K_1C_0} \qquad [H^+]_2 = C_0\alpha_2 = \sqrt{K_2C_0}$$

Relative acidic strengths $= \dfrac{[H^+]_1}{[H^+]_2} = \dfrac{\alpha_1}{\alpha_2} = \dfrac{K_1}{K_2}$

51.(ABCD)

(A) $[CH_3COOH] > [NaOH]$

$\rightarrow$ gives a mixture of $CH_3COOH + CH_3COONa$

(B) $[CH_3COONa] > [HCl]$

$\rightarrow$ gives a mixture of $CH_3COONa + CH_3COOH$

(C) NH_4CN – Salt of weak acid & weak base

$\rightarrow$ Acts as simple buffer

(D) $HCN + NaCN$

$\rightarrow$ weak acid & its salt

52.(CD) All Arrhenius acids & bases are Bronsted acids and bases

All Bronsted acids & bases are Lewis acids & bases but not vice-versa

Eg. BF_3 is a Lewis acid (electron acceptor) but not Bronsted acid

Conjugate base of a strong acid is a weak base

Eg. $HI \longrightarrow H^+ + I^-$

HI is a strong acid & I^- is a weak base

53.(AB) $\underset{\text{Colour P}}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour Q}}{In^-}$

Solution assumes colour P, when $[HIn] \geq 10[In^-]$

$\therefore \quad pH \leq pK_{In} - 1$

Solution assumes colour Q, when $[In^-] \geq 10[HIn^-]$

$pH \geq pK_{In} + 1$

54.(ABC) KCN is a basic salt so its addition in water increases the pH of water.

55. **[A-p, s] → [B-q, r] → [C-p, r] → [D-p]**

(A) As CH_3COONa is formed

(B) As $CH_3COOH + CH_3COONa$ is left

(C) As $NH_4Cl + NH_4OH$ is left

(D) As NaOH is left

56. **[A-p, s] → [B-q] → [C-p, r] → [D-p, q]**

(A) 50 mol of 0.1 M CH_3COOH + 25 ml of 0.1 M NaOH

$\downarrow$

$CH_3COOH + CH_3COONa$

(B) 50 ml of 0.1 M NaOH + 50 ml of 0.1 M HCl

$\downarrow$

NaCl

(C) 50 ml of 0.1 M NH_4OH + 25 ml of 0.1 M HCl

$\downarrow$

$NH_4Cl + NH_4OH$

(D) 50 ml 0.1 M CH_3COOH + 50 ml of 0.1 M NH_4OH

$\downarrow$

CH_3COONH_4 (salt of weak acid & weak base)

57.(3)

	$Ag^+(aq)$	+	$Fe^{2+}(aq)$	$\rightleftharpoons$	$Ag(s)$	+	$Fe^{3+}(aq)$
No. of moles initially	$500 \times 0.15 = 75$		$500 \times 1.09 = 545$		0		0
Moles at equilibrium.	$75 - x$		$545 - x$		x		x

On titration of reaction mixture with $KMnO_4$, only Fe^{2+} reacts with it.

$\therefore$ Equivalents of Fe^{2+} in 25 ml = Equivalents of $KMnO_4$

$$\frac{(545-x)}{1000} \times 25 \times 10^{-3} \times 1 = 30 \times 10^{-3} \times 0.0833 \times 5$$

$$\frac{(545-x)\times 25}{1000} \approx 12.5 \;;\; 545 - x = 500 \;;\; x = 45$$

$$\therefore \quad K_c = \frac{[Fe^{3+}]}{[Ag^+]\,[Fe^{2+}]} = \frac{\frac{45}{1000}}{\frac{(75-45)}{1000} \times \frac{(545-45)}{1000}} = \frac{45 \times 1000}{30 \times 500} = 3.0$$

58.(6) Let the molarity and volume of HX be M_1 and V_1 ml respectively while the molarity of NaOH be M_2.

	HX	+	NaOH	$\longrightarrow$	NaX	+	H_2O
Initial millimoles	M_1V_1		$10M_2$		–		–
After the addition of 10 c.c of NaOH	$M_1V_1 - 10M_2$		0		$10\ M_2$		–

Since weak acid HX and NaX are left after the reaction, they will constitute an acidic buffer.

$$\therefore \quad pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$5.7 = pK_a + \log \frac{10\ M_2}{(M_1V_1 - 10M_2)} \qquad \textbf{...(1)}$$

Let V_2 ml be the volume of NaOH required to neutralize given HX completely.

$\therefore$ At equivalence point, $M_1V_1 = M_2V_2$

$$V_2 = \frac{M_1V_1}{M_2}$$

Dividing the numerator and denominator of log term by M_2, we get

$$\therefore \quad 5.7 = pK_a + \frac{\frac{10M_2}{M_2}}{\frac{M_1V_1 - 10M_2}{M_2}} = pK_a + \log \frac{10}{V_2 - 10} \qquad \textbf{...(2)}$$

Similarly, after the addition of 20 c.c of NaOH, we have

$$6.3 = pK_a + \log \frac{20}{V_2 - 20} \qquad \textbf{...(3)}$$

Subtracting equation (2) from equation (3) $6.3 - 5.7 = \log \frac{20}{V_2 - 20} - \log \frac{10}{V_2 - 10}$

$$0.6 = \log\left(\frac{20}{V_2 - 20} \times \frac{V_2 - 10}{10}\right)$$

Taking antilog, $4 = \frac{2(V_2 - 10)}{(V_2 - 20)}$ $\qquad \therefore \qquad V_2 = 30$ ml.

Putting V_2 in equation (2), $5.7 = pK_a + \log\frac{10}{30-10} = pK_a + \log\frac{1}{2}$

$pK_a = 5.7 + \log 2 = 5.7 + 0.3 = 6.0.$

59. The equilibrium constant for the precipitation reaction is the inverse of K_{sp} for $Cd(OH)_2$.

	$Cd^{2+}(aq)$	+	$2OH^-(aq)$	$\rightleftharpoons$	$Cd(OH)_2(s)$
Initial conc.	1.8×10^{-5}		6×10^{-2}		–
Conc. at equilibrium	y		$6\times10^{-2}-2\times1.8\times10^{-5}$ $=6\times10^{-2}$		1.8×10^{-5}

$$K_{eq} = \frac{1}{\left[Cd^{2+}\right]_{eq}\left[OH^-\right]_{eq}^2} = \frac{1}{K_{sp}} = \frac{1}{2.5\times10^{-14}} = 4.0\times10^{13}$$

$$M_2 = \frac{M_1V_1}{V_2} = \frac{(6.0M)(1.0L)}{1.00\times10^2 L} = 6.0\times10^{-2}M = \left[OH^-\right]_{initial}$$

$$K_{sp} = (y)\left(6.0\times10^{-2}+2y^2\right) \approx (y)\left(6.0\times10^{-2}\right)^2 = 2.5\times10^{-14}$$

$$y = \frac{2.5\times10^{-14}}{\left(6.0\times10^{-2}\right)^2} = 6.9\times10^{-12}$$

$$\left[Cd^{2+}\right]_{eq} = 6.9\times10^{-12}M$$

mol of $Cd(OH)_2$ = mol of Cd^{2+} = MV = $(1.8 \times 10^{-5}$ M$)(1.00 \times 10^2$L$) = 1.8 \times 10^{-3}$ mol

Mass of $Cd(OH)_2$ = (mol)(MM) = $(1.8 \times 10^{-3}$ mol) (146 g/mol) = 0.26 g

60. $\left[Cl^-\right] = \left[Ag^+\right] = \sqrt{K_{sp_{AgCl}}} = \sqrt{1\times10^{-10}} = 10^{-5}M$

Mixing with NaBr has $\left[Ag^+\right] = \frac{10^{-5}\times100}{200}$ and $\left[Br^-\right] = \frac{100\times0.03}{200}$

$$\left[Ag^+\right]\left[Br^-\right] = \left[\frac{10^{-5}\times100}{200}\right]\times\left[\frac{100\times0.03}{200}\right] = 7.5\times10^{-8}$$

The product of ionic concentration is greater than K_{sp} and thus AgBr will be precipitated.

61. $\underset{x-y}{Ag^+} + \underset{1-2y}{2NH_3} \rightleftharpoons \underset{y}{[Ag(NH_3)_2]^+}$ **...(1)** $K_c' = \frac{1}{K_c}$

$AgCl(s) \rightleftharpoons \underset{x-y}{Ag^+(aq)} + \underset{x}{Cl^-}(aq)$ **...(2)** K_{sp}

$AgCl(s) + \underset{1-2y}{2NH_3} \rightleftharpoons \underset{y}{[Ag(NH_3)_2]^+} + \underset{x}{Cl^-}$ **...(3)** $K_c'' = \frac{K_{sp}}{K_c}$

As the value of $K_c' = \frac{1}{K_c}$ is very large, so $x \approx y$

$$K_c'' = \frac{[Ag(NH_3)_2]^+[Cl^+]}{[NH_3]^2}$$

$$\frac{K_{sp}}{K_c} = \frac{y^2}{(1-2y)^2}$$

$$\frac{y}{1-2y} = \sqrt{\frac{1.8\times10^{-10}}{6.2\times10^{-8}}}$$

$$\frac{y}{1-2y} = 0\cdot 05$$

$$y = 0\cdot 05 - 0\cdot 1y$$

$$1\cdot 1y = 0\cdot 05$$

$$y = \frac{0\cdot 05}{1\cdot 1} = 0\cdot 0489$$

62.(9) $[Cl^-] = 0.1M \quad [Br^-] = 0.01M \quad [I^-] = 0.001M$

$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad K_{sp}(AgCl) = 10^{-10}$

$[Ag^+][Cl^-] = K_{sp} \quad \Rightarrow \quad [Ag^+] = \frac{10^{-10}}{0.1} = 10^{-9}M$

AgCl will start precipitating after $[Ag^+]$ is greater than 10^{-9}.

$AgBr \rightleftharpoons Ag^+ + Br^- \qquad K_{sp}(AgBr) = 10^{-13}$

$[Ag^+][Br^-] = K_{sp} \quad \Rightarrow \quad [Ag^+] = \frac{10^{-13}}{0.01} = 10^{-11}$

AgBr starts precipitating after the concentration of $[Ag^+]$ is greater than 10^{-11}.

$AgI \rightleftharpoons Ag^+ + I^- \qquad K_{sp}(AgI) = 10^{-17}$

$[Ag^+][I^-] = K_{sp} \quad \Rightarrow \quad [Ag^+] = \frac{10^{-17}}{0.001} = 10^{-14}$

AgI precipitate when $[Ag^+]$ is greater than 10^{-14}.

Order of precipitation : AgI > AgBr > AgCl

Concentration of Ag^+ required to ppt. all three ions $= 10^{-9}$.

63.(5.97) $pK_{a_1} = 2.34$

$pK_{a_2} = 9.60$

The first inflection point $pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.34 + 9.60}{2} = 5.97$

64.(3.88)

At equivalence point,

$pH = 8.15$

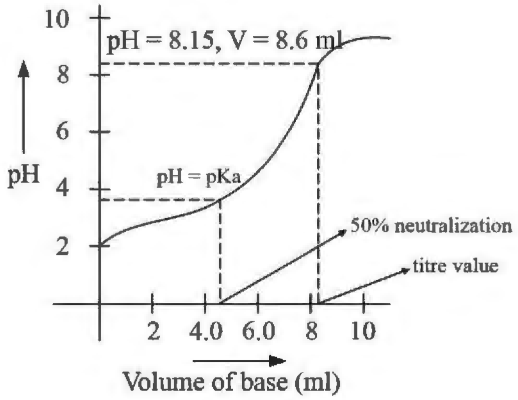
$V_{base} = 8.6mL$

At half equivalence point,

$[salt] = [acid]$

$\Rightarrow \quad pH = pK_a$

$\Rightarrow \quad pH = 3.88$



65.(3.31) $K_a = 6.46\times10^{-5}(C_6H_5COOH)$

$K_{SP}(C_6H_5COOAg) = 2.5\times10^{-13}$

Solubility in water

$$C_6H_5COOAg \rightleftharpoons \underset{S}{C_6H_5COO^-} + \underset{S}{Ag^+}$$

$$K_{sp} = [C_6H_5COO^-][Ag^+]$$

$$S^2 = 2.5\times10^{-13} \quad \Rightarrow \quad S = 5\times10^{-7}$$

Solubility in a buffer of $pH = 3.19$

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+ \qquad K_a$$

$$S = \left\{\frac{K_{SP}}{K_a}\left[[H^+]+K_a\right]\right\}^{1/2}$$

$$S = \left\{\frac{2.5\times10^{-13}}{6.46\times10^{-6}}\left(64.6\times10^{-5}+6.46\times10^{-5}\right)\right\}^{1/2}$$

$$S = 16.5\times10^{-7}$$

$$\frac{S_{buffer}}{S_{water}} = \frac{16.55\times10^{-7}}{5\times10^{-7}} = 3.31$$

Thermochemistry & Thermodynamics

1.(A) $H_2O + C \longrightarrow CO + H_2$ (131 kJ) ....(i)

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$ (–282 kJ) ....(ii)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ (–242 kJ) ....(iii)

(i) + (ii) + (iii)

$\Rightarrow \quad H_2O + C + CO + H_2 + O_2 \longrightarrow CO + H_2 + CO_2 + H_2O$

$\equiv C + O_2 \longrightarrow CO_2 \quad (131 - 282 - 242)\text{ kJ} = -393\text{ kJ}$ (A) –393 kJ

2.(D) $P_{white} \longrightarrow P_{red} \quad \Delta H = -18.4\,kJ$

The energy considerations, i.e., the thermodynamics of reaction does not tell us of the kinetics of the reaction. We can not say that P_{red} is readily formed from P_{white}.

But, it can be said that P_{red} is more stable as energy is released in its production

(D) White P can be converted to red P and red P is more stable.

3.(C) $NH_3 + HCl \longrightarrow NH_4Cl$ (–176 kJ / mol) ....(i)

$N_2 + 3H_2 \longrightarrow 2NH_3$ (–92 kJ / mol) ....(ii)

$N_2 + 4H_2 + Cl_2 \longrightarrow 2NH_4Cl$ (–629 kJ / mol) ....(iii)

(iii) – 2(i) – (ii)

$\Rightarrow \quad N_2 + 4H_2 + Cl_2 + 2NH_4Cl + 2NH_3 \longrightarrow 2NH_4Cl + 2NH_3 + 2HCl + N_2 + 3H_2$

$\Rightarrow \quad \equiv H_2 + Cl_2 \longrightarrow 2HCl\ (-629 - 2(-176) - (-92))\,kJ/mol = -185\,kJ/mol$

$\Rightarrow \quad \frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl\ (-92.5\text{ kJ}/mol = \Delta_f H^{o}_{HCl})$ (C) –92.5 kJ / mol

4.(B) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

At equilibrium, $\Delta G^\circ \Rightarrow \Delta H^\circ - T\Delta S^\circ \quad \Rightarrow \quad T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{30000\,cal}{40\,cal/K} = 750\,K$ (B) 750 K

5.(A) $3N_2H_4(\ell) \longrightarrow 4NH_{3(g)} + 2N_{2(g)}$

1 mol $N_2H_{4(\ell)}$ would produce 2 mol gases

(3 mol N_2H_4 produces 6 mol of gaseous products)

$P = 1.0\,atm, \quad T = 27°C = 300K$

Work done by system = $P\Delta V = RT\Delta n = (8.314\,J/mol/K)\ (300K)\ (2mol) = 4988.4\,J$ (A) –4988.4 J

6.(A) CaO (s) + $CO_2(g) \longrightarrow CaCO_3(s)$

$\Delta H_f^o = \Delta H_f^o\ (CaCO_3) - \Delta H_f^o\ (CaO) - \Delta H_f^o\ (CO_2)$

$= -1207 - (-635) - (-394)$

$\Delta H_f^o = -178$ kJ/mol

$\therefore \quad \Delta E = \Delta H - \Delta n_{(g)}RT$

$\Delta E = -178 - \frac{(-1) \times 8.3 \times 300}{1000} = -175.51$

$n_{CaO} = \dfrac{280}{56} \Rightarrow 5.0$ ∴ $q_V = \Delta E$

For n moles $q_V = \Delta E = 5 \times (-175.51) = -877.55$ kJ

$|q| \Rightarrow 877.55$ kJ

7.(A) $P_iV_i = nRT \Rightarrow V_i = \dfrac{nRT}{P_i} = \dfrac{(0.5)\,(0.08)\,(300)}{(2)} = 6 \text{ L initial}$

As T is constant, PV is also constant at the end of each step.

$$P_iV_i = P_1V_1 = P_2V_2 = P_3V_3 \qquad \Rightarrow \qquad V_1 = \frac{P_iV_i}{P_1} - V_2 = \frac{P_iV_i}{P_2},\ V_3 = \frac{P_iV_i}{P_3}$$

$$\therefore \qquad W_1 = -P_1(V_1 - V_i) = -(P_i - P_1)V_i$$

Similarly,

$$W_2 = -P_2(V_2 - V_1) = -(P_1 - P_2)V_1$$
$$W_3 = -P_3(V_3 - V_2) = -(P_2 - P_3)V_2$$

$$\therefore \qquad |W| = (2-1.6)(6) + (1.6-1.2)\left(\frac{12}{1.6}\right) + (1.2-1)\left(\frac{12}{1.2}\right) = (0.4)(6) + (0.4)(7.5) + (0.2)(10)$$
$$= 2.4 + 3 + 2 = 7.4 \text{ atm-L}$$

(A) 7.4 atm-L

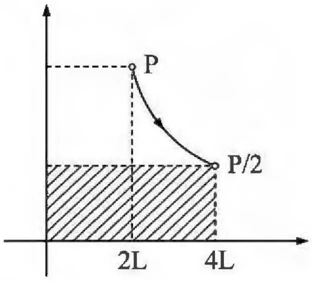
Alter : $|W| = nRT\left(\dfrac{P_i - P_1}{P_i} + \dfrac{P_1 - P_2}{P_1} + \dfrac{P_2 - P_3}{P_2}\right) = 12\left(\dfrac{0.4}{2} + \dfrac{0.4}{1.6} + \dfrac{0.2}{1.2}\right) = 2.4 + 3.2 = 7.4$ atm-L

8.(B) Work calculated by student

$$= \frac{P}{2}.4L = P.2L = W_0$$

Work required $= P.2L.\ell n\left(\dfrac{4L}{2L}\right) = W_0 \ell n2$

$$= 49.26 \text{ L atm} \times 0.69 = 34.14 \text{L-atm}$$



Since, this work is done by the system, work done on system = –34.14.

(B) –34.14

9.(C) Pressure is constant, P

Volume doubles from V to 2V ⇒ Temperature double from T to 2T

$$\Delta u = nC_V\Delta T = \frac{C_VP\Delta V}{R} = \frac{C_VPV}{R}$$

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V} \qquad \Rightarrow \qquad \frac{R}{C_V} = \gamma - 1 \ \Rightarrow\ \frac{C_V}{R} = \frac{1}{\gamma - 1}$$

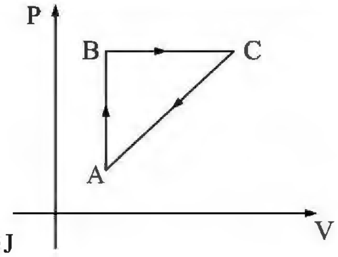
$$\therefore \qquad \Delta u = \frac{PV}{\gamma - 1} \qquad \text{(C)} \quad \frac{PV}{\gamma - 1}$$

10.(B) Work done by gas in A : 2W ; Work done by gas in B : W

Temperature rise is same in both processes.

∴ More heat is absorbed in A than B for same temperature rise ⇒ $C_A > C_B$

(B) $C_A > C_B$



11.(A) In AB : 600 J heat is added

$q_{AB} = 600\,J,\ W_{AB} = 0 \Rightarrow\ 600\,J$

For BC, 200 J heat is added

$W_{BC} = P_B(V_C - V_B) = P_B(V_C - V_A) = 8\times10^4(5-2)\times10^3 = 240\,J$

$q_{BC} + W_{BC} = \Delta U_{BC} \qquad \Rightarrow \qquad \Delta u_{BC} = 200\,J - 240\,J = -40\,J$

$\Delta U_{AB} + \Delta U_{BC} = \Delta U_{AC}$ internal energy is state function $\qquad \Rightarrow \qquad \Delta U_{AC} = 560\,J$

12.(D) Proceeding without external influence once it has begun. (Defn)

13.(A) $C + O_2 \longrightarrow CO_2$ (–393.5 kJ/mol) **. . . .(i)**

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ (–285.8 kJ/mol) **. . . .(ii)**

$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$ (–2598.8 kJ/mol) **. . . .(iii)**

$2(i) + (ii) - \frac{1}{2}\ (iii)$

$= 2C + H_2 \longrightarrow C_2H_2 \ \left(2(-393.5) + (-285.8) - \frac{1}{2}(-2598.8)\right)\text{kJ / mol}$

$= 226.6\,\text{kJ / mol}$

14.(D) All spontaneous processes are those where total entropy i.e. system + surroundings increases.
Thus, (a), (c), (d) are true.
Basically, time moves in the direction where entropy of universe increases.
Now, in (b), we have a closed system, i.e. even through matter can't move into or out of system, energy can.
Clearly, (b) can also be true of entropy of surroundings increase more than decrease of entropy of system.

15.(D) $C - Cl$ energy is calculated from

$CCl_{4(g)} \longrightarrow C_{(g)} + 4Cl_{(g)}$

$\Delta_f H^{\circ}_{CCl_4\text{-}\ell}$ gives : $C_{(s)} + 2Cl_{2(g)} \longrightarrow CCl_{4(\ell)}$

$\Delta_{vap} H^{\circ}_{CCl_4}$ gives : $CCl_{4(\ell)} \longrightarrow CCl_{4(g)}$

$\Delta_f H^{\circ}_{C(g)}$ gives : $C_{(s)} \longrightarrow C_{(g)}$

$BeCl_2$ gives : $Cl_{2(g)} \longrightarrow 2Cl_{2(g)}$

Clearly, we need all these values to calculate $C - Cl$ bond energy.

16-18. Heat of formation : Heat absorbed/evolved when one mol of a compound is formed from constituent element in standard state.
Heat of combustion : Heat absorbed/evolved when one mol of compound is burnt completely in excess of oxygen.

16.(A) Energy released $= x$

$\therefore \quad \Delta H = -x$

(A) $-x$

17.(C) $\Delta H^{\circ}_{\text{combustion},\ C_6H_{12}O_6}$

18.(B) $x + z$ (Hess' law)

19-21. $\gamma = \frac{C_P}{C_V} = \frac{5}{3}$ for monoatomic gas

19.(A) 1.66

20.(B) Argon : molar mass 40 g

Energy required $= \dfrac{20\text{g}}{40\text{g/mol}} \times 5\,\text{cal/mol/°C} \times 1\text{°C} = 2.5\,\text{cal}$

21.(C) Constant volume, specific heat

$\Rightarrow \quad \left[\dfrac{\delta E}{\delta T}\right]_V$

22-24.

22.(A) –ve $\quad \Delta S \Rightarrow$ randomness of system decreases

Clearly in adsorption, the movement, i.e. randomness of absorbed particles decreases.

(A) adsorption

23.(A) Clearly, ΔS_{fusion} is at melting point.

$\Delta S_{\text{vap.}}$ is at boiling point.

(A) T, is MP, T_2 is BP

24.(D) Absolute entropy is determined using 3rd law which states that entropy of system at 0K is zero.

(D) 3rd law.

25-27.

25.(D) Isochoric $\Rightarrow \Delta V = 0$

$\Delta u = q + w$ is always true (1st law)

As $\Delta V = 0,\ \Delta u = q_V$

(D) all of these

26.(D) In isothermal process, $\Delta T = 0$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ is not true for isothermal processes. It is true for adiabatic processes.

(D) $T_1V_1^{-1} = T_2V_2^{\gamma-1}$

27.(C)

28.(ABC) Isolated system

$\Rightarrow$ matter and energy cannot be exchanged through it.

(BC) impermeable, adiabatic

29.(AB) $\Delta E = 0 \Rightarrow \Delta T = 0$

(A) cyclic process, isothermal expansion.

30.(AB) If both temperature are less than critical temperature on increasing temperature, Z would increase. Gas would become less compressible and volume would become more than double.

However, above Boyle temperature, on increasing temperature, Z decreases. Gas becomes more compressible and volume would be less than doubled.

31.(ABC) Molar internal energy is intensive property. Heat capacity is extensive property

Reversible processes take place quasistatically.

32.(AD) Reversible adiabatic process has $\Delta S = 0$ as $\Delta G = 0$

$\Delta S_{surr} = 0,\ \Delta S_{sys} > 0$: Irreversible adiabatic expansion

$\Delta S_{surr} = 0,\ \Delta S_{sys} > 0$: Free expansion

$\Delta S_{surr} > 0,\ \Delta S_{sys} < 0$: Irreversible isothermal compression

33.(ACD) All spontaneous processes are irreversible (ABC)

At 0.1 atm, BP of water < 373 K.
So, at T = 373 K vaporization is spontaneous

34.(ACD) 3^{rd} law: At 0 K, entropy of perfectly crystalline substance = 0
At all temperatures above 0 K, entropy > 0 (ACD) are false

35.(AD) $\Delta_f H^\circ \cdot H^+(aq), Br_2(l) = 0$

36.(ABC) Isothermal irreversible expansion $\Delta U = 0$

$$w = -p_{ext.}(V_2 - V_1)$$
$$p_{ext} = p_2,$$
$$p_2V_2 = p_1V_1 = RT$$
$$\therefore \quad w = -p_2(V_2 - V_1) = (p_2 - p_1)V_1 = -\left(1 - \frac{p_2}{p_1}\right)RT$$
$$q = -w = RT\left(1 - \frac{p_2}{p_1}\right) = \Delta H$$

37.(BC) $C_{graphite} + O_2, g \longrightarrow CO_2; \Delta H = -94.05 \text{ k cal/mol}$ **...(i)**

$C_{diamond} + O_2, g \longrightarrow CO_2; \Delta H = -94.5 \text{ k cal/mol}$ **... (ii)**

(ii) – (i) $\Rightarrow \quad C_{diamond} \longrightarrow C_{graphite} (-450 \text{ cal/mol})$

$\Rightarrow \quad C_{graphite} \longrightarrow C_{diamond} (450 \text{ cal/mol})$

Clearly, graphite is more stable allotrope

38.(B) $C_2H_6(g) \to 2C(g) + 6H(g) : 1\,C\overset{x}{-}C, \quad 6\,C\overset{y}{-}H$

$C_3H_8(g) \to 3C(g) + 8H(g) : 2\,C-C, \quad 8\,C-H$

$x + 6y = 620 \quad \ldots(i)$

$2x + 8y = 880 \quad \ldots(ii)$

2 (i) –(ii) $\Rightarrow \quad 4y = 360 \Rightarrow y = 90 kJ/mol$

$\Rightarrow \quad x = 80 kJ/mol$ (B) 80 and 90 kJ/mol

39.(AB) $ds = \dfrac{dq}{T} = \dfrac{du - dw}{T} = \dfrac{nC_v dT + pdV}{T} = nC_v\dfrac{dT}{T} + nR\dfrac{dV}{V}$

$\Rightarrow \quad \int ds = nC_v\int\dfrac{dT}{T} = nR\int\dfrac{dV}{V} \quad \Rightarrow \quad \Delta S = nC_v \ln\left(\dfrac{T_2}{T_1}\right) + nR\ln\left(\dfrac{V_2}{V_1}\right)$

(A) $nC_v \ln\left(\dfrac{T_2}{T_1}\right) + nR\ln\left(\dfrac{V_2}{V_1}\right)$ Modify the equal to get (B) also

40.(B) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_1 -393 kJ/mol \quad \ldots(i)$

$CO_{2(g)} \longrightarrow C_{(g)} + 2O_{(g)} \quad \Delta H_2 = 2BE_{C=0}$

$C_{(s)} \longrightarrow C_{(g)} \; 718 kJ/mol \;\; \Delta H_3 \quad \ldots(ii)$

$O_{2(g)} \longrightarrow 2O_{(g)} \; 498 \text{ kJ/mol} \;\; \Delta H_4 \quad \ldots(iii)$

Thus expected value $\Delta H_2 = \Delta H_3 + \Delta H_4 - \Delta H_1 = 1609$ kJ/mol

Actual value of $\Delta H_2 = 2BE_{C=0} = 678$ kJ/mol

Difference: (678 – 1609) kJ/mol = – 931 kJ/mol

41.(ABD) $-\Delta G^\circ = RT\ln k$

$\Delta G = \Delta G^\circ + RT\ln Q$

At equilibrium, $\Delta G = 0$

Thus, (ABC) are true

42.(BCD) According to IInd law $dS_m = C_V\frac{dT}{T} + R\frac{dV}{V}$

$dG = dH - SdT$

$dH = dq$ (D) are true

43.(ACD) Free expansion : $\Delta U = 0,\ \Delta T = 0,\ \ q = 0$

$\Delta S_{sys} > 0,\ \Delta_{Surr} = 0,\ W_{sys} = 0,$

$\Delta G < 0$

(ACD)

44.(BC) $\Delta G_{sys} < 0 \quad \Rightarrow \quad \Delta H_{sys} - T\Delta S_{sys} < 0$

Reaction need not always be exothermic.

$\Delta_f H^\circ{}_{s,\text{rhombic}} = 0, \Delta_f H^\circ{}_{s,\text{ monoclinic}} \neq 0$

$CH_4 : 4C - H$: 1656 kJ/mol

$\Rightarrow$ $C - H$: 414 kJ/mol

C_2H_6 : $C - C$, 6 $C - H$: 2812 kJ/mol

6 $C - H$: 2484 kJ/mol

$\Rightarrow$ $C - C$: 328 kJ/mol

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O(l)$ –56 kJ/mol

$\Delta_f H^\circ H_2O_g = -242$ kJ/mol

$\Delta_{vap} H^\circ H_2O = 44$ kJ/mol

$\therefore$ $\Delta_f H^\circ H_2O,l = (-242 - 44)$ kJ/mol $= -286$ kJ/mol

$\Delta_r H^\circ = \Delta_f H^\circ{}_{H_2O,l} - \Delta_f H^\circ{}_{OH^-,aq} \Rightarrow \Delta_f H^\circ{}_{OH^-,aq} = (-286 \text{ kJ/mol}) - (-56 \text{ kJ/mol}) = -230 \text{ kJ/mol}$

45.(ABD) We know,

$\Delta G = \Delta H - T\Delta S; \Delta G$ will be negative for spontaneous process.

$\therefore$ When $\Delta H = -ve$ and $\Delta S = +ve$, then $\Delta G = -ve$ and process will be spontaneous.

In all other conditions, the process may be non spontaneous.

46.(ABC) During adiabatic expansion or compression of an ideal gas, q = 0

$\therefore$ $w = \Delta U = nC_V\Delta T$

As, $C_V = \frac{R}{\gamma - 1}$

$\Rightarrow$ $W = \frac{nR}{\gamma - 1}(T_2 - T_1)$

47.(BC) For the cyclic process, ABCA,

$\Delta H = 0,\ \ \Delta U = 0,\ \ \Delta S = 0$

Total work done = Total heat exchange

i.e., W = q

48.(BC) $\Delta H = \Delta U + (\Delta n_g)RT$

For $\Delta H < \Delta U, \quad \Delta n_g > O$

In options A & D, $\Delta n_g = O$

In options B & C, $\Delta n_g > O$

49.(ABCD) Refer to Theory

50. **[A-q] → [B-p, s] → [C-r]**

Isochoric : $w = 0,\ \Delta V = 0$

Isothermal reversible expansion : $\Delta T = 0,\ \Delta E = 0, \Delta H = 0$

Adiabatic work : $w = \frac{nR}{\gamma - 1}(T_2 - T_1) = nC_V\Delta T$

51. **[A-p] → [B-r] → [C-q] → [D-t]**

10 mL HA + 10 mL BOH produces 5°C temperature rise

Heat evolved : 5°C from 20 mL $\quad q = 20 \times s \times 5 = 20 \times 4.2 \times 5 = 40\,\text{cal}$

100 mL HA + 100 mL BOH : $\frac{420}{20} \times 200 = 200 \times 4.2 \times \Delta T,\ \Delta T = 5°C$

10 mL HA + 20 mL BOH : $\frac{420}{20} \times 20 = 30 \times 4.2 \times \Delta T,\ \Delta T = 333°C$

20 mL HA + 30 mL BOH : $\frac{420}{20} \times 40 = 50 \times 4.2 \times \Delta T,\ \Delta T = 4°C$

50 mL HA + 150 mL BOH : $\frac{420}{20} \times 100 = 200 \times 4.2 \times \Delta T,\ \Delta T = 2.5°C$

52. **[A-q] → [B-q, r, s] → [C-q, r] → [D-p]**

$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ combustion

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$ combustion, formation, fuel cell

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ combustion, formation

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(\ell)}$ neutralisation

53. **[A-s] → [B-p] → [C-r] → [D-q]**

$H_2O_{(\ell)} \rightleftharpoons H_2O_{(s)} \quad \Delta H < 0,\ \Delta S < 0$

$2A(s) + 1/2\,O_2(g) \rightleftharpoons A_2O(s) \quad \Delta H > 0,\ \Delta S < 0,\ \Delta G > 0$

$C_{diamond} \rightleftharpoons C_{graphite}$

Diamond forms at high T, P

$\therefore$ $\Delta S > 0,\ \Delta H > 0$ formation of diamond $\quad \therefore\ \Delta H > 0$ formation of diamond, $\Delta S < 0$ formation of graphite.

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta S > 0$

E_a forward = 57.2 kJ, E_a, backward = 3.2 kJ $\quad \Rightarrow \quad \Delta H > 0$

54.(8) 2 kcal heat added to system and 6 kcal heat added to system

55.(5) T : 300 K to 400 K

P_{ext} = constant $\quad$ Work done by gas = 4.157 kJ

$W = -P_{ext}\ \Delta V = -nR\Delta T \quad \Rightarrow \quad n = \frac{W}{R\Delta T} = 5$

56.(6) $\Delta H = \Delta U + \Delta PV = 14 + \big((2)(1) - (5)\ (2)\big) = 14 + 2 - 10 = 6$

57.(8) 4.0 L 20 K

Adiabatic expansion to 25 L

$\gamma = 1.5$

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \quad \Rightarrow \quad (4)^{1/2}(20) = T_2 (25)^{1/2} \quad \Rightarrow \quad T_2 = \frac{(20)(2)}{(5)} = 8$$

58.(8) $\Delta H_{vap} = 3600\ J$

$BP = 177°C = 450K$

$$\Delta S = \frac{\Delta H}{T} = 8J/K$$

59.(27.20)

$$\begin{matrix} P_1 = 20\,atm & & P_2 = 10\,atm \\ & \longrightarrow & \\ V_1 = 15\,L & & V_2 = 60 \end{matrix}$$

$C_{p,m} = 30.96$

$$\Delta S = nC_p \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

$$= 30.96 \ln\left(\frac{7308}{3654}\right) - 8.314 \ln\left(\frac{10}{20}\right) = 21.46 + 5.76$$ (temperature calculated using PV = nRT)

$\Delta S = 27.22\, JK^{-1} mol^{-1}$

60.(15) $\begin{matrix} 1L & & 4L \\ 10\,atm & \longrightarrow & 5\,atm \end{matrix}$ $\quad P_{ext} = 1\,atm$

$T = 300K$ $\quad C = 50\,J/°C$

Work done during process,

$$w = -P_{ext}(V_2 - V_1) = -1\,atm(4L - 3L) = -3L\,atm = -300\,J$$

Using ideal gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\Rightarrow \quad T_2 = \frac{4 \times 5 \times 300}{1 \times 10} \quad \Rightarrow \quad T_2 = 600\,K$$

$\Delta T = (600\,K - 300\,K) = 300\,K = 300°C$

$\Delta H = C\Delta T = 50\,J/°C \times 300°C = 15000\,J = 15\,kJ$

61. (−557)

$$2CO \ + \ O_2 \ \longrightarrow \ 2CO_2 \qquad \Delta H = -560\,kJ$$

2 mol 1 mol –

$V = 1L$ $\quad P_1 = 70\,atm$ $\quad P_2 = 40\,atm$

$\Delta H = \Delta U + \Delta(PV)$ (Since volume remains constant)

$-560\,kJ = \Delta U + V\Delta P$

$\Delta U = -560\,kJ - (1 \times -30 \times 0.1)\,kJ = -557\,kJ$

62.(10.9) The complete reaction is

$$3I_2(s)+6OH^-(aq) \rightleftharpoons 5I^-(aq)+IO_3^-(aq)+3H_2O(\ell)$$

$$K_{eq}=\frac{\left[IO_3^-\right]\left[I^-\right]^5}{\left[OH^-\right]^6} \qquad \text{....... (i)}$$

$$\Delta G^\circ_{rxn}=3\Delta G^\circ_{f(I^-)}+\Delta G^\circ_{f(IO_3^-)}+3\Delta G^\circ_{f(H_2O)}-\left\{6\Delta G^\circ_{f(OH^-)}\right\}$$

$$=3(-50\,kJ\,mol^{-1})+(-123.5\,kJ\,mol^{-1})+3(-233\,kJ\,mol^{-1})-6(-150\,kJ\,mol^{-1})$$

$$=-72.5\,kJ\,mol^{-1}$$

$$\Delta G^\circ=-RT\ln K_{eq}$$

$$-72.5\,kJ\,mol^{-1}=-2.3\times\frac{25}{3}JK^{-1}mol^{-1}\times\log K_{eq}\times 300\,K$$

$$\Rightarrow \quad \log K_{eq}=12.6 \quad \Rightarrow \quad K_{eq}=3.98\times10^{12}$$

Substitution in (i)

$$3.98\times10^{12}=\frac{(0.1)(0.1)^5}{[OH^-]^6}$$

$$\Rightarrow \quad [OH^-]^6=2.51\times10^{-19} \quad \Rightarrow \quad [OH^-]=0.00079$$

$$\Rightarrow \quad pOH=-\log(0.00079)$$

$$pOH=3.09$$

$$\Rightarrow \quad pH=14-pOH=10.9$$

Chemical Kinetics

1.(B) $M \rightarrow N$

Rate $\propto [M]^x$

Rate $= k\,[M]^x$

Rate $\times 8 = k\,[2M]^x$

$$\frac{8R}{R} = \frac{k[2M]^x}{k[M]^x} \Rightarrow [2]^3 = [2]^x$$

$\Rightarrow x = 3$

2.(D) We know, $\log_{10} k = \log_{10} A - \frac{E_a}{2.303R} \times \frac{1}{T}$ **. . . . (i)**

The given equation is $\log_{10} k = 6 - \frac{2000}{T}$ **. . . . (ii)**

Comparing eqns. (i) and (ii)

$\log_{10} A = 6 \;\therefore A = 10^6\ \text{sec}^{-1}$ (for first order reaction)

$$\frac{E_a}{2.303R} = 2000$$

$E_a = 2000 \times 2.303 \times 8.314 = 38294\ \text{J mol}^{-1} = 38.3\ \text{kJ mol}^{-1}$

3.(A) $2A \overset{k}{\rightleftharpoons} B$; $B + C \xrightarrow{k_f} P$

$K = \frac{[B]}{[A]^2}$ **. . . .(i)** $\qquad \frac{d[P]}{dt} = k_f[B][C]$ **. . . .(ii)**

From (i) and (ii), $\frac{d[P]}{dt} = Kk_f[A]^2[C]$

4.(A) $t = \frac{0.693}{k}$ for first order reaction

$$k = \frac{2.303}{\text{time}} \log\left(\frac{a}{a-x}\right)$$

$$\frac{0.693}{t} = \frac{2.303}{\text{time}} \log\left(\frac{100}{100-99.9}\right)$$

$$\text{time} = \frac{6.909}{0.693} \approx 10t$$

5.(A) Rate $\propto \frac{kP}{1+kP}$

At high pressure, $kP >>> 1 \quad \therefore kP + 1 \approx kP$

$\therefore$ Rate = Constant and the reaction will be a zero order reaction.

6.(B) $PV = nRT$

$$P = \frac{n}{V}RT = CRT$$

$$\frac{1}{RT}\frac{dP}{dt} = \frac{1}{V}\frac{dn}{dt} = \frac{dC}{dt}$$

7.(A) For the given reaction, $-\frac{1}{2}\frac{d[NH_3]}{dt}=\frac{d[N_2]}{dt}=\frac{1}{3}\frac{d[H_2]}{dt}$

$\frac{1}{2}k_1=k_2=\frac{1}{3}k_3$

$1.5k_1=3k_2=k_3$

8.(D) $\log_{10}\left(\frac{k_2}{k_1}\right)=\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$

$\log\frac{4.5\times10^7}{1.5\times10^7}=\frac{E_a}{2.303\times8.314}\left[\frac{1}{323}-\frac{1}{373}\right]$

$E_a=2.2\times10^4\,J\,mol^{-1}$

9.(D) (i) Molecularity can never be fractional

(ii) Zero order reaction completes

(iii) first order reaction may be homogeneous or heterogenous

(iv) $K=\frac{A}{e^{Ea/RT}}$ as temperature increases, K increases

10.(B) Photo chemical reactions generally are zero order

11.(A) $k_2=Ae^{-E_{a_2}/RT}$, $k_1=Ae^{-E_{a_1}/RT}$

$\therefore\ \frac{k_2}{k_1}=e^{\left(-E_{a_2}+E_{a_1}\right)/RT}$

$\frac{k_2}{k_1}=e^{-E_{a_1}/RT}$ (Since, $E_{a_2}=2E_{a_1}$)

$k_2=k_1e^{-E_{a_1}/RT}$

12.(C) Collision theory is given for Biomolecular reaction.

13.(C) Statement 1 incorrect because, rate does not depend on concentration for zero order reactions.

14.(B) Half - life of the given reaction is independent of concentration. Hence, it will be a first order reaction.

15.(C) Mechanism-I

$\text{rate}\propto[NO_2]^1[O_3]^1$

Mechanism-II

$\text{rate}\propto[NO_2]^1[O]$ ....(1)

Apply steady state approximation.

$K_{eqm}=\frac{[O_2][O]}{[O_3]}$

$[O]=K_{eqm}\frac{[O_3]}{[O_2]}$ ....(2)

on putting (2) in (1)

$\text{rate}\propto\frac{[NO_2]^1[O_3]^1}{[O_2]}$

16.(B) For maximum increase of k, E_a should be high & ΔT as high as possible

17.(B) $\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1}-1}{4^{n-1}-1}$

It depends only on 'n'

18.(B) $t_{1/2} \propto \frac{1}{a^{n-1}}$

n = 2, for second order reaction

$\therefore \qquad t_{1/2} \propto \frac{1}{a}$

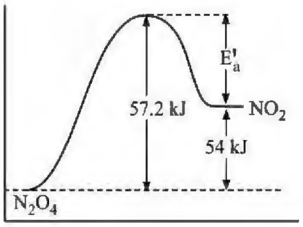
19.(A) $[C_t] = \frac{[C_0]}{2^n} \Rightarrow 1 = \frac{16}{2^n} \Rightarrow n = 4$ where n is the no. of half lives

$\Rightarrow n = \frac{\text{total time taken}}{\text{Half life}}$

$4 = \frac{\text{total time}}{30}$

Total time = 120 mins.

20.(B)



$E'_a = E_a - \Delta H$

$= 57.2 - 54$

$= 3.2\,\text{kJ}$

21.(C) Step 1 : $2NO \rightleftharpoons N_2O_2$

Step 2 : $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

Step 3 : $N_2O + H_2 \longrightarrow N_2 + H_2O$

Rate = $k[N_2O_2][H_2]$

From step 1, $\quad k = \frac{[N_2O_2]}{[NO]^2}$ or $[N_2O_2] = k[NO]^2$

$\therefore \qquad \text{Rate} = kK[NO]^2[H_2] = k'[NO]^2[H_2]$

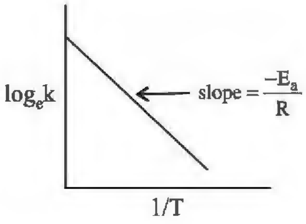
22.(C) $-\frac{d[A]}{dt} = k_1[A] - k_2[B]$

23.(B) $k = Ae^{-E_a/RT}$

$\log_e k = \log_e A - \frac{E_a}{RT}$

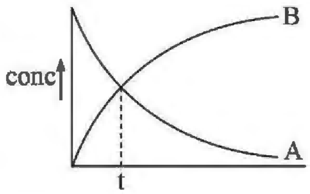
$y = c + mx$

$\text{Slope} = \frac{-E_a}{R}$



24.(C) Catalyst forms new intermediate in the reaction, therefore, provides alternative path for climbing the activation energy barrier. In other words. Catalyst alters the reaction mechanism.

25.(A)



At the point of intersection

$[A]_t = \frac{[A]}{2}$

$\therefore$ Point of intersection of two curves represents $t_{1/2}$.

26.(D) Specific rate constant depends only on temperature

$$K = A\ e^{-Ea/RT}$$

27.(C) Statement-I For complex reaction molecularity is not applicable.

Statement-II Molecularity & order are same only for elementary reaction & not for complex reaction

28.(B) Statement-I Order of reaction may be, zero, fractional positive & negative

Statement-II Order of reaction is the mathematical number that describes the effect of change of concentration on rate of reaction.

29.(C) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Rate = $k[CH_3COOC_2H_5][HOH]$

Water is present in large excess, therefore, concentration of water will be almost constant.

Thus, rate law may be given as

Rate = $k'[CH_3COOC_2H_5]$

$\therefore$ It is pseudo first order reaction.

30.(B) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt} = \text{Rate of reaction}$$

31.(D) For the reaction, $m_1A + m_2B \longrightarrow n_1C + n_2D$

$$-\frac{1}{m_1}\frac{d[A]}{dt} = +\frac{1}{n_1}\frac{d[C]}{dt}$$

$$-\frac{d[A]}{dt}\Big/\frac{d[C]}{dt} = \frac{m_1}{n_1}$$

32.(B) In the reaction

$$\begin{array}{ccc} 2SO_2(g) + O_2(g) & \longrightarrow & 2SO_3(g) \\ 1mol & & 2\ mol \\ 32g & & 160\ g \end{array}$$

$\because$ 160 g of SO_3 is formed by 32 g of O_2

$\therefore$ 100 g of SO_3 will be formed by $\frac{32}{160} \times 100$ or 20 g of O_2

$\therefore$ Rate of disappearance of O_2 = 20 g min^{-1}

33.(B) $O_3(g) \rightleftharpoons O_2(g) + [O]$ (fast) .... (i)

$O_3 + [O] \longrightarrow 2O_2$ (slow) ....(ii)

$\text{Rate} = k'[O_3][O]$ .... **(iii)**

From eqn. (i) $K = \dfrac{[O_2][O]}{[O_3]}$

$$[O] = \frac{K[O_3]}{[O_2]}$$

From eqn. (ii) rate $= k'[O_3]\dfrac{K[O_3]}{[O_2]} = k''[O_3]^2[O_2]^{-1}$

34.(C) Step 1 : $NO + Br_2 \rightleftharpoons NOBr_2$ (fast)

Step 2 : $NOBr_2 + NO \longrightarrow 2NOBr$ (slow)

$\text{Rate} = k'[NOBr_2][NO]$ .... **(i)**

From step 1, $K = \dfrac{[NOBr_2]}{[NO][Br_2]}$

$[NOBr_2] = K[NO][Br_2]$ .... **(ii)**

From eqns. (i) and (ii), $\text{Rate} = k'K[NO][Br_2][NO]$

$= k[NO]^2[Br_2]$

$\text{Order} = 2 + 1 = 3$

35.(D) Slowest step is rate determining.

Thus $\text{Rate} = k[A_2]$ and $\text{Order} = 1$

36.(B) Slowest step is rate determining, therefore $B \rightarrow C$ will be rate determining. Its rate constant is lowest

37.(AD) (A) $A \longrightarrow B$

$t = 0 \quad C \quad -$

$t = t \quad C - C\alpha \quad C\alpha$

for first order reaction

$$Kt = \ell n\frac{a}{a-x}$$

$$Kt = \ell n\frac{C}{C - C\alpha}$$

$$e^{kt} = \frac{1}{1-\alpha}$$

$$1 - \alpha = e^{-Kt}$$

$$-\alpha = e^{-Kt} - 1$$

$$\alpha = 1 - e^{-Kt}$$

(B) $\dfrac{1}{C_t}$ vs t is straight-line for second order reaction

(C) $t_{3/4} = \dfrac{3}{2} \times t_{1/2}$

(D) $K = Ae^{-Ea/RT}$, exponential factor is unit less. & K has unit of $(\text{time})^{-1}$. So A will also has unit of $(\text{time})^{-1}$.

38.(BC) Rate = k [RCl]. It is of first order, therefore, rate of reaction will be halved when the concentration of halide is reduced to half.

Rate of reaction increases with increase in temperature. We have to consider only forward reaction.

As $T\uparrow \Rightarrow k\uparrow \Rightarrow r\uparrow$

39.(ABD) Only option (C) is incorrect because half - life order reaction is independent of initial concentration of reactant.

$$t_{1/2} = \frac{0.693}{k}$$

40.(ACD) Catalyst does not alters the equilibrium constant because it affects the rate constant of forward and backward reaction equally.

41.(AB) In the equation : $k = Ae^{-E_a/RT}$; k will be equal to 'A' when either $E_a = 0$ or $T = \infty$ K

42.(ABD) Rate = $k[A]^{2/3}[B]$

$$\text{Order} = \frac{2}{3} + 1 = \frac{5}{3}$$

$$\text{Unit of } k = \left[\frac{L}{mol}\right]^{n-1} \times sec^{-1} = \left[\frac{L}{mol}\right]^{\frac{5}{3}-1} \times sec^{-1} = L^{2/3}\ mol^{-2/3}\ sec^{-1}$$

43.(CD) Arrhenius equation is : $k = Ae^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{.... (i)}$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT} \qquad \text{....(ii)}$$

From eq. (i)

$$\ln A = \ln k + \frac{E_a}{RT} \qquad \text{.... (iii)}$$

44.(AD) Large slope corresponds to large activation energy. Thus E_{a_1} will be greater than E_{a_2} and D, E will be the favorable products.

45.(AB) $t_{3/4} = 2 \times t_{1/2}$

$t_{15/16} = 4 \times t_{1/2}$

These are standard relation of first order reaction.

46.(AC) $\Delta H = E_f - E_b = (60 - 40) = +20$ kJ

$\Delta H = +$ ve ; hence it is an endothermic reaction.

47.(BD) Rate of zero order reactions do not depend on the concentration of reactant.

In the equation, $k = Ae^{-E_a/RT}$

$k = A$ when $E_a = 0$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303} \times \frac{1}{RT}$$

$$y = c + mx$$

When log k is plotted against $\frac{1}{T}$, we get straight line with negative slope.

48. **[A-p, q] → [B-s] → [C-r] → [D-r]**

Half – life of a reaction depends on initial concentration or initial pressure of the reactant as

$$t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{or} \quad t_{1/2} \propto \frac{1}{p^{n-1}}$$

INTEGER TYPE :

49.(2) According to rate law, $\frac{dc}{dt}=k[A_2]^x[B_2]^y$

$$\frac{0.04}{0.08}=\frac{k[0.2]^x[0.2]^y}{k[0.2]^x[0.4]^y}$$

$$\left[\frac{1}{2}\right]=\left[\frac{1}{2}\right]^y \quad \Rightarrow\ y=1$$

$$\frac{0.04}{0.08}=\frac{k[0.1]^x\ [0.4]^y}{k[0.2]^x\ [0.4]^y}$$

$$\left[\frac{1}{2}\right]=\left[\frac{1}{2}\right]^x \quad \Rightarrow x=1$$

Order = 1 + 1 = 2

50.(9) $$\frac{t_{1/8}}{t_{1/10}}=\frac{\frac{2.303}{k}\log\frac{1}{1/8}}{\frac{2.303}{k}\log\frac{1}{1/10}}$$

$$\frac{t_{1/8}}{t_{1/10}}\times 10=\left[\frac{\log 8}{\log 10}\right]\times 10=9$$

51.(3) $$\frac{t_2}{t_1}=\left(\frac{a_1}{a_2}\right)^{n-1}$$

$$16=\left(\frac{1}{1/4}\right)^{n-1} \qquad \therefore \qquad n=3\text{, i. e, third order reaction.}$$

52.(4) $t_{99.9\%}=10\times t_{50\%}=10\times 0.4=4$ min

53.(4)

$$\begin{array}{llll} & X_2(g) & \longrightarrow Z(g) + & \frac{1}{2}Y(g) \\ t_0 & 150 & \quad 0 & 0 \\ 10\,\text{min} & 150-x & \quad x & \frac{x}{2} \end{array}$$

Total pressure of reaction after 10 min $=150-x+x+\frac{x}{2}=170 \ \Rightarrow\ x=40$

thus rate of disappearance of $X_2=\frac{-d[X_2]}{dt}=\frac{40}{10}=4\text{mm}/\text{min}$.

54.(9) $\frac{k_2}{k_1}=2^n$ where $n=\frac{\text{change in temp}}{10}$ $\qquad \Rightarrow n=\frac{115-25}{10}=\frac{90}{10}=9$

55.(2) $K=[A][B]^2$, if ‘A’ is taken in excess, then change in concentration of [A] wont effect rate of reaction. So, reaction rate will only depend upon concentration of B & hence reaction will be 2nd order reaction.

56.(60) $N_2+3H_2\longrightarrow 2NH_3$

$$\text{rate}=-\frac{d[N_2]}{dt}=-\frac{1}{3}\frac{d[H_2]}{dt}=\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$\frac{d[NH_3]}{dt}=40\times10^{-3}\text{mol L}^{-1}\text{s}^{-1} \quad \Rightarrow \quad \frac{d[H_2]}{dt}=\frac{3}{2}(40\times10^{-3}\text{ mol L}^{-1}\text{s}^{-1})=60\times10^{-3}\text{ mol L}^{-1}\text{s}^{-1}$$

57.(490) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Rate constant $= k = 3.38\times10^{-5}s^{-1}$

Order of reaction $= 1 \quad \Rightarrow \quad$ Rate $\propto [N_2O_5]^1$

Rate $= k[N_2O_5] \qquad t = 10\,\text{min} = 600\,s$

$A_t = A_0e^{-kt} \quad \Rightarrow \quad A_t = 500e^{-3.38\times10^{-5}\times600} \quad \Rightarrow \quad A_t = 490\,\text{atm}$

58.(3.44) $\qquad A \longrightarrow B$

At $t = 0 \qquad 1M \qquad 0$

After $1h \qquad (1-x)M \qquad xM$

Rate of reaction after $1h = k(1-x) \qquad$ .... (i)

For the calculation of $1-x$, first order kinetic equation is used as follows :

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

or $\qquad 4.5\times10^{-3}\,\text{min}^{-1} = \frac{2.303}{1\times60}\log_{10}\frac{1}{(1-x)}$ or $\log\frac{1}{(1-x)} = \frac{4.5\times10^{-3}\times60}{2.303} = 0.1172$

$\therefore \qquad \frac{1}{1-x} = 1.310 \quad \therefore \quad (1-x) = 0.7633M$

Rate of reaction after $1h = 4.5\times10^{-3}\times0.7633 = 3.435\times10^{-3}\,M\,\text{min}^{-1}$

59.(5.2) Let initial conc$(a) = 100$, $t = 10h = 36000s$, $x = (?)$

$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$; $\qquad 1.5\times10^{-6} = \frac{2.303}{3.6\times10^4}\log\frac{100}{(100-x)} \qquad \therefore \qquad x = 5.2$

Thus, initial concentration changed into product is 5.2%.

60.(12500)

For a second order reaction $\frac{1}{A_t} = \frac{1}{A_0} + kt \quad \Rightarrow \quad \frac{1}{0.5} = \frac{1}{1} + 8.0\times10^{-5}\times t \quad \Rightarrow \quad \frac{1}{8\times10^{-5}} = t \quad \Rightarrow$

$t = 12500\,\text{min}$

61.(1.93) $N_0 = 0.1g$ atom

$t = 10$ days and $t_{1/2} = 5$ days

$\lambda = \frac{2.303}{t}\log\frac{N_0}{N} \qquad \frac{0.693}{5} = \frac{2.303}{10}\log\frac{0.1}{N}$

$\therefore \qquad$ Amount left after 10 days $= 0.0250g$ atom

Similarly if $t = 11$ days

$\frac{0.693}{5} = \frac{2.303}{11}\log\frac{0.1}{N} \qquad \therefore \qquad$ Amount left after 11 days $= 0.0218g$ atom

$\therefore \qquad$ Amount decayed in 11th day $= 0.0250 - 0.0218$

$$= 3.2\times10^{-3}g \text{ atoms} = 3.2\times6.023\times10^{23}\times10^{-3}\text{atoms} = 1.93\times10^{21}\text{atoms}$$

62.(75)

63.(4.5) ${}^{238}_{92}U \longrightarrow {}^{206}_{82}Pb$

The rock contains equal number of U and Pb atoms $\quad \Rightarrow \quad$ U is half decayed

$\therefore \qquad$ Age of rock $= t_{1/2} = 4.5\times10^9$ years

64.(60) $\Delta H = E_{a,f} - E_{a,b}$

$$-10\,\text{kJ mol}^{-1} = 50\,\text{kJ mol}^{-1} - E_{a,b} \Rightarrow \qquad E_{a,b} = 60\,\text{kJ mol}^{-1}$$

65.(0.693)

$$\frac{\left(-\frac{dN}{dt}\right)_1}{-\left(\frac{dN}{dt}\right)_2} = \frac{1}{1/10} = 10 \quad \Rightarrow \quad \frac{N_0}{N_t} = 10$$

$$k = \frac{2.303}{t}\log\left(\frac{N_0}{N_t}\right) \quad \Rightarrow \quad k = \frac{2.303}{2.303}\log(10) \quad \Rightarrow \quad k = 1 \qquad \Rightarrow \qquad t_{1/2} = \frac{0.693}{k} = 0.693\,\text{s}$$

66.(5) $k_{app} = \dfrac{k_1 C}{1+\alpha C}$ $\qquad \alpha = 9\times 10^5$

Limiting value of k'_{app} when $C \to \infty$ $\qquad \Rightarrow \qquad \alpha C >> 1 \quad \Rightarrow \quad 1+\alpha C \simeq \alpha C$

$$k_{app} = \frac{k_1 C}{\alpha C} = \frac{k_1}{\alpha}$$

To calculate the values of C for which k_{app} has 90% of k'_{app}

$$k_{app} = \frac{90}{100}k'_{app} = \frac{k_1 C}{1+\alpha C}$$

$$\Rightarrow \qquad \frac{9}{10}\cdot\frac{k_1}{\alpha} = \frac{k_1 C}{1+\alpha C} \quad \Rightarrow \quad 9(1+\alpha C) = 10\alpha C \quad \Rightarrow \quad 9 + 9\alpha C = 10\alpha C$$

$$\Rightarrow \qquad 1\alpha C = 9 \quad \Rightarrow \quad C = \frac{9}{9\times 10^5} = 10^{-5}\,\text{mol L}^{-1}$$

67.(1.188) $Fe^{2+} + 3\text{dipy} \longrightarrow [Fe(\text{dipy})_3]^{2+}$

$$r_f = 1.45\times 10^{13}[Fe^{2+}][\text{dipy}]^3$$

$$r_b = [Fe(\text{dipy})_3]^{2+}(1.22\times 10^{-4})$$

At equilibrium, $r_f = r_b$

$$\Rightarrow \qquad 1.45\times 10^{13}[Fe^{2+}][\text{dipy}]^3 = 1.22\times 10^{-4}[Fe(\text{dipy})_3]^{2+}$$

$$\Rightarrow \qquad \frac{[Fe(\text{dipy})_3]^{2+}}{[Fe^{2+}][\text{dipy}]^3} = \frac{1.45\times 10^{13}}{1.22\times 10^{-4}} \quad \Rightarrow \quad K_{(\text{stability constant})} = 1.188\times 10^{17}$$

68.(70.8) $Q_{10} = \dfrac{k_{37°C}}{k_{27°C}} = \dfrac{A e^{-E_a/RT'}}{A e^{-E_a/RT}} = 2.5$

$$\ln 2.5 = -\frac{E_a}{R}\left(\frac{1}{310} - \frac{1}{300}\right) \qquad \Rightarrow \qquad E_a = \frac{0.9163\times 8.314\times 300\times 310}{10} \quad \Rightarrow \quad E_a = 70.8\,\text{kJ mol}^{-1}$$

69.(6) $-\dfrac{d[H^+]}{dt} = 1\times 10^7\,\text{mol L}^{-1}\,\text{s}^{-1}$

A drop $\equiv 0.05\,\text{mL}$ solution contains 3×10^{-6} mol H^+

$$\Rightarrow \qquad \text{Concentration of } H^+ \text{ in drop} = \frac{3\times 10^{-6}\,\text{mol}\times 1000}{0.05\,\text{mL}} = 0.06\,\text{mol L}^{-1}$$

$1\times 10^7\,\text{mol L}^{-1}$ will disappear in 1 second

$$\Rightarrow \qquad 0.06\,\text{mol L}^{-1} \text{ will disappear in } \frac{1}{10^7}\times 0.06 = 6\times 10^{-9}\,\text{sec}$$

70.(2.30) By observing reading 1 and 2, the reaction is first order w. r. t. B. Also by 3 and 4, the reaction is found to be 2nd order w.r.t. A.

$\Rightarrow \quad \text{rate} = k[A]^2[B]^1 \Rightarrow \quad 1.15\times10^{-4} = k[0.50]^2(0.02)^1 \Rightarrow \quad k = 230\times10^{-4} = 2.30\times10^{-2}\ L^2\ mol^{-2}\ min^{-1}$

71.(48) $t_{99\%} = 32\,\text{min}$

$$k = \frac{2.303}{32}\log\left(\frac{100}{1}\right)$$

$$k = 0.144\,\text{min}^{-1}$$

$$k_{99.9\%} = \frac{2.303}{0.144}\log\left(\frac{100}{0.1}\right) = 48\,\text{min}$$

72.(0.75) $\text{Rate} = k[A]^{1/2}[B]^{1/4}[C]^0$

$$\text{Overall order} = \frac{1}{2}+\frac{1}{4}+0 = \frac{3}{4}$$

73.(1)

$$\begin{array}{lll} & A \longrightarrow & B \\ t=0 & 0.8 & - \\ t=1\,h & 0.2 & 0.6 \end{array} \qquad \text{rate} = k[A]$$

$$k = \frac{2.303}{1}\log\left(\frac{0.8}{0.2}\right) \qquad k = 1.387\,h^{-1}$$

If $A_0 = 0.9\,\text{mol}$ and $B_t = 0.675\,\text{mol} \quad \Rightarrow \quad A_t = 0.9 - 0.675 = 0.225$

$$t = \frac{2.303}{1.387}\log\left(\frac{0.9}{0.225}\right) \quad \Rightarrow \quad t = 1\,h$$

74.(7.33) $k_f = 1.1\times10^{-2}$

$k_b = 1.5\times10^{-3}$

$$\text{Equilibrium constant } k_{eq} = \frac{k_f}{k_b} = \frac{1.1\times10^{-2}}{1.5\times10^{-3}} = 7.33$$

75.(3.2) $E_a = 0$

$k = 3.2\times10^6\,s^{-1}$ at 300 K

$k_{(at\,310K)} = ?$

$\Rightarrow \quad k = Ae^0 \quad \Rightarrow \quad k = A$

At 310 K,

$$k = (3.2\times10^6)e^{-Ea/RT} \quad \Rightarrow \quad k = 3.2\times10^6\,s^{-1}$$

76.(4) $A \longrightarrow B$

$\text{rate}(r) = k[A]^2$

On doubling the concentration of A

$r' = k[2A]^2 = 4k[A]^2 \quad \Rightarrow \quad r' = 4r$

Colligative Properties of Solution

1.(C) Solution with positive deviation from Raoult's law forms low boiling azeotrope.

2.(A) K_2SO_4 has highest van't Hoff factor, therefore, aqueous solution of K_2SO_4 has lowest freezing point.

3.(B) $2KI(aq)+HgI_2(s) \longrightarrow K_2[HgI_4](aq)$

Number of solute particles decreases, therefore, freezing point is raised.

4.(C) $\dfrac{\Delta P}{P_0}=X_B \approx \dfrac{n_B}{n_A}$

$\dfrac{3000-2985}{3000}=\dfrac{5/m_B}{100/18}$; $m_B=180$

5.(B) Increase in temperature has no effect on mass

$\therefore$ Molality does not change nor does % w/w

However, volume increases and $\therefore$ Molarity decreases.

6.(A)

$$\begin{array}{lcccc} & HX & \rightleftharpoons & H^+ & + & X^- \\ t=0 & 1 & & 0 & & 0 \\ t_{eq} & (1-0.2)\,0.2\text{m}, & & 0.04\text{ m}, & & 0.04\text{ m}, \end{array}$$

Total molality $=0.16\text{m}+0.04+0.04$

$=0.24\text{m}$

$\Delta T=k_f\times m=1.86\times 0.24=0.45$

Freezing point $-0.45°C$

7.(A) Freezing point is the temp. at which vapour pressure of liquid solvent is equal to vapour pressure of solid solvent

So, equilibrium exists between

Solvent$(l) \rightleftharpoons$ solvent(s)

8.(A) $\pi(Na_2SO_4) \rightleftharpoons \pi(\text{glucose})$

$i\times 0.004\times RT=0.01\times RT$

$i=2.5$

$\alpha=\dfrac{i-1}{n-1}=\dfrac{2.5-1}{3-1}=0.75$

9.(B) $\alpha=\dfrac{i-1}{n-1}=\dfrac{2.74-1}{3-1}=\dfrac{1.74}{2}=0.87$

10.(A) $\Delta T=i\times K_f\times\dfrac{w_B\times 1000}{M_B\times w_A}$

$2=i\times 1.72\times\dfrac{20\times 1000}{172\times 50}$; $i=0.5$

11.(C) For isotonic solutions,

$\pi_1=\pi_2$

$C_1RT=C_2RT$

or $C_1=C_2$ (same molar concentration)

12.(B) $\alpha=\dfrac{i-1}{n-1}$

Here, $n=$ number of ions formed $=x+y$ $\therefore$ $\alpha=\dfrac{i-1}{x+y-1}$

13.(C) Greater is the molar concentration of solution, more is the osmotic pressure.

$\therefore \quad P_2(\text{urea}) > P_1(\text{glucose}) > P_3(\text{sucrose})$

14.(B) Due to increase in the inter-molecular force, the rate of evaporation is lowered. Thus, the solution of acetone and chloroform will give negative deviation.

15.(B) $\Delta T = K_b \times \dfrac{w_B \times 1000}{M_B \times w_A} = K_b \times \dfrac{Y \times 1000}{M \times 250} = \dfrac{4K_bY}{M}$

16.(C) $\dfrac{\Delta P}{P_0} = X_B \approx \dfrac{n_B}{n_A} = \dfrac{w_B \times M_A}{M_B \times w_A}$

$$\left(\frac{w_B \times M_A}{M_B \times w_A}\right)_{\text{glu cos e}} = \left(\frac{w_B \times w_A}{M_B \times w_A}\right)_{\text{urea}}$$

$\dfrac{w_B \times 18}{180 \times 100} = \dfrac{1 \times 18}{60 \times 50}$; $w_B = 6$ g

17.(C) $\Delta T = K_f \times \dfrac{w_B \times 1000}{M_B \times w_A}$

$9.3 = 1.86 \times \dfrac{50 \times 1000}{62 \times w_A}$

$w_A = 161.29\,\text{gm}(\text{water})$

Amount of ice $= 200 - 161.29 = 38.71\,\text{g}$

18.(A) $P_{\text{Total}} \times y_A = P_A$

$$\frac{1}{P_{\text{Total}}} = y_A \times \frac{1}{P_A}$$

When $\dfrac{1}{P_{\text{Total}}}$ is plotted against y_A, we get straight line passing through origin having

Slope of $\dfrac{1}{P_A}$.

19.(A) Urea and glucose do not dissociate in aqueous medium, hence their solution has lowest depression in freezing point.

20.(C) When $X_A = 1,\ P = P_A^0$ $\quad\therefore\quad P_A^0 = 254 - 119 = 135\,\text{torr}$

When $X_A = 0,\ P = P_B^0$ $\quad\therefore\quad P_B^0 = 254\,\text{torr}$

21.(A) $i = \dfrac{\text{Normal molar mass}}{\text{Observed molar mass}} = \dfrac{164}{65.6} = 2.5$

$\alpha = \dfrac{i-1}{n-1},\quad n = 3\ (\text{number of ions})$

$= \dfrac{2.5-1}{3-1} = \dfrac{1.5}{2} = 0.75$ $\quad\therefore$ Percentage ionization of MX_2 will be 75%

22.(B) $X_A = \dfrac{1}{3},\ X_B = \dfrac{2}{3}$

$P = P_A^0X_A + P_B^0X_B = 150 \times \dfrac{1}{3} + 240 \times \dfrac{2}{3} = 50 + 160 = 210$ mm

$P_{\text{exp.}} < P_{\text{calculated}}$; $\therefore$ There is negative deviation from Raoult's law.

23.(C) If 2 liquids are mixed the entropy of mixture is always more than entropy of components.

$\Delta S_{mix} > 0$

$\Delta G_{mix} < 0$

$\Delta H_{mix} = 0$ (for ideal solution)

$\because$ Interaction between molecules in components are equal to interaction between molecules in mixture

24.(A) A : Benzene B : Toluene

$$P = P_A + P_B$$

$$P = P_A^0 X_A + P_B^0 X_B = 75 \times \frac{1}{2} + 22 \times \frac{1}{2} = 37.5 + 11 = 48.5$$

Mole fraction of benzene in vapour, $Y_A = \frac{P_A}{P} = \frac{37.5}{48} = 0.78$

Similarly, mole fraction of toluene in vapour, $Y_B = 0.22$

$\therefore$ The vapour will contain higher percentage of benzene.

25.(B)
$$\frac{(\Delta T)_P}{(\Delta T)_Q} = \frac{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A}\right)_P}{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A}\right)_Q}$$

$$\frac{0.2}{0.4} = \frac{\left(\frac{0.1 \times 1000}{100 \times 100}\right)_P}{\left(\frac{0.1 \times 1000}{100 \times m_B}\right)_Q}$$

$$\frac{1}{2} = \frac{(m_B)_Q}{100}$$

$m_B = 50 \quad \therefore \quad (m_B)_P : (m_B)_Q = 100 : 50 = 2 : 1$

26.(A) For X, $i = 2$

For Y, $i = 0.5$ as Y dimerizes in solution

$\therefore$ Elevation in boiling point $\Delta T_b = iK_b m$

ΔT_b for $X > \Delta T_b$ for Y

Depression in freezing point $\Delta T_f = iK_f m$

ΔT_f for $X > \Delta T_f$ for Y

Osmotic pressure, $\pi = iCRT$

$\therefore$ π for $X > \pi$ for Y

Relative lowering of vapour pressure, $\frac{\Delta P}{P} = iX_B$ since value of i is not same, $\therefore$ $\frac{\Delta P}{P}$ will not be same.

27.(B)

	X	0.010	0.015	0.020
	P	82	122	166
$\Rightarrow$	$K_H = \frac{P}{X}$	8200	8133.33	8300

So, average $K_H = 8211 kP_a$

Also, graph of P v/s × is a straight line which cannot pass through origin.

28.(B) For $NaCl \rightarrow i = 2$

$BaCl_2 \rightarrow i = 3$

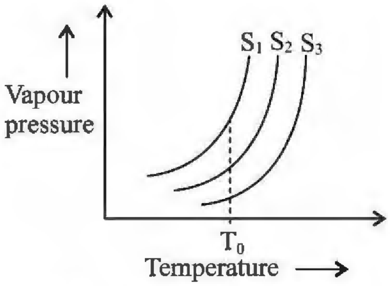
$\therefore$ C_{eff} for $NaCl = 0.1 \times 2 = 0.2\ M$.

C_{eff} for $BaCl_2 = 0.05 \times 3 = 0.15 M$

$\Rightarrow$ NaCl(aq) solution S_1 is more concentrated than S_2.

So, S_1 solution is hypotonic while S_2 is hypertonic and osmosis will take place from S_2 to S_1.

29.(B) At a particular temperature, more the concentration of solute in the solution, lesser will be the vapour pressure.
As vapour of $S_1 > S_2 > S_3$



$\therefore$ concentration order is $S_3 > S_2 > S_1$

30.(A) According to Dalton's law of partial pressures, total vapour pressure = sum of partial vapour pressure of all components

$\therefore$ OP = Partial vapour pressure of B at composition O

OQ = Partial vapour pressure of A at composition O

$\therefore$ OR = Total vapour pressure at composition O.

So, OR = OP + OQ

31.(B) $p = K_H x$ Henry's law

At a particular partial pressure P,

$$k_H \propto \frac{1}{x}$$

$\therefore$ lower the x (solubility), higher the value of k_H.

$\Rightarrow$ O_2 has the highest solubility and

$\therefore$ has the lowest k_H

So, we have $O_2 < N_2 < He$

32.(B) For a particular gas, increase in temperature decreases the solubility of gas in the solution. So, $T_1 > T_2 > T_3 > T_4$

33.(C) $\alpha = \dfrac{1-i}{1-1/n} = \dfrac{1-i}{1-1/2}$

$\dfrac{\alpha}{2} = 1 - i$; $i = 1 - \dfrac{\alpha}{2}$

34.(B) $\alpha = \dfrac{1-i}{1-\frac{1}{n}} = \dfrac{1-i}{1-\frac{1}{3}} \Rightarrow \dfrac{2}{3}\propto = 1 - i$ For $\propto = 1, i = \dfrac{1}{3}$

35.(C) Non-electrolytes neither dissociate nor associate in water $\therefore$ i remains equal to 1.

36.(C) $\alpha = \dfrac{i-1}{n-1}$, $\alpha = 0.6$, $n = 5$ $\therefore$ $0.6 = \dfrac{i-1}{5-1}$

$i = 0.6 \times 4 + 1 = 3.4$

37.(A) CH_3OH is the most volatile out of the other

38.(C) $\Delta T_f = K_f m$

$$\text{Molality(m)} \propto \frac{1}{\text{Molar mass}}$$

$\therefore$ For 124 g, glycerol will have lower molality than glycol.

39.(B) $\Delta T_f = K_f m$

$$= 1.86 \times \frac{620}{62 \times 4} = 4.65$$

$\therefore$ Freezing point decreases by 4.65.

Freezing point $= -4.65°C$

Let amount of water left after freezing be x kg

$\therefore$ If depression = 6°C

$$6 = k_f \times \frac{10}{x} \Rightarrow 6 = \frac{18.6}{x} \Rightarrow x = 3.1\text{kg}$$

Amount of water freezing = 9 kg = 900 g

40.(B) The work of anti-freeze is to decrease the freezing point. Hence forth, more will be the depression in freezing point, the better will be the anti-freeze property.

$\therefore$ $\Delta T_g \propto \frac{1}{M_B}$ where, M_B = molecular wt. of solute

As order of molecular wt. is Glycerol > Glycol > Methanol

Hence, the order of usage / economy is Methanol > Glycol > Glycerol

41.(ABC) If solvent and solute react with each other then solution becomes non-ideal and relations of colligative properties do not give accurate molecular mass of solute.

42.(ABD) Azeotropes are non-ideal solutions, hence they do not obey Raoult's law.

43.(ABC) In case of solutions showing negative derivation from Raoult's law, the A – B interactions are stronger than that between A – A and B – B.

$\therefore$ Stronger bonds are formed.

As a result, $\Delta H_{mix} < 0$ and $\Delta V_{mix} < 0$

Also, $p_T < p_A^0 x_A + p_B^0 x_B$

44.(AB) $(H_2O + C_2H_5OH)$ and $(C_6H_6 + C_2H_5OH)$ show positive deviation from Raoult's law while $(H_2O + HCl)$ and $\left[CHCl_3 + (CH_3)_2 CO\right]$ show negative deviation from Raoult's law.

45. **[A-q, r] → [B-q, r] → [C-p, r] → [D-s]**

Elevation in boiling point and depression in freezing point are both colligative properties.

$$\Delta T_b = k_b m \quad \text{and} \quad \Delta T_f = k_f m$$

Osmotic pressure is also a colligative property

46.(69.6) Given that :

$p° = 640\,\text{mmHg}$, $p_s = 600\,\text{mmHg}$ and $w = 2.175\text{g}$, $W = 39.0$ also $M = 78$

$$\frac{p° - p_s}{p°} = \frac{w \times M}{m \times W} \text{ therefore } \frac{640 - 600}{640} = \frac{2.175 \times 78}{m \times 39} \text{ or } m = 69.6$$

47.(46.9) $n_{H_2O} = \frac{500}{18} = 27.78$ mol, $n_{(glucose)} = \frac{20}{180} = 0.11\text{mol}$

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{(glucose)}} = \frac{27.78}{27.78 + 0.11} = \frac{27.78}{27.89} = 0.996$$

According to Raoult's law,

Vapour pressure of solution $= P_{H_2O} = P^o_{H_2O} X_{H_2O} = 47.1 \times 0.996 = 46.9\,\text{torr}$

Lowering of vapour pressure $= P^o_{H_2O} - P_{H_2O} = 47.1 - 46.9 = 0.2\,\text{torr}$

48.(3.35) Given : $P^\circ_A = 59.2\,\text{torr},\ P_A = 51.3\,\text{torr}$

By RLVP $\Rightarrow$ $X_{solute} = \dfrac{7.9}{59.2} = 0.1334$

$\because$ $$(\text{molality})\, m = \frac{X_B}{X_A} \times \frac{1000}{M_{solvent}} = \frac{X_B}{(1 - X_B)} \times \frac{1000}{M_{solvent}} \qquad (\because X_A + X_B = 1)$$

$$m = \frac{0.1334}{0.8666} \times \frac{1000}{46} = 3.346\,\text{molal}$$

49.(100.25) Urea solution, $\Delta T_b = K_b m$

$$0.25 = K_b \cdot \frac{1\,\text{g}}{60\,\text{g mol}^{-1}} \times \frac{1}{1}$$

$\Rightarrow$ $K_b = (0.25 \times 60)\,\text{k kg mol}^{-1}$

Glucose solution

$$\Delta T_b = K_b m = (0.25 \times 60) \times \frac{3}{180} \times \frac{1}{1} = 0.25$$

Boiling point of solution $= 100.25°\text{C}$

50.(4.48) Concentration $= \dfrac{68.4\,\text{g}}{342\,\text{g mol}^{-1}} \times \dfrac{1}{1} = 0.2\,\text{M}$

$\pi = CRT = 0.2\,\text{mol L}^{-1} \times 0.0821\,\text{L atm K}^{-1}\text{mol}^{-1} \times 273\,\text{K}$

$\pi = 4.48\,\text{atm}$

51.(0.478) Pentane : hexane mole ratio $= 1 : 4$ (1n solution phase)

$P^\circ_{pentane} = 440\,\text{mm Hg}$

$P^\circ_{hexane} = 120\,\text{mm Hg}$

$$y_A = \frac{P^\circ_A x_A}{P_T}$$

$$P_T = P^\circ_A x_A + P^\circ_B x_B = 440\left(\frac{1}{5}\right) + 120\left(\frac{4}{5}\right) = 184\,\text{mm Hg}$$

$$y_{pentane} = \frac{440 \times \frac{1}{5}}{184} = 0.478$$

52.(84.86°C) Using the result :

$$\Delta T_b = K_b\left(\frac{\frac{g_B}{M_B}}{g_A} \times 1000\right) = 2.57\left(\frac{\frac{5}{180}}{15} \times 1000\right) = 4.76°\text{C}$$

$T_b = T_b^0 + \Delta T_b$ $\qquad$ $[T_b^0 = \text{Boiling point of pure solvent}]$

$= 80.1 + 4.76 = 84.86°C$

53.(2736 gm) $\Delta T_f = 3.72°C,\ M_{sugar} = 342$

$$\Delta T_f = K_f\left(\frac{\frac{g_B}{M_B}}{g_A} \times 1000\right) \quad \Rightarrow \quad g_B = \frac{\Delta T_f\, g_A\, M_B}{1000\, K_f}$$

$$\Rightarrow \qquad g_B = \frac{3.72 \times 4 \times 10^3 \times 342}{1000 \times 1.86} = 2736\,gm$$

54.(83.5%) *i* for $AgNO_3 = \dfrac{\text{Normal mol .wt}}{\text{Oberved mol. wt.}} = 1 + \alpha \Rightarrow \alpha = \dfrac{170}{92.64} - 1 = 0.835 = 83.5\%$

55.(2.24 mg) Solubility of oxygen $C = k \times P$

$= 1.4 \times 10^{-3}\,mol\,L^{-1}\,atm^{-1} \times 0.5\,atm$

$= 0.7 \times 10^{-3}\,mol\,L^{-1}$

$\Rightarrow$ 1 L of solution contains $= 0.7 \times 10^{-3}$ moles O_2

$\Rightarrow$ 0.1 L of solution contains $= 0.7 \times 10^{-4}$ moles O_2

$= (0.7 \times 10^{-4} \times 32)\,g\,O_2 = 2.24\,mg\,O_2$

Electrochemistry

1.(D)

$$\begin{array}{ll} Cr^{3+}+e^{-}\longrightarrow Cr^{2+} & \Delta G_1^0=-F(-0.41)=0.41F \\ \underline{Cr^{2+}+2e^{-}\longrightarrow Cr} & \underline{\Delta G_2^0=-2FE_2^0} \\ Cr^{3+}+3e^{-}\longrightarrow Cr & \Delta G_3^0=-3F(-0.74)=2.22F \end{array}$$

$$\Delta G_1^0+\Delta G_2^0=\Delta G_3^0$$

$$-1.81\text{ F}=2FE_2^0 \quad ; \quad E_2^0=-0.905$$

2.(A) $Be^{2+}+2e^{-}\longrightarrow Be$

$$w_{Be}=\frac{5\times1\times60\times60}{96500}\times\frac{1}{2}\times9=0.84g$$

3.(C) $In^{+x}+xe^{-}\longrightarrow In$

$$\frac{3.2\times40\times60}{96500}\times\frac{1}{x}=\frac{3.05}{114.8},x\simeq3.$$

4.(A) $Cr^{3+}+3e^{-}\longrightarrow Cr \qquad 3Ag^{+}+3e^{-}\longrightarrow 3Ag$

Equivalents of Cr = Equivalents of Ag

$$\frac{W_{Cr}}{52}\times3=\frac{0.54}{108}\times1$$

$$W_{Cr}=0.0866g.$$

5.(C) $(C):\ 2Ag^{+}+2e^{-}\rightarrow 2Ag$

$(A):\ H_2O\rightarrow\frac{1}{2}O_2+2H^{+}+2e^{-}$

6.(D) $$E=E^{o}-\frac{RT}{nF}\ln\frac{\left[Cr^{3+}\right]}{\left[Ag^{+}\right]^3}=1.5-\frac{0.059}{3}\log\frac{0.1}{(0.1)^3}=1.5-0.039=1.461$$

$$\Delta G=-nFE=-3\times96500\times1.461=-422959J=-422.96KJ.$$

7.(B)

$$\begin{array}{l} 2e^{-}+2NO_3^{-}+4H^{+}\longrightarrow 2NO_2+2H_2O \\ \underline{\qquad\qquad Cu\longrightarrow Cu^{2+}+2e^{-}} \\ Cu+2NO_3^{-}+4H^{+}\longrightarrow Cu^{2+}+2NO_2+2H_2O \end{array}$$

$$E=\left(E^{o}{}_{NO_3^{-}/NO_2}-E^{o}{}_{Cu^{2+}/Cu}\right)-\frac{0.059}{2}\log\frac{\left[Cu^{2+}\right]\left(P_{NO_2}\right)^2}{\left[NO_3^{-}\right]^2\left[H^{+}\right]^4}$$

$$E=(0.79-0.34)-\frac{0.059}{2}\log\frac{0.1\times10^{-6}}{[HNO_3]^4}$$

$$0=0.45-\frac{0.059}{2}\log\frac{10^{-7}}{[HNO_3]^4};\quad 15.2=\log\frac{10^{-7}}{[HNO_3]^4}\ \Rightarrow\ 1.58\times10^{15}=\frac{10^{-7}}{[HNO_3]^4}\ \Rightarrow\left[HNO_3\right]=2.82\times10^{-6}M.$$

8.(C) $\Lambda_{eq}=\Lambda_m$ / Total cationic or anionic change in 1 mole of electrolyte

$$\Lambda_{eq}=\frac{150}{3}=50\text{ S Cm}^2\text{ eq}^{-1}.$$

9.(D) $\mathrm{Pt}\,|\,\mathrm{H_2}\,|\,\mathrm{HA(cM)}\,||\,\mathrm{H^+(1M)}\,|\,\mathrm{H_2}\,|\,\mathrm{Pt}$

Net Reaction: $\mathrm{H_c^+} \longrightarrow \mathrm{H_A^+}$

$$E_{cell} = \frac{0.059}{1}\log\frac{\left[\mathrm{H_c^+}\right]}{\left[\mathrm{H_A^+}\right]} = 0.059\log\frac{1}{\left[\mathrm{H_A^+}\right]}$$

To get maximum E_{cell}, the $\left[\mathrm{H_A^+}\right]$ must be least.

10.(D) $\Delta S = nF\left(\frac{dE}{dT}\right)$

$$\Delta G = -nFE = \Delta H - T \times nF\left(\frac{dE}{dT}\right)$$

$$\Delta H = nF\left[T\left(\frac{dE}{dT}\right) - E\right] = 1 \times 965000\left[\left\{298 \times \left(-5.5 \times 10^{-4}\right)\right\} - 0.265\right]$$

$$\Delta H = -41388.85\mathrm{J} = -41.38\mathrm{kJ}$$

11.(B) $k_{soln} = k_{AgCl} + k_{water}$

$$\therefore k_{AgCl} = k_{soln} - k_{water} = 1.26 \times 10^{-6} = k_{Ag^+} + k_{Cl^-}$$

$$1.26 \times 10^{-6} = \frac{\lambda_{Ag^+}\left[\mathrm{Ag^+}\right]}{1000} + \frac{\lambda_{Cl^-}\left[\mathrm{Cl^-}\right]}{1000}$$

$$1.26 \times 10^{-3} = (53.9 + 72.1)\left[\mathrm{Ag^+}\right]$$

$$\left[\mathrm{Ag^+}\right] = \frac{1.26 \times 10^{-3}}{126} = 10^{-5}\,\mathrm{moles/L}$$

Or $1.435 \times 10^{-3}\,\mathrm{g/L}$.

12.(D) The conducting ability of an electrolyte is measured using its equivalent conductivity.

	$AgCl$	$BaSO_4$	$AlPO_4$	$Ba_3(PO_4)_2$
$\Lambda_{eq} =$	$\frac{200}{1} = 200$	$\frac{300}{2} = 150$	$\frac{500}{3} = 166.6$	$\frac{700}{6} = 116.6$

The one with highest equivalent conductivity is the most conducting.

13.(C) $\propto = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{5.5}{275} = 0.02$

$$Ka = \frac{C\propto^2}{1-\propto} = \frac{0.1(0.02)^2}{0.98} = 4.08 \times 10^{-5}$$

14.(C) The reactions during discharging is

(A) : $\mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-}$

(C) : $\mathrm{2e^- + 4H^+(aq) + PbO_2(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2H_2O(\ell)}$

Net Reaction $\mathrm{Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)}$

15.(A) First conductance decreases due to replacement of H^+ by Na^+ till the equivalence point and then increases due to presence of free OH^- ions.

16.(B) Potential of the cell will be same as that of the Fe^{3+}/Fe^{2+} couple.

$$E_{cell} = E_{Fe^{3+}/Fe^{2+}} = E^{o}_{Fe^{3+}/Fe^{2+}} - \frac{0.059}{1}\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]} \Rightarrow E_{cell} = 0.8 - \frac{0.059}{1}\log\frac{\frac{2}{3}}{\frac{1}{3}} \Rightarrow E_{cell} = 0.782V$$

17.(D) At equivalence point, $\left[Fe^{2+}\right]$ and $\left[Fe^{3+}\right]$ will be equal.

$\therefore E_{cell} = E_{Fe^{3+}/Fe^{2+}} = E^{o}_{Fe^{3+}/Fe^{2+}} = 0.8V$

18.(B) $E_{cell} = E^{o}_{Ce^{4+}/Ce^{3+}} - E^{o}_{Fe^{3+}/Fe^{2+}} - \frac{0.059}{1}\log K$

$0 = (1.64 - 0.8) - 0.059 \log K$

$\log K = \frac{0.84}{0.059},\ K = 10^{0.84/0.059}$

19.(BD)

$$2e^{-} + Sn^{2+} \longrightarrow Sn$$
$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^{-}$$

Net Reaction: $2Sn^{2+} \longrightarrow Sn + Sn^{4+}$

$E^{o}_{cell} = E^{o}_{Sn^{2+}/Sn} - E^{o}_{Sn^{4+}/Sn^{2+}} = -0.14 - (-0.13) = -0.01$

Sn^{2+} is stable and does not undergo disproportionation.

20.(CD) $\Lambda^{\infty}_{AcOH} = (91 + 426.2 - 126.5) = 390.7$

$\Lambda^{\infty}_{HNO_3} = (426.2 + 145) - 149.9 = 421.3$

21.(ABC)(C) : $2H^{+} + 2e^{-} \longrightarrow H_2$

(A) : $2OH^{-} \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^{-}$

$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^{+} + 2e^{-}$

Equivalents of H_2 formed = Equivalents of O_2 formed + Equivalents of $H_2S_2O_8$ formed.

22.(ABD)

(A) $H^{+}_{C} \longrightarrow H^{+}_{A}$

$$E_{cell} = \frac{0.059}{1}\log\frac{\left[H^{+}_{C}\right]}{\left[H^{+}_{A}\right]}$$

The reaction would be spontaneous when $\left[H^{+}_{C}\right] > \left[H^{+}_{A}\right]$.

(B) $H_2(A) \longrightarrow H_2(C)$

$$E_{cell} = \frac{0.059}{2}\log\frac{\left(P_{H_2}\right)_A}{\left(P_{H_2}\right)_C}$$

This cell reaction is spontaneous when $\left(P_{H_2}\right)_A > \left(P_{H_2}\right)_C$.

(C)/(D) $Ag^{+}_{C} \longrightarrow Ag^{+}_{A}$

$$E_{cell} = \frac{0.059}{1}\log\frac{\left[Ag_C^+\right]}{\left[Ag_A^+\right]}$$

The cell reaction is spontaneous when $\left[Ag_C^+\right] > \left[Ag_A^+\right]$.

23.(ACD) $\Delta G^\circ = -RT\ln K_{eq}$.

24.(AC) (Cathode) : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ (Anode) : $2Cl^- \longrightarrow Cl_2 + 2e^-$

P^H of solution increases after electrolysis.

25.(ACD) $Ag \mid Ag^+\left(10^{-5}\right) \| Ag^+\left(4\times10^{-4}\right) \mid Ag,\quad Ag_C^+ \longrightarrow Ag_A^+$

$$E_{cell} = \frac{0.059}{1}\log\frac{4\times10^{-4}}{1\times10^{-5}} = 0.059\times1.6 = 0.0944$$

It is an electrolyte concentration cell and the reaction occurring in it is spontaneous.

26.(CD) (A) : $2Ag + 2Cl^- \longrightarrow 2AgCl + 2e^-$

(C) : $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

$$Hg_2Cl_2(s) + 2Ag(s) \longrightarrow 2AgCl(s) + 2Hg(\ell)$$

$$E_{cell} = E^\circ_{Cl^-/Hg_2Cl_2/Hg} - E^\circ_{Cl^-/AgCl/Ag}$$

27.(BD) $Cu^{2+} + 2e^- \rightarrow Cu \qquad {}^{m}Cu = \frac{1}{2}\times63.5g$

$Mg^{2+} + 2e^- \rightarrow Mg \qquad {}^{m}Mg = \frac{1}{2}\times24 = 12g$

$Na^+ + e^- \rightarrow Na \qquad {}^{m}Na = \frac{1}{1}\times23 = 23g$

$Al^{3+} + 3e^- \rightarrow Al \qquad {}^{m}Al = \frac{1}{3}\times27 = 9g$

28.(BC) At anode, H_2O gets oxidized in preference to SO_4^{2-} to form O_2 gas.

At cathode, the possible reactions are

$Ni^{2+} + 2e^- \longrightarrow Ni \qquad E_{Ni^{2+}/Ni} = E^\circ_{Ni^{2+}/Ni} = -0.25V$

$2H^+ + 2e^- \longrightarrow H_2 \qquad E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.059}{2}\log\frac{1}{10^{-14}}$

$= 0 - 0.059\times7 = -0.413V$

$\therefore$ Ni^{2+} will be reduced in preference to H^+.

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

$E^\circ = 1.5 - 0.77 = 0.73V$

$MnO_4^- + 5Cl^- + 8H^+ \longrightarrow \frac{5}{2}Cl_2 + Mn^{2+} + 4H_2O$

$E^\circ = 1.5 - 1.4 = 0.1V$

Equivalents of MnO_4^- used = Equivalent of Fe^{2+} + Equivalent of Cl^-.

Estimation of Fe^{2+} can not be done unless and until amount of Cl^- is known using MnO_4^- in aqueous HCl.

30.(CD) $Ag(s) \longrightarrow Ag^+(aq) + e^-$ $\quad \Delta G_1^\circ = -nFE_1^\circ, \Delta G_1 = -nFE_1$

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ $\quad \Delta G_2^\circ = -RT\ln\frac{1}{K_{sp}}, \Delta G_2 = 0$

$Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^-$ $\quad \Delta G_3^\circ = -nFE_3^\circ, \Delta G_3 = -nFE_3$

Using Hess's law,

$\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ \qquad \Delta G_1 + \Delta G_2 = \Delta G_3$

$-nFE_1^\circ + RT\ln K_{sp} = -nFE_3^\circ \qquad -nFE_1 + 0 = -nFE_3$

$E_1^\circ \neq E_3^\circ \qquad E_1 = E_3$

31.(AC) $Cu^{2+} + Sn \longrightarrow Cu + Sn^{2+}$ $\quad E^\circ = 0.34 - (-0.136) = 0.476V$

$Cu^{2+} + H_2 \longrightarrow Cu + 2H^+$ $\quad E^\circ = 0.34 - 0 = 0.34V$

$2H^+ + Sn \longrightarrow Sn^{2+} + H_2$ $\quad E^\circ = 0 - (-0.136) = 0.136V$

32.(AC)

(A)	Anode :	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$	Cathode :	$2Na^+ + 2e^- \rightarrow 2Na$
(B)	Anode :	$Cu \rightarrow Cu^{2+} + 2e^-$	Cathode :	$2H^+ + 2e^- \rightarrow H_2$
(C)	Anode :	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$	Cathode :	$2H^+ + 2e^- \rightarrow H_2$
(D)	Anode :	$2Cl^- \rightarrow Cl_2 + 2e^-$	Cathode :	$2Na^+ + 2e^- \rightarrow 2Na$

33.(ACD) Redox half cell.

(A) $Pt \mid Fe^{2+}(0.1M), Fe^{3+}(0.01M)$

Represents conversion of Fe^{2+} to Fe^{3+} if half cell behaves as anode.

Fe^{3+} to Fe^{2+} $\rightarrow$ if half cell behaves as cathode.

(B) $Pt \mid H_2(1\,atm) \mid H^+(0.05M)$

Represent anode (oxidation half cell, not redox half cell)

(C) $Pt \mid Mn^{2+}(0.1M), MnO_4-(0.1M), H^+(0.8M) \mid$

Mn^{2+} converts to MnO_4^- if half cell forms anode.

MnO_4-convert to Mn^{2+} if half cell forms cathode.

(D) Cr^{+3} gets converted to $Cr_2O_7^{2-}$ if the cell behaves as anode

$Cr_2O_7^{2-}$ gets converted to Cr^{+3} if the cell behaves as cathode

34.(ABD) A more electronegative halogen displaces a less electronegative halogen from its solution.

35.(ABC) Discharging reactions:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(\ell)$$

Reactions during charging is exactly reverse of the above.
With the lowering of temp, the viscosity of electrolyte increases which leads to difficulty in movement of ions.

36.(AC) A spontaneous electrolyte concentration cell will have concentration of ion at cathode, greater than that of anode.

37. **[A-p, s] → [B-s] → [C-p, q, s] → [D-q, r, s]**

(A) $Cu \mid Cu^{2+} \mid (C,M) \parallel Cu^{2+}(C_2M) \mid Cu$

$C_2 > C_1 \rightarrow$ concentration cell

In A concentration cell anode and cathode are made up of same metal metal ion but different concentration of ion in both halves.

It represents an electrochemical cell.

(B) $Al \mid Al^{+3} \parallel Zn^{2+} \mid Zn$

Represents Galvanic cell

(C) $Pt \mid O_2(P_1\,atm) \mid OH^- \parallel OH^- \mid O_2(P_2\,atm) \mid Pt$

→ Represents concentration cell

∵ Partial pressure of O_2 in both the halves are different

→ It also represents gas-gas ion electrode (O_2 gas, OH^- ion)

→ Represents Galvanic cell.

(D) H^+ / H_2 is gas gas ion electrode.

→ pH measurement can be done from H^+ concentration.

→ represents Galvanic cell

38. **[A-q, s] → [B-p, r, s, t] → [C-r, s, t] → [D-p, s]**

(A) Electrolysis of aqueous $CuSO_4$ using Cu electrode

→ In electrolytic cell, positive electrode is Anode and negative electrode is cathode.

At Cathode :- Cu^{2+} gets deposited into Cu

At Anode :- Cu forms Cu^{2+}

∴ $[SO_4^{2-}]$ remains constant

$[Cu^{2+}]$ remains constant

(B) Electrolysis of dil H_2SO_4

At cathode : - $2H^+ + 2e^- \rightarrow H_2$

+ve cathode:- Anode

–ve cathode : - Cathode.

At anode : - O_2 is liberated

(C) Electrolysis of aqueous NaF using Pt electrodes.

Cathode H_2O gets reduced to H_2

In electrolytic all – cathode –ve charged

Anode → +ve charged

Anode - H_2O gets oxidized to O_2

(D) Recharging of lead storage battery.

→ It behaves as electrolytic cell during recharging

∴ cathode → –ve charged electrode

Anode → +ve charged electrode

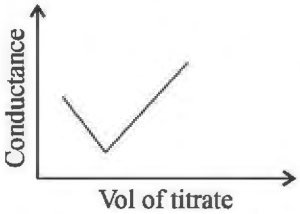
39.(C) (1) $HCl + NaOH \rightarrow NaCl + H_2O$

On titration conc of H^+ ion decreases

$\therefore$ conductance decreases. (since H^+ converts to H_2O)

When titration is complete, conductance becomes minimum.

On further addition of OH^-, conduction increases

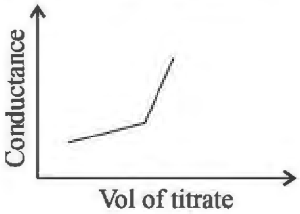


(2) Titration of CH_3CO_2H V/S NaOH

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$\therefore$ Conc. of ions increases with titration when titration is complete and even then NaOH is added $[OH^-] \uparrow$ es. And

$\therefore$ Conductance increases



(3) Titration of $(HCl + CH_3CO_2H)$ V/S NaOH

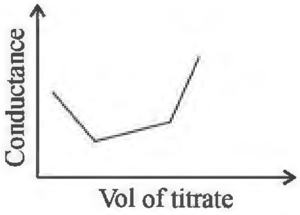
Firstly HCl + NaOH $\rightarrow$ NaCl + H_2O

Conductance decreases

Then $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Buffer is formed

No. of ion increases $\therefore$ Conductance increase slowly.



(4) $AgNO_3$ & KCl

$AgNO_3 + KCl \longrightarrow AgCl \downarrow + KNO_3$

$\because$ AgCl is ppt.

Conductance decreases & when ppt is complete on further addition of KCl, conductance again starts increasing.

40.(2) Overall Reaction : $M(s)+nH^+(aq)\longrightarrow M^{n+}(aq)+\frac{n}{2}H_2(g)$

$$E_{cell}=E^o{}_{H^+/H_2}-E^o{}_{M^{n+}/M}-\frac{0.059}{n}\log\frac{\left[M^{n+}\right]\left(P_{H_2}\right)^{\frac{n}{2}}}{\left[H^+\right]^n}$$

$0.81=0-\ -0.76\ -\frac{0.059}{n}\log\ 0.02$; $0.81-0.76=-\frac{0.059}{n}\log\ 0.02$

$$0.05=\frac{0.059\times1.7}{n}$$

$n=2$

41.(2) The cell is reduced to,

$$Ag\,|\,Ag^+\left(\frac{Ksp}{\left[Br^-\right]}\right)\|\ \left|Ag^+\left(\frac{Ksp}{\left[Cl^-\right]}\right)\right|Ag$$

The overall reaction is : $Ag^+_c\longrightarrow Ag^+_A$

∴ $$E_{cell}=E^o{}_{cell}-\frac{0.059}{1}\log\frac{\left[Ag^+_A\right]}{\left[Ag^+_c\right]}$$

$0.118=\frac{0.059}{1}\log\frac{Ksp\ \ AgCl}{\left[Cl^-\right]}\times\frac{\left[Br^-\right]}{Ksp\ \ AgBr}$; $2=\log\frac{1\times10^{-10}\times\left[Br^-\right]}{5\times10^{-13}\times\left[Cl^-\right]}$

$2=\log200\frac{\left[Br^-\right]}{\left[Cl^-\right]}$; $\therefore\frac{\left[Cl^-\right]}{\left[Br^-\right]}=2$.

42.(4) Let the charge on metal cation be n+. The reduction half reaction would be

$M^{n+}+ne^-\rightarrow M$

The quantity of electricity required to deposit 106.4 g metal = n mole of electron $=n\times96500\ C$.

∴ 2.977 g metal will be deposited by $=\frac{n\times96500\times2.977}{106.4}=n\times2700C$ of electricity

The electricity actually passed = $4\times45\times60C$ ∴ $n=\frac{4\times45\times60}{2700}=4$.

43.(8) $Pt\,|\,H_2\ \ g\ \,|\,Buffer\,\|\,Cl^-\ \ 1M\ \,|\,Hg_2Cl_2\,|\,Hg\ \ \ell$

Cell reaction : $Hg_2Cl_2\ \ s\ +H_2\ \ g\ \rightarrow2H^+\ \ aq\ +2Hg\ \ \ell\ +2Cl^-\ \ aq$

$$E_{cell}=E^o{}_{calomel}-E^0{}_{H^+/H_2}-\frac{0.06}{2}\log\frac{\left[H^+\right]^2\left[Cl^-\right]^2}{p_{H_2}}$$

∴ $0.76=0.28-0-\frac{0.06}{2}\log\frac{\left[H^+\right]^2 1^2}{1}$; $0.48=0.06\ pH$

$$pH=\frac{0.48}{0.06}=8$$

44.(8) $\underset{a-s}{CaF_2(s)}\rightleftharpoons\underset{s}{Ca^{2+}(aq)}+\underset{2s}{2F^-(aq)}$

$K_{sp}=[Ca^{2+}]\,[F^-]^2=s(2s)^2=4s^3$

$\kappa_{\text{solution}}-\kappa_{\text{water}}=\kappa_{CaF_2}=\kappa_{Ca^{2+}}+\kappa_{F^-}$

$$\left(5.2\times10^{-5}-0.2\times10^{-5}\right)=5\times10^{-5}=\frac{\left[Ca^{2+}\right]\approx_{Ca^{2+}}}{1000}+\frac{\left[F^{-}\right]\approx_{F^{-}}}{1000}$$

$$5\times10^{-5}=\frac{\left[Ca^{2+}\right]}{1000}\left(\approx_{Ca^{2+}}+2\approx_{F^{-}}\right)=\frac{\left[Ca^{2+}\right]}{1000}(120+130)$$

$$5\times10^{-5}=\frac{\left[Ca^{2+}\right]}{1000}\times250\quad;\qquad\left[Ca^{2+}\right]=2\times10^{-4}=s$$

$$K_{sp}=4(s)^3=4\left(2\times10^{-4}\right)^3=4\times8\times10^{-12}\quad;\qquad\therefore x=8$$

45.(4)

$$\begin{array}{c}A\ :Sn^{2+}\longrightarrow Sn^{4+}+2e^{-}\\ C\ :Sn^{2+}+2e^{-}\longrightarrow Sn\\ \hline \text{Net Reaction}\ :\ 2Sn^{2+}\longrightarrow Sn+Sn^{4+}\end{array}$$

No. of moles of e^- passed = $\frac{96.5\times100\times60}{96500}=6$

Moles of Sn^{2+} consumed = 6

Initial moles of Sn^{2+} = 8

Moles of Sn^{2+} left = 2

$\left[Sn^{2+}\right]_{left}=4M$.

46.(9) Number of moles of e^- passed = $\frac{9650\times100}{96500}=10$

$Al^{3+}+3e^{-}\longrightarrow Al(s)$

Moles of Al produced = $\frac{10}{3}$

Mass of Al produced = $\frac{10}{3}\times27=90$ g

No of cans of Al that can be made = 9

47. (–1.66 V)

$$E^{\circ}_{Ag^{+}/Ag}=0.80V$$

$$E^{\circ}_{cell}=\underset{\substack{\text{Reduction}\\ \text{potential of Al}}}{-E^{\circ}_{Al^{3+}/Al}}+\underset{\substack{\text{Reduction}\\ \text{potential of Ag}}}{E^{\circ}_{Ag^{+}/Ag}}$$

$$\Rightarrow\qquad 2.46=-E^{\circ}_{Al^{3+}/Al}+0.80V$$

$$\Rightarrow\qquad E^{\circ}_{Al^{3+}/Al}=-1.66V$$

48.(18.99 g)

Power = 100 watt

Voltage = 110 V

Current $I=\frac{100}{110}=0.909$ Ampere

$Cd^{2+}+2e^{-}\longrightarrow Cd(s)$

$$W=zIt=\frac{112}{2\times96500}\times0.909\times10\times60\times60=18.99g$$

49.(193 coulombs)

Cathode : $2H^+ + 2e^- \longrightarrow H_2$

$\Rightarrow$ $2F \equiv 1 \text{mole of } H_2 \equiv 22400 \text{mL}$

or $1F \equiv 0.5 \text{mole of } H_2 \equiv 11200 \text{mL}$

Anode : $2OH^- \longrightarrow O_2 + 4e^- + 2H_2O$

$\Rightarrow$ $4F \equiv 1 \text{mole of } O_2 \equiv 22400 \text{mL}$

or $1F \equiv 0.25 \text{mole of } O_2 \equiv 5600 \text{mL}$

From two electrode reactions, it clear that hydrogen and oxygen are evolved in the mole ratio of $2:1$, hence their volumes will also be in the same ratio.

$\Rightarrow$ $\text{volume of } H_2 = \frac{2}{3}(33.6) = 22.4 \text{mL}$

As $2F \equiv 22400 \text{mL } H_2$

$\Rightarrow$ $0.002F$ of charge is passed through the electrolytic cell.

$\Rightarrow$ Amount of electricity $= 0.002 \times 96500 C = 193.0$ Coulombs

50.(0.521V)

From given data,

$\because$ $E^\circ_{Cu^{2+}/Cu^+} = 0.153 V$

$\therefore$ $E^\circ_{Cu^+/Cu^{2+}} = -0.153 V$

(i) $Cu^{2+} + 2e^- \to Cu, E^\circ = +0.337 V,$

$\therefore$ $\Delta G_1^\circ = -2 \times 0.337 \times F = -0.674 F$

(ii) $Cu^+ \to Cu^{2+} + e^-, E^\circ = -0.153 V$

$\therefore$ $\Delta G_2^\circ = -1 \times F(-0.153)$

$Cu^+ + 1e^- \longrightarrow Cu, E^\circ = ? \quad \therefore \quad G_3^\circ = -1 \times E^\circ \times F$

$\Delta G_3^\circ = \Delta G_2^\circ + \Delta G_1^\circ$

$-E^\circ \times F = -0.674F + 0.153F$

or $-E^\circ F = -0.521F$

$\therefore$ $E^\circ = 0.521 V$

The Solid State

1.(B) Packing efficiency = $\dfrac{\text{Volume occupied by particles}}{\text{Volume of unit cell}}$

2.(C) Relation between edge length and radius of atom in simple cubic is a = 2r, body centred cubic is $\sqrt{3}a = 4r$ and face centred cubic is $\sqrt{2}a = 4r$.

3.(C)

4.(B) O_2 molecule is non polar and at very low temperature it crystallises into molecular crystal having O_2 molecule at lattice points. The type of interaction in this solid will be induce dipole induce dipole (or) London forces.

5.(D) Position of B represents octahedral void, whose coordination number is 6.

6.(A) This kind of planes have closest arrangement of atoms.

7.(A) In FCC, octahedral and tetrahedral voids are located on body diagonal at a distance of $\dfrac{\sqrt{3}a}{4}$.

8.(B) For the given formula, 18 copper ions present with 10 sulphide ions. Let (18 – x) Cu^{+} and x Cu^{2+} are present. Using charge balance, $(18 - x) + 2x = 20$, $x = 2$, % of $Cu^{2+} = 11.11$.

9.(A) Shortest inter ionic distance is $\sqrt{3}a/2$.

10.(B) Replacement of every $2Na^{+}$ ions by one Sr^{2+} ion produces one cation vacancy.

11.(C) Occupying CCP lattice with A atoms, there are 4A per unit cell while occupying 50% tetrahedral voids by B, there are 4B per unit cell and coordination number of A with respect to B is 4.

12.(B) On heating oxygen gets evaporated, leaving excess zinc metal whose electrons cab be excited by absorbing visible light (Learn as a fact & Read NCERT)

13.(A) $\dfrac{\rho_{BCC}}{\rho_{FCC}} = \dfrac{Z_{BCC}}{Z_{FCC}}$

14.(C) In FCC arrangement, $4O^{2-}$, $\dfrac{1}{5}^{th}$ tetrahedral voids i.e. $\dfrac{8}{5}X^{2+}$ and $\dfrac{1}{2}$ octahedral voids i.e. $2Y^{3+}$ are present. Thus the formula is $X_4Y_5O_{10}$.

15.(D) $x\left(4 - \dfrac{1}{4}\right)y(4-1)z(8-2) = x_5y_4x_8$

16.(B) With respect to corner position, there are 12 equidistant face centre positions exist.

17.(C) There is no direct contact of tetrahedral and octahedral voids.

18.(A) Tetrahedral void is located over body diagonal at a distance of $\dfrac{\sqrt{3}a}{4}$ from corner. We can see it by cutting a cube into 8 sub cubes. Distance between centres of two sub cubes = distance between two nearest tetrahedral voids in FCC (As centre of sub cube represents a tetrahedral void).

19.(C)

20.(A) Volume = Area of basal plane × height = $6\sqrt{3}\,r^2 \times 2\left[2r\sqrt{\dfrac{2}{3}}\right] = 24\sqrt{2}\,r^3$

21.(D)

H. C. P.	C. C. P
One-unit cell have 12 tetrahedral voids	One-unit cell have 8 tetrahedral voids

In close packing of "N" identical spheres there will be "N" octahedral voids and "2N" tetrahedral voids. For C.C.P arrangement N = 4 and for H.C.P arrangement N = 6.

22.(C) Distance between two layers is equal to height of tetrahedron

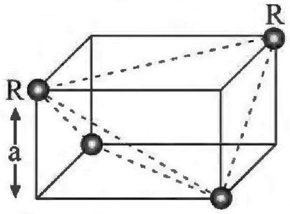
23.(B) $\text{density} = \dfrac{ZM}{N_A V}$

24.(D) In Zinc blende type of structure S^{2-} occupy CCP arrangement while Zn^{2+} present in half of tetrahedral voids.

25.(C) B is present in tetrahedral void, whose coordination number is 4.

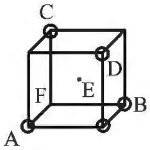
26.(C) Closest packed lattice of four atoms resembles tetrahedral arrangement and these four atoms are assumed to present at four corners of a imaginary cube.

27.(C) Face diagonal $= a\sqrt{2} = 2R;\ a = \sqrt{2}R$



Body diagonal $= \sqrt{3}a = \sqrt{6}R$.

28.(B)



Length AB = $\sqrt{2}x = 2R$

Length DF = $\sqrt{3}x = \sqrt{6}R$

Length DE = $\dfrac{\sqrt{3}x}{2} = R + r_t$

$$r_t = \left(\sqrt{\frac{3}{2}} - 1\right)R$$

29.(ACD)

Crystal systems	Inter axial angles $[\alpha, \beta, \gamma]$
Cubic	$\alpha = \beta = \gamma = 90°$
Hexagonal	$\alpha = \beta = 90°, \gamma = 120°$
Monoclinic	$\alpha = \gamma = 90°, \beta \neq 90°$
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90°$

30.(ABC) In a close pack arrangement within a layer the voids are trigonal and the voids created by adjacent arrangement of layer's are tetrahedral and octahedral.

31.(ACD)

(A) In Cs^+Cl^- structure a cation is surrounded by 8 anions and an anion is surrounded by 8 cations then coordination number of the ions is 8.

(B) In a B.C.C arrangement of identical spheres C.N. of a sphere = 8

(C) In a NaCl type structure.

$a = 2[r^+ + r^-]$

Here $r^+ = 95$ pm

$r^- = 181$ pm $\quad \therefore \quad a = 2[95 + 181] = 552$ pm

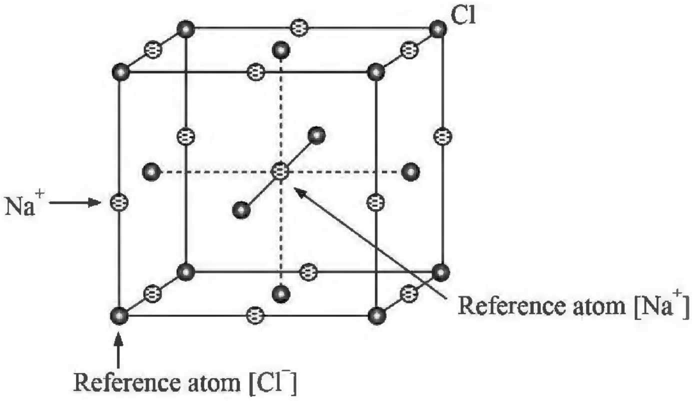
(D) Ionic crystals are formed by close packing of ions and in close packing sharing of atoms by adjacent unit cell is a common feature.

32(BD) (B) In H.C.P structure effective number of atom = 6
Number of tetrahedral voids = 12
$\therefore$ Number of tetrahedral voids/atom = 2.

(D) In antifluorite structure (Li_2O, Rb_2S etc).

Cation occupy tetrahedral voids and anions form a C.C.P lattice.

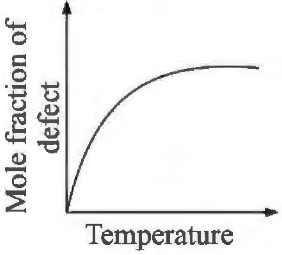
33.(ABC)



It can be visualise that a Na^+ is surrounded by $6\,Cl^-$ ions and a Cl^- ion is surrounded by $6\,Na^+$

The next nearest neighbour of Na^+ ion will be 12 Na^+.

34.(ABCD)
(A) Schottky defect is usually favoured by a very small difference in size of cation and anion.
(B) Each defect has its energy barrier (E) and the fraction of defects is proportional to the Boltzmann factor $[e^{-E/kt}]$. Hence mole fraction of Frenkel defect increases exponentially with temperature.



(C) Trapping of an electron in a lattice is the cause of F-centre.
(D) Usually ionic solids having F-centre act as a semiconductor.

35.(ABC) Unpaired electron doesn't exist in-case of schottky defect.
(D) Usually ionic solids having F-centre act as a semiconductor.

36.(AD) Doping of solids NaCl with $CaCl_2$ cause.

Replacement of some Na^+ ions by Ca^{+2}. As charge of the dopant is greater than charge of the source hence it will create metal deficiency [cationic vacancy] as well as decrease in density of the host solid.

$$\underset{(\text{mass} = 4 \times 23\text{ u})}{Na^+ \quad Na^+ \quad Na^+ \; Na^+} \xrightarrow[-2Na^+]{+1Ca^{+2}} \underset{(\text{mass} = 2 \times 23 + 40)}{Na^+ \quad Na^+ \quad Ca^{+2}}$$

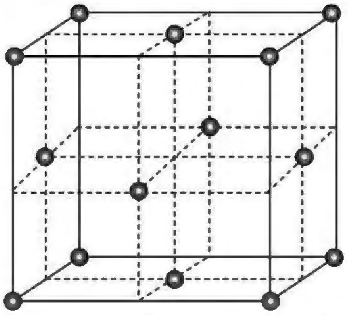
Hence doping will cause decrease in mass of the host lattice.

37.(ABCD)
(A) CsCl structure can show Schottky defect due to comparable sizes of ions.
(B) ZnS structure can show Frenkel defect due to smaller radius ratio $\left(\dfrac{r_{Zn^{2+}}}{r_{S^{2-}}}\right)$
(C) Both H.C.P and C-C.P arrangements of identical spheres have C.N = 12.
(D) Increase in pressure over solids can forcefully change arrangement of atoms into more compact arrangement with higher coordination number.

38.(ABCD)

Crystal system	Inter axial angles
Cubic	$\alpha=\beta=\gamma=90^\circ$
Tetragonal	$\alpha=\beta=\gamma=90^\circ$
Orthorhombic	$\alpha=\beta=\gamma=90^\circ$
Rhombohedral/Trigonal	$\alpha=\beta=\gamma\neq 90^\circ$

39.(ACD)



Out of these 8 small cubes only 4 are having carbon atoms. The centres of these small cubes are tetrahedral voids.

In diamond.

→ 4 out of 8 tetrahedral voids are occupied

→ Packing efficiency of diamond unit cell = 34%

→ All octahedral voids are vacant.

→ C.N. of a carbon atom = 4 in this unit cell.

40.(C) **(1)** NaCl type crystal.
$$\begin{bmatrix}\text{CN. of cation} = 6\\ \text{CN. of anion} = 6\\ a = 2[r_C + r_a]\\ \text{Anion forming C.C.P lattice}\end{bmatrix}$$

(2) CsCl type crystal
$$\begin{bmatrix}\text{C.N. of cation or anion} = 8\\ a\sqrt{3} = 2\left[r_c + r_a\right]\\ \text{Both ions forming simple cubic lattice}\end{bmatrix}$$

(3) ZnS type crystal
$$\begin{bmatrix}\text{CN. of ions} = 4\\ a\sqrt{3} = 4[r_c + r_a]\\ \text{Anion forming C.C.P lattice (Zinc blende)}\end{bmatrix}$$

(4) CaF_2 type crystal
$$\begin{bmatrix}\text{CN. of cation} = 8\\ \text{CN of anion} = 4\\ a\sqrt{3} = 4[r_c + r_a]\end{bmatrix}$$
$$\left[\text{cation forming C.C.P lattice}\right]$$

41(A)

	(Set – I)		(Set – II)
(1)	Cubic	(p)	All angles are equal
		(R)	Have maximum elements of symmetry
(2)	Ortho rhombic	(P)	All angles are equal
(3)	Monoclinic	(S)	Contain only two Bravais lattices [Primitive and End centred].
(4)	Hexagonal	(Q)	Only two sides have equal length

42.(A) In simple cubic system face of the unit cell has Q type of atomic arrangement

In body centred cubic system, diagonal plane of symmetry has R type of atomic arrangement. In face centred cubic system, diagonal plane of symmetry has S type of atomic arrangement.

In hexagonal close packing system, basal plane has P type atomic arrangement.

43.(4) This kind of arrangement is observed in F.C.C. system.
Rank of the unit cell i.e. effective no. of atoms per unit cell is equal to 4.

44.(2) In body centred cubic crystal, the nearest distance between two atoms is $\frac{\sqrt{3}a}{2}$. Its effective no. of atoms per unit cell is 2.

45.(4) Cubic, tetragonal, orthorhombic, rhombohedral.

46.(2) The given arrangement follows face centred cubic system which contain 8 tetrahedral voids and 4 octahedral voids per unit cell.

47.(4) Body diagonal length is $\sqrt{3}a$ while the nearest distance between octahedral and tetrahedral voids is $\frac{\sqrt{3}a}{4}$.

48.(3) The given axis is 4 fold axis. Removal of body centred Na^+ will give 3 Na^+ ions per unit cell.

49.(7) Formula of the compound is $Zn\,Al_2\,O_4$.

50.(4) $Ni_{0.98}\,O_1$ contain 98 Nickel ions with total charge of 200 units.

$$3x + (98 - x)\,2 = 200$$
$$x = 4$$

51.(0) None of the face of a truncated octahedron is octahedral face.

52.(3) In ABC packing, that is in F.C.C. system, distance between two successive layers of 'A' is $\sqrt{3}$ times of lattice parameter.

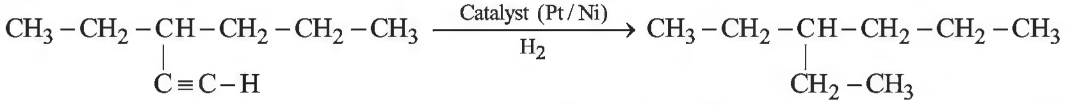
53.(5) Density = $\frac{ZM}{N_A V}$, $Z = 4$, $M = 6.023y$ amu / formula unit $= y \times 10^{-26}$ kg /formula unit, $V = a^3 = (2y^{1/3})^3$ nm^3

54.(8) Formula of the compound is A_4B_3C.

IOC & Hydrocarbons

1.(B) $C_6H_5CH=CH_2 \xrightarrow{Br_2} C_6H_5CHBrCH_2Br \xrightarrow[\text{3 equivalents}]{NaNH_2} C_6H_5C\equiv CNa \xrightarrow{CH_3I} C_6H_5C\equiv CCH_3$

2.(D)



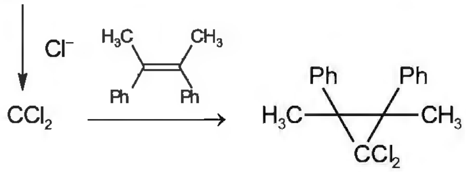
$$\underset{\displaystyle C\equiv C-H}{CH_3-CH_2-\overset{|}{C}H-CH_2-CH_2-CH_3} \xrightarrow[H_2]{\text{Catalyst (Pt/Ni)}} \underset{\displaystyle CH_2-CH_3}{CH_3-CH_2-\overset{|}{C}H-CH_2-CH_2-CH_3}$$

In catalytic hydrogenation double bonds and triple bonds are reduced.

3.(C) sp hybridized carbons are more electro negative then sp^2-hybridized carbons so alkynes are more acidic than alkenes.

4.(A) Br_2 gives Anti addition.

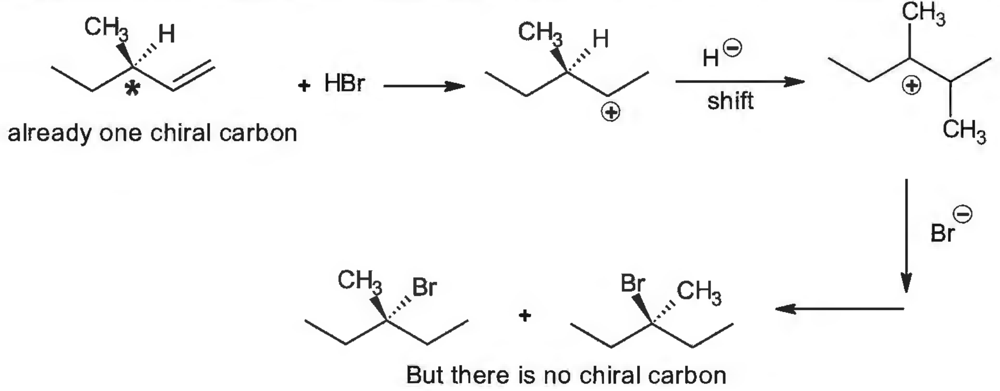
5.(A) $CHCl_3 + OH^- \longrightarrow CCl_3^- + H_2O$



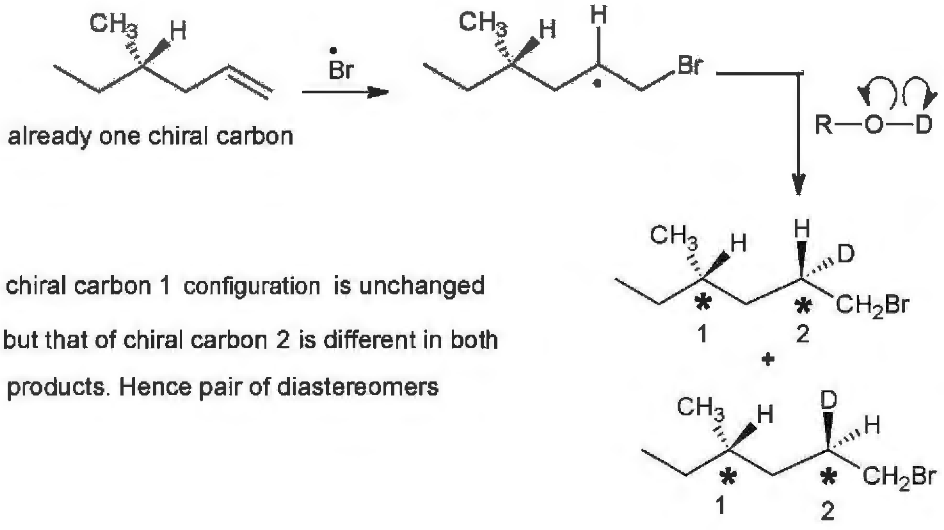
6.(B) Reaction I :

Chiral carbon 1 configuration is unchanged, but configuration are different at chiral carbon 2. Thus diastereomers.

Reaction II :

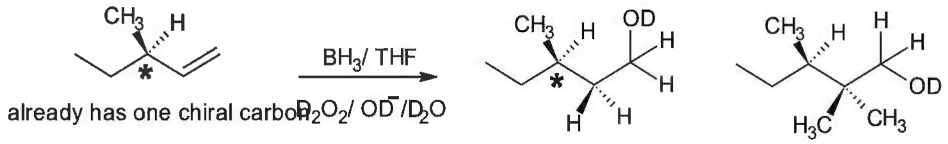


Reaction III :

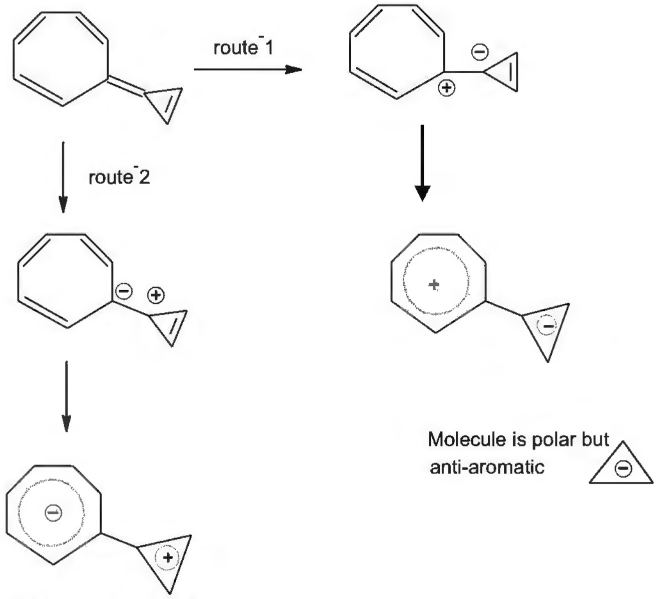


chiral carbon 1 configuration is unchanged but that of chiral carbon 2 is different in both products. Hence pair of diastereomers

Reaction IV :



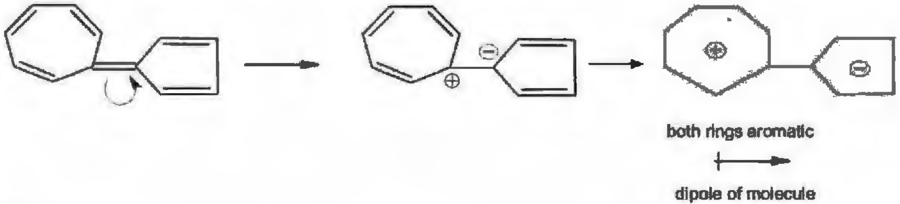
7.(B) **(A)**



Molecule is polar but anti-aromatic

Molecule is polar but not aromatic as seven - membered is anti aromatic

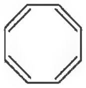
(B)



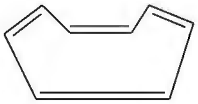
(C)

is non-polar in nature.

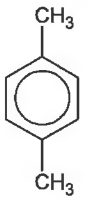
(D)



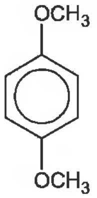
is non-aromatic in nature because of non-polar tub-like structure.



8.(C)



&



Have all 4 positions identical for mono substitution and both compounds are activating in nature.

9.(A) A meso compound must have at least 1 chiral centre and then it must have at least one element of symmetry.

10.(C) Benzene ring activated for electrophilic aromatic substitution can easily undergo Friedel Craft's alkylation reaction.

11.(D) % enantiomeric excess = $\frac{\text{measured specific rotation of mixture}}{\text{specific rotation of pure enantiomer}} \times 100 = \frac{11.55}{23.1} \times 100 = 50\ \%$

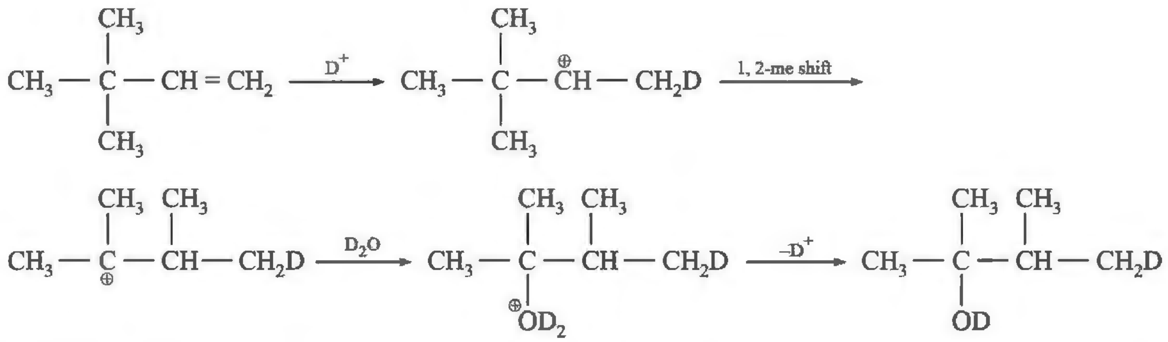
or $11.55 = 23.1 \times a + (1-a)(-23.1)$ [Where 'a' is the fraction of dextro form.]

⇒ a = 0.75, so dextro form is 75% and 25% form is laevo form

It means 50% is the enantiomeric excess of dextro or (+) form

12.(C) Extended conjugation.

13.(B)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{D^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{C}H-CH_2D \xrightarrow{1,\,2\text{-me shift}}$$

$$CH_3-\underset{\oplus}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2D \xrightarrow{D_2O} CH_3-\underset{\oplus OD_2}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2D \xrightarrow{-D^+} CH_3-\underset{OD}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2D$$

14.(C) Hint: meso product is formed

15.(B) Hydroboration-oxidation

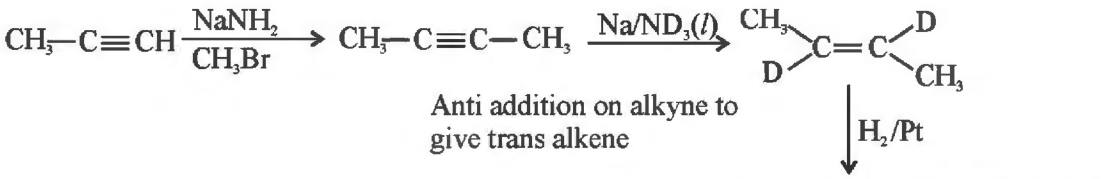
16.(A) $CH_3-CH_2-C\equiv C-(CH_2)_2-C\equiv CH \xrightarrow{\text{Ozonolysis}}$

$CH_3-CH_2-COOH+HOOC-(CH_2)_2-COOH+HCOOH$

17.(AB) In option (A) elimination product is the minor product, in option (D) first product is the major product because E2 elimination is carried out by anti-planar arrangement.

18.(AC) In option (B) isopropyl-Benzene is formed.

19.(BD)

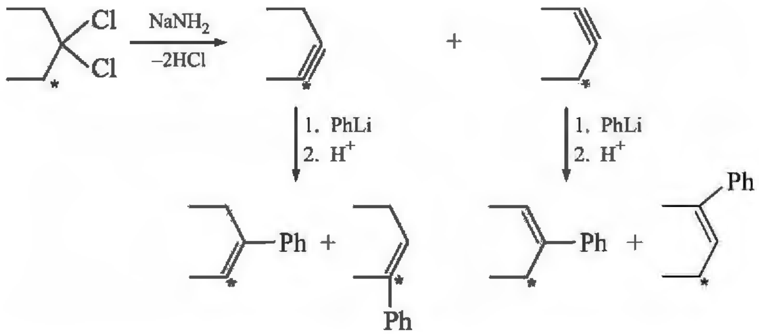


$CH_3-C\equiv CH \xrightarrow[CH_3Br]{NaNH_2} CH_3-C\equiv C-CH_3 \xrightarrow{Na/ND_3(l)}$

Anti addition on alkyne to give trans alkene

Syn addition on trans alkene give racemic mixture

20.(ABCD)



21.(BD) In first reaction addition takes place via Markonikov's rule.

In second reaction addition takes place via anti- Markonikov's rule forming more stable intermediate

$$\underset{\oplus}{CH_2}-CH_2-COOH$$

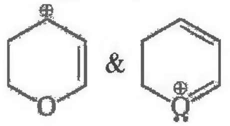
22.(BD) The structure must have three active H-atoms; red P and HI cannot reduce $-C\equiv C-$

23.(AD) $Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$

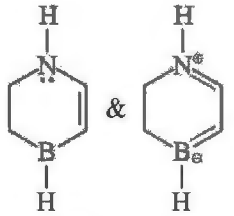
$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_3$

24.(ACD) It decreases the energy of system by delocalisation. Resonating structure are hypothetical structure having decrease energy than resonance hybrid.

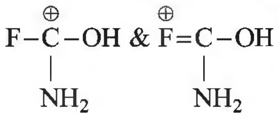
25.(ABC)



Second structure having more Number of double bond



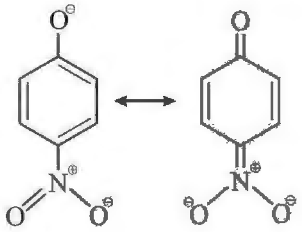
Second structure having more Number of double bond



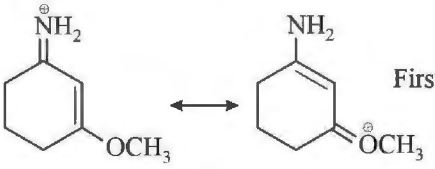
$$F-\underset{NH_2}{\overset{\oplus}{C}}-OH \ \& \ \overset{\oplus}{F}=\underset{NH_2}{C}-OH$$

Second structure having more number of double bond.

26.(BC)

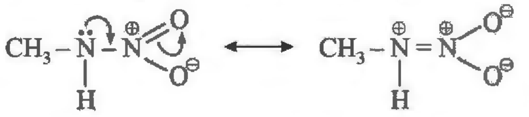


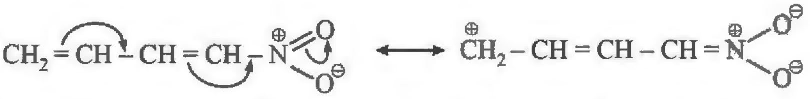
First structure having more number of double bond



First structure having positive charge on less electronegative atom

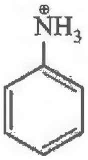
27.(BC)

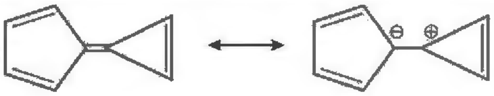


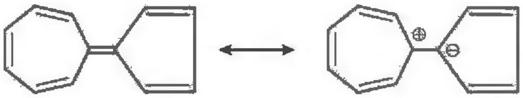


28.(C) It can not show –M effect Because nitrogen cannot form five bonds

It can not show +M effect because nitrogen neither having lone pair nor –ve charge

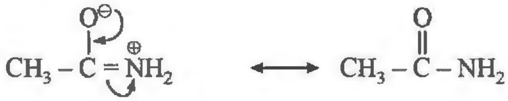


29.(BD)  Both the rings are aromatic now

 Both the rings are aromatic now

30.(ABCD) **(A)** $\overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}-CH_3 \longleftrightarrow CH_2=CH-O-CH_3$

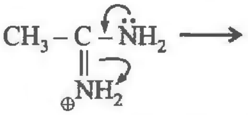
(B) $\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{O} \longleftrightarrow CH_2=CH-CH=O$

(C) 

$CH_3-\overset{O^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{N}H_2 \longleftrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

(D) $\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2 \longleftrightarrow CH_2=CH-CH=CH_2$

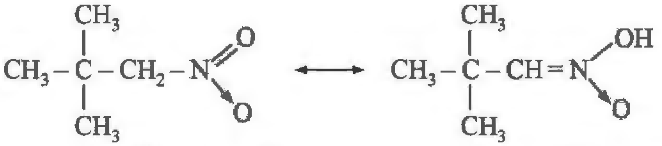
31.(ABD) (A) a' > a → Because of resonance single bond acquire some double bond character. Hence, the bond length decreases

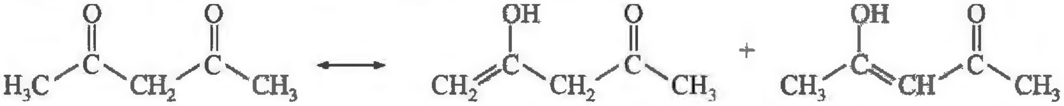
(B) 

$CH_3-\underset{\overset{\oplus}{N}H_2}{\underset{\|}{C}}-\ddot{N}H_2 \longrightarrow$ Resonance is in between b and b' bond
So they will have equal bond length

(D) d > d' → Because of resonance, double bond acquire some single bond character. Here, the bond length along d will increase

32.(BCD) Equivalent contributing structures make resonance very important because of equal stability
Contributing structures are hypothetical and less stable than resonance hybrid.

33.(BC) **(B)** 

(C) 

34.(ABC)

(A) More electronegative atom having –ve charge
(B) More electronegative atom having –ve charge
(C) Molecule having more No. of double bond

35.(ACD)

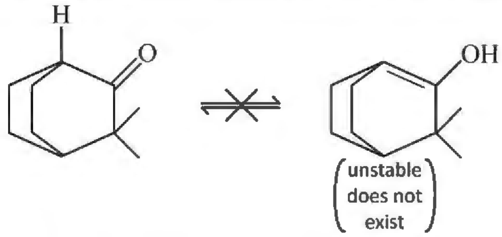
It is free radical allylic substitution reaction. For allylic bromination NBS, $Br_2 / h\nu$ and Br_2 / Δ can be used.

36.(ABC)

(A) Free radical bromination is highly regioselective. 3°H atom is easily substituted by Br atom.
(B) It is allylic bromination
(C) It is free radical benzylic bromination of side chain.
(D) It is electrophilic substitution reaction. In this reaction iodination of benzene takes place

$$I-Br+FeBr_3 \longrightarrow I^{\oplus} + FeBr_4^{\ominus}$$

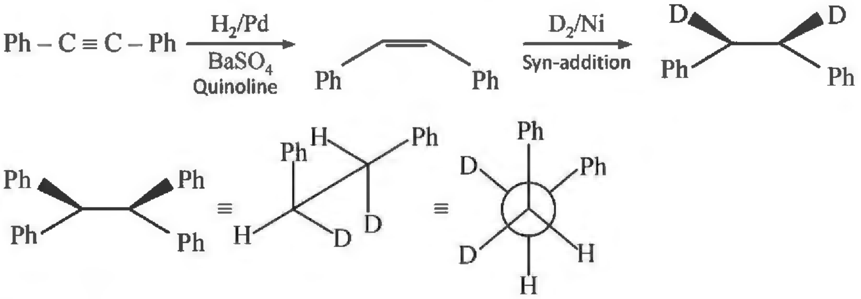
37.(AB) In case of bicyclic carbonyl compound, bridge head position can't be planar hence may not exhibit tautomerism



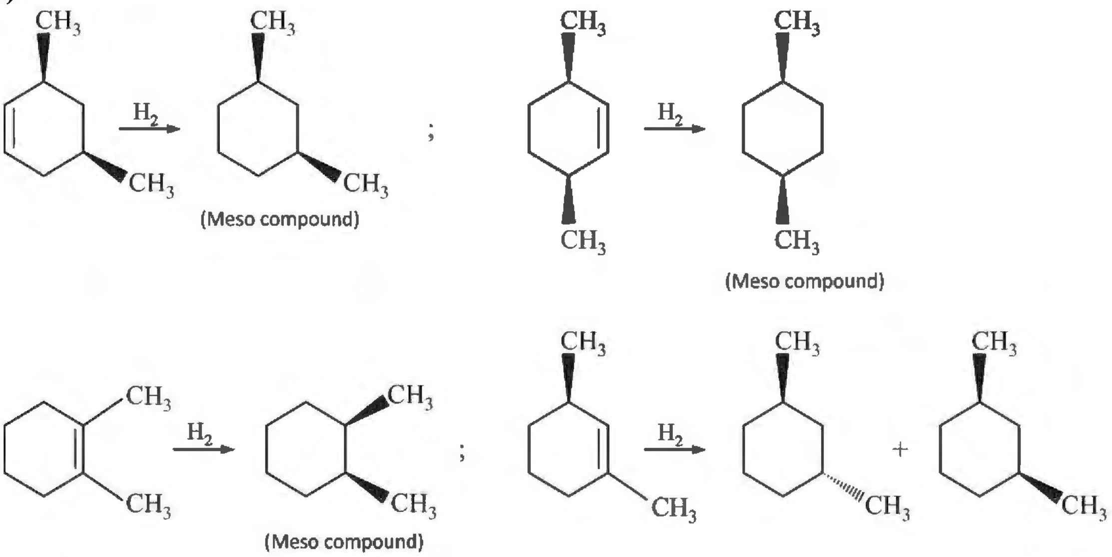
38.(ABCD)

All are suitable catalyst for partial reduction of alkyne to alkene. Rosenmund catalyst is $Pd-CaCO_3$ poisoned with sulphur and quinoline.

39.(BC)



40.(ABC)

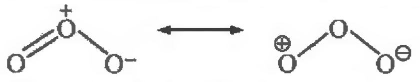


41.(ABC)

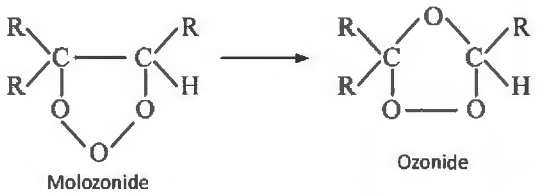
Cold alk·$KMnO_4$ and OsO_4 & Na_2CO_3 are used for syn hydroxylation of alkene.

42.(ABCD)

(A) Ozone is 1, 3-dipolar ion and acts as both electrophile as well as nucleophile

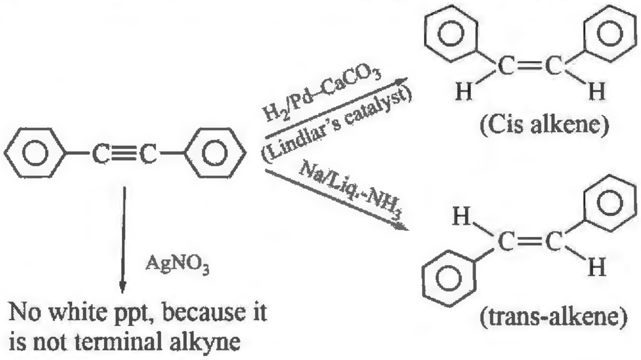


(B) Alkene is nucleophilic substrate hence O_3 interact with alkene as electrophile



43. **[A-p, q, s]** **[B-p, r, s]** **[C-p, q, s]** **[D-p, r, s]**

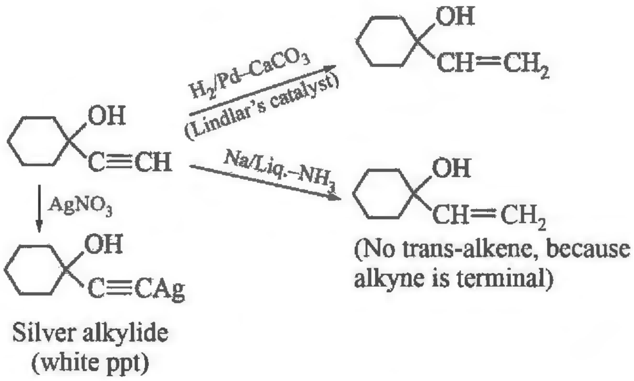
(A)



$$D.B.E = \frac{2C+2+N-X-H}{2} = \frac{2(14)+2-10}{2} = 10$$

So, $A \rightarrow p, q, s$

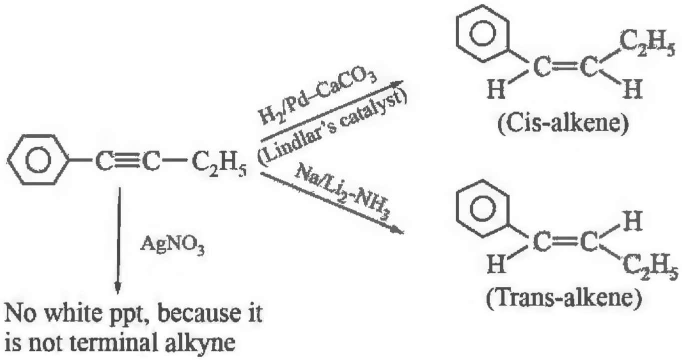
(B)



$$\textbf{D.B.E} = \frac{2C+2+N-X-H}{2} = \frac{2(8)+2-12}{2} = 3$$

So, $B \rightarrow p, r, s$

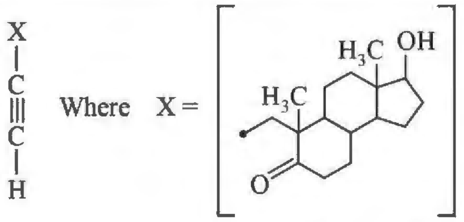
(C)

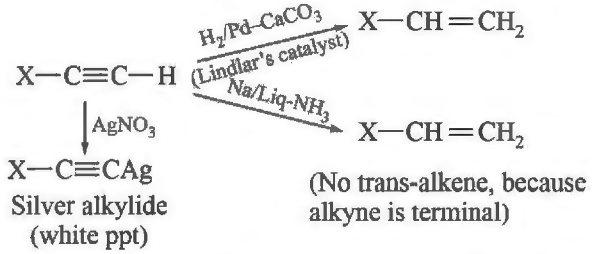


$$\textbf{D.B.E} = \frac{2C+2+N-X-H}{2} = \frac{2(10)+2-10}{2} = 6$$

So, $C \rightarrow p, q, s$

(D)



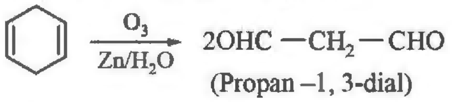


$$\textbf{D.B.E} = \frac{2C+2+N-X-H}{2} = \frac{2(19)+2-28}{2} = 6$$

So, $D \rightarrow p, r, s$

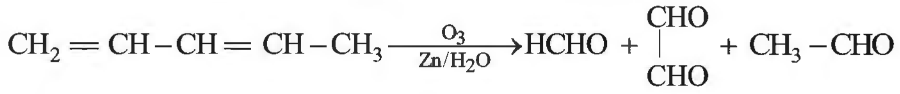
44. **[A-r] → [B-p, q, s] → [C-q, s] → [D-p, s]**

(A)



So, $A \rightarrow r$

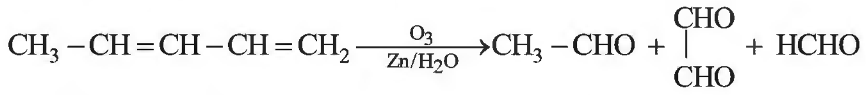
(B)



$$CH_2 = CH-CH = CH-CH_3 \xrightarrow[Zn/H_2O]{O_3} HCHO + \begin{matrix} CHO \\ | \\ CHO \end{matrix} + CH_3-CHO$$

So, $B \rightarrow p, q, s$

(C)



$$CH_3-CH=CH-CH=CH_2 \xrightarrow[Zn/H_2O]{O_3} CH_3-CHO + \begin{matrix} CHO \\ | \\ CHO \end{matrix} + HCHO$$

So, $C \rightarrow p,q,s$

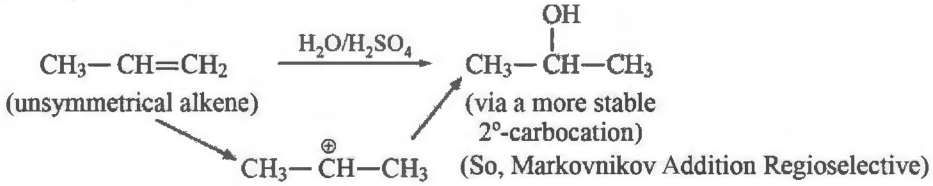
(D) $CH_3-CH=CH_2 \xrightarrow[Zn/H_2O]{O_3} CH_3-CHO+HCHO$

So, $D \rightarrow p,s$

45. **[A-p, s] → [B-p, s, r] → [C-q, s] → [D-r, s]**

(A) Acid catalyzed hydration of alkenes

Example,

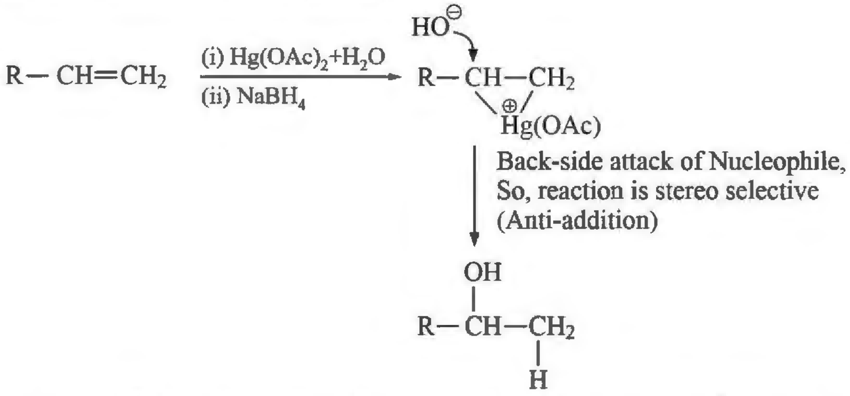


- No stereoselectivity, because carbocation is planar, and attack of nucleophile on carbocation can be from both above the plane as well as below the plane.

  So, $A \rightarrow p, s$

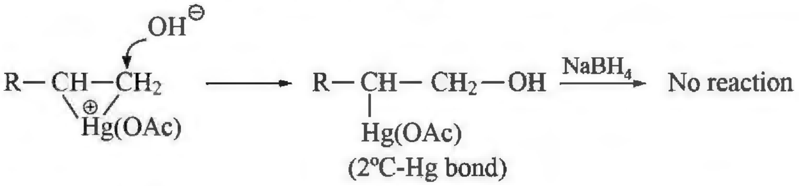
(B) **Oxymercuration-Demercuration of Alkenes**

Example,



Back-side attack of Nucleophile,
So, reaction is stereo selective
(Anti-addition)

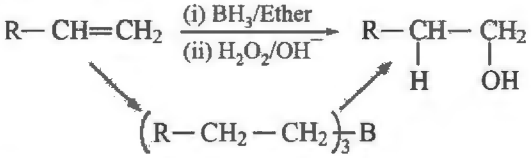
- **The reaction is also Regioselective, because only 1°C-Hg bond can be reduced by $NaBH_4$. So, Markovnikov Addition takes place.**



So, $B \rightarrow p, r, s$

(C) Hydroboration-Oxidation of Alkenes

Example,



- The reaction is Regioselective, because Boron always attached to sterically less hindered carbon. So, Anti-Markovnikov Addition takes place.
- The reaction is stereoselective, because it proceed through cyclic transition state [So, syn Addition]

So, $C \rightarrow q, r, s$

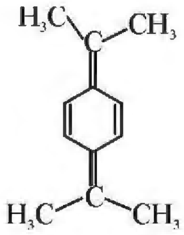
(D) Dehydration of Alcohols to Alkenes

For 2° and 3° Alcohols, elimination in acidic medium takes place through E1 mechanism, where carbocation may undergo rearrangement, and a Saytzeff product is always formed. So, regioselectivity is there.

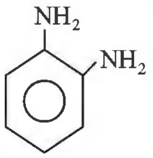
For 1° alcohols, elimination in acidic medium takes place through E2 mechanism, where principle of anti-peri planarity is followed i.e. Anti-elimination. So, stereoselectivity is there.

So, $D \rightarrow r, s$

46.(4) Compound A is



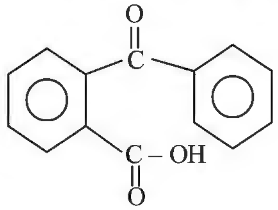
47. (4) Product (P) is



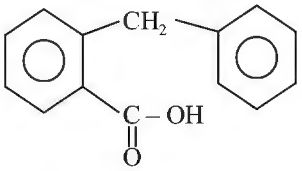
Molecular weight = M = 108 $\therefore \frac{M}{27}=\frac{108}{27}=4$

48. (194)

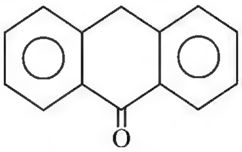
A =



B =



C =

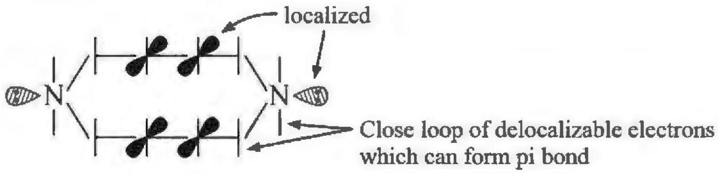


Molecular weight = M = 194

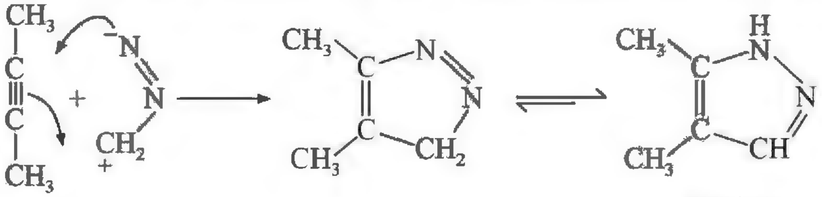
49.(5) It is intramolecular wurtz reaction.

50.(10) Given compound obey Huckel's rule hence it possess a close loop of ten delocalizable pi electrons.

$x\pi = 10\pi \Rightarrow x = 10$



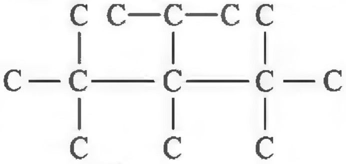
51.(6) Diazomethylene also acts as 1, 3-dipolar ion and it may add across carbon-carbon multiple bond.



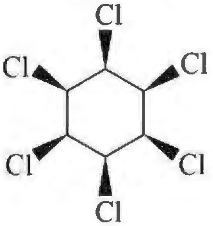
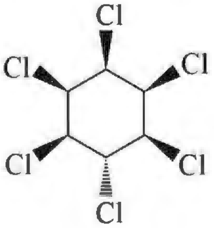
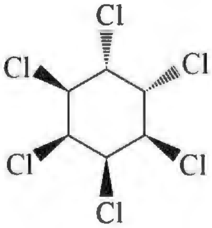
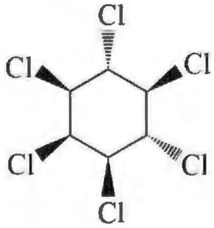
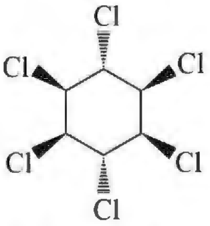
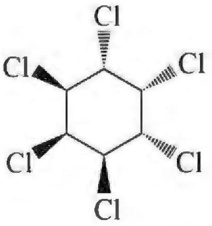
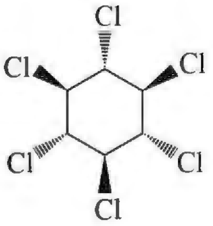
(Major)
Aromatic (More stable)

Major product is aromatic and it possess six delocalizable pi electrons.

52.(5)

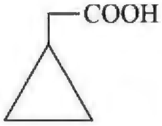


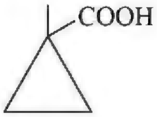
53.(7)

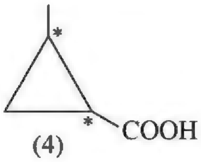








54.(6) (2, 3, 4, 5, 6, 8)

55.(6)

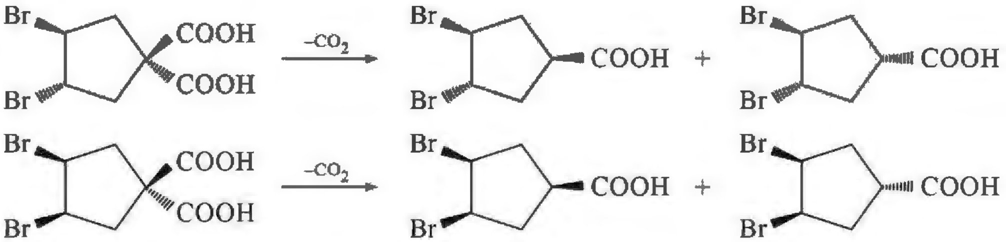






(4)

56.(4)



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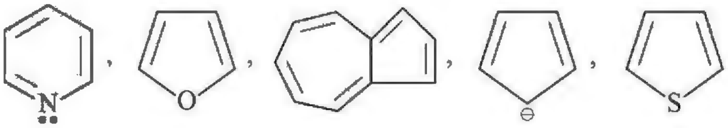
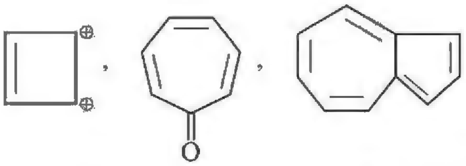
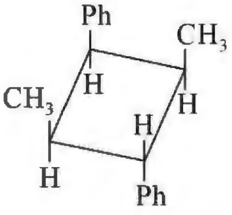


58.(3)

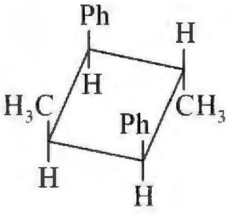


are Aromatic species

59.(05)



POS



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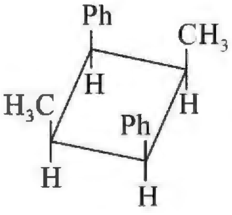

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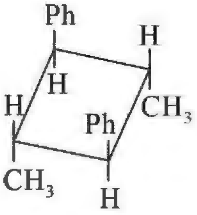

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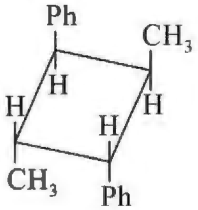
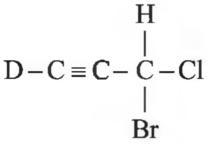


COS & POS

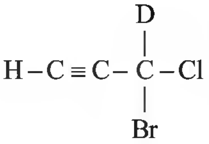
05 all optically inactive

60.(08)



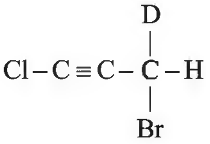
$\mathrm{D-C\equiv C-\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}-Cl}$

enantiomer



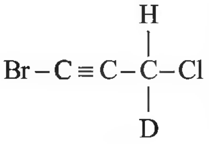
$\mathrm{H-C\equiv C-\overset{\overset{D}{|}}{\underset{\underset{Br}{|}}{C}}-Cl}$

enantiomer



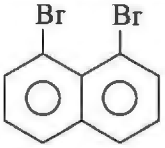
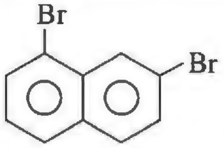
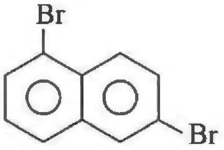
$\mathrm{Cl-C\equiv C-\overset{\overset{D}{|}}{\underset{\underset{Br}{|}}{C}}-H}$

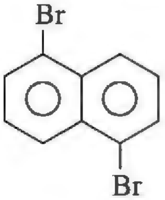
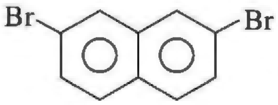
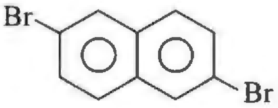
enantiomer



$\mathrm{Br-C\equiv C-\overset{\overset{H}{|}}{\underset{\underset{D}{|}}{C}}-Cl}$

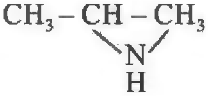
enantiomer

61.(06)  ,  , 

 ,  , 

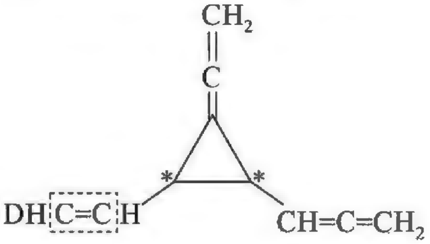
62.(5) (iii), (iv), (vi), (vii), (viii)

63.(3) $CH_3-CH_2-CH=NH$, $CH_3-CH=CH-NH_2$, $CH_3-CH=N-CH_3$

$CH_2=N-CH_2CH_3$,  , 

64.(8) The molecule contains 3 stereocenters

$\therefore$ Total stereoisomers = $2^3=8$



Organic Halides & Organic Concepts

1.(D) 2° allylic halides undergo S_N1 reaction faster than simple 2° halides. 3° bridged halides undergo S_N1 reaction too slowly because of difficulty in forming a planar sp^2 hybridized carbon at bridge head.

2.(B) Cl atom is substituted by PhS^- and inversion of configuration takes place as reaction is S_N2.

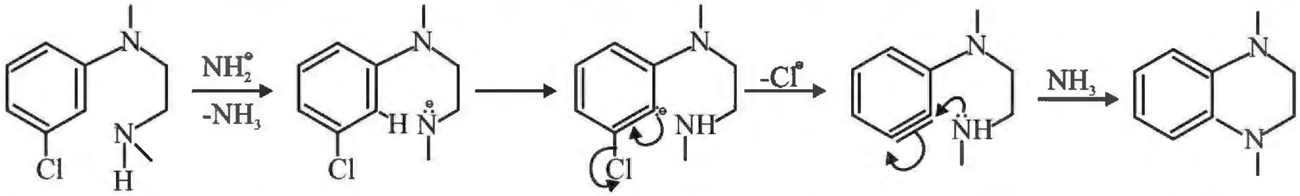
3.(A) The unhybridized p-orbital in the S_N2 transition state will be capable of delocalization of e^- density into the benzene ring and then to the carbonyl group. 1° benzyl halide would react faster than a 2° benzyl halide.

4.(B) 2° benzyl halide which gives the most stable carbocation after loss of leaving group, will undergo S_N1 reaction fastest.

5.(C) In presence of a strong base like NaOEt in EtOH and heating, the elimination would be preferred by E2 route as the substrate is 2°.

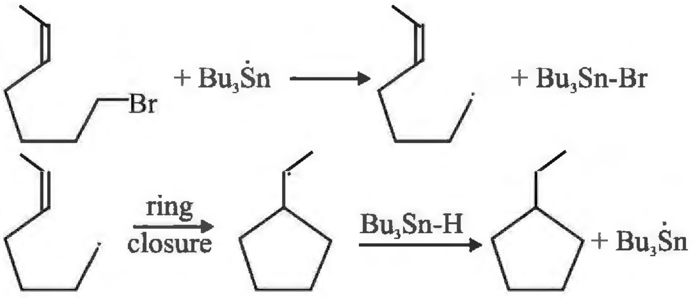
6.(B) Rate of those S_N2 reactions can be increased by increasing the polarity of the solvent when the reactants are uncharged.

7.(B)



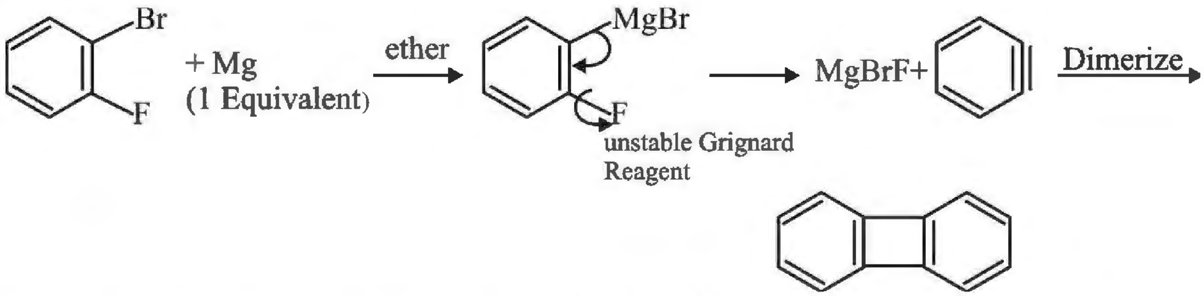
8.(C) $Me_2C(CN)N=N(CN)CMe_2 \xrightarrow{\Delta} N_2\uparrow + 2Me_2\dot{C}-CN$

$Me_2\dot{C}-CN + Bu_3Sn-H \rightarrow Me_2CH-CN + Bu_3\dot{S}n$



9.(B) Since H_2O is a far better ion –solvating agent than ethanol, so H_2O would be the preferred nucleophile to give product as alcohol.

10.(D)

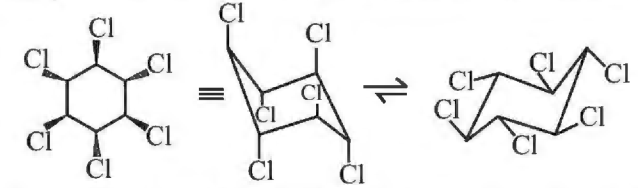


11.(B) α - Halo ketones are more reactive than simple 2° halides towards S_N2 attack.

12.(B) In presence of dilute OH^-, the reaction proceeds via neighbouring group participation to form product with retention of configuration.

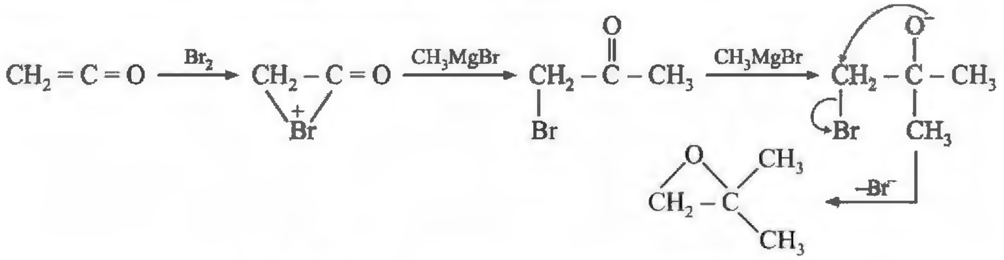
13.(A) A 1° halide cannot undergo elimination by E_1 pathway, so E_2 elimination route is preferred. C – H bond is more easily broken than a C – D bond, so deuterium remains in the product.

14.(C)

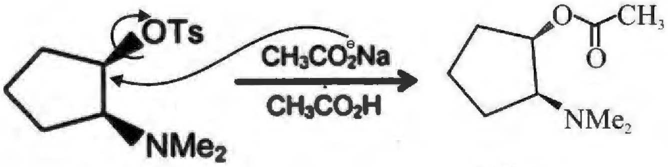


Since, H and Cl are not at anti positions, so elimination by E2 route is least favoured.

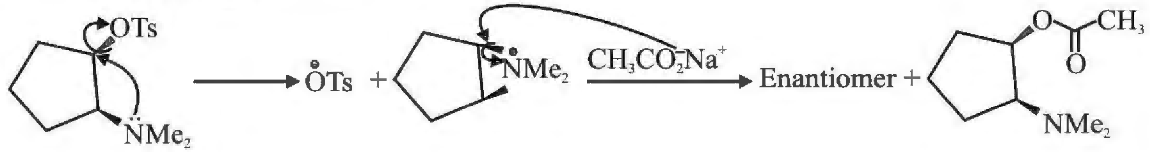
15.(C)



16.(A) Reaction - 1



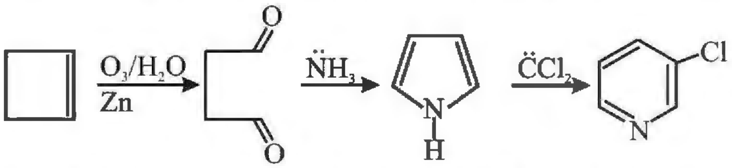
Reaction - 2



17.(D) Br and H atoms are in anti-position in compound 3 to undergo E_2 elimination giving Saytzeff's product. In compound 1, it undergoes elimination to give Hofmann product. ∴ Order of reactivity is 3 > 1 > 2.

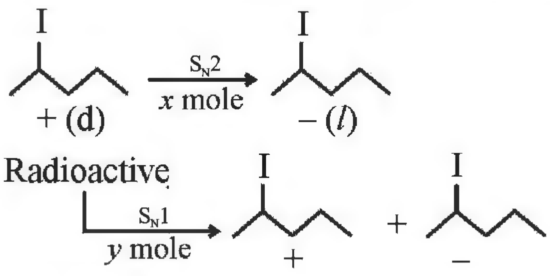
18.(C) Hofmann's product can be obtained by bulky and sterically crowded bases.

19.(D)



20.(B) α - hydrogen of carbonyl compounds is more acidic than β - hydrogen, so elimination becomes rapid.

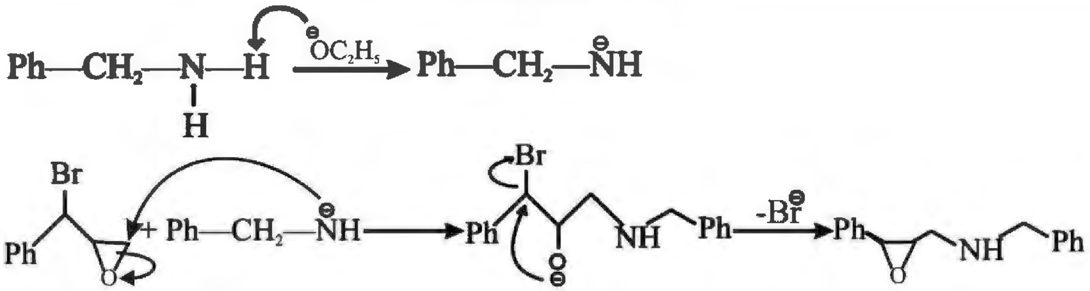
21.(D)



Loss in Radio activity = x
Loss in Radio activity= y
Loss in optical activity = $2x$
Loss in optical activity = y
Total loss in Radio activity= $x+y$

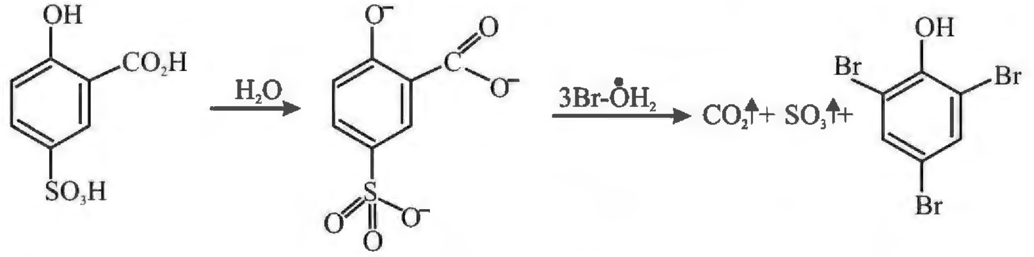
$(2x+y)=1.80(x+y)=\frac{x}{y}=4$; $\%\ S_N2=\frac{x}{x+y}\times100=\frac{4}{5}\times100=80\%$

22.(B)

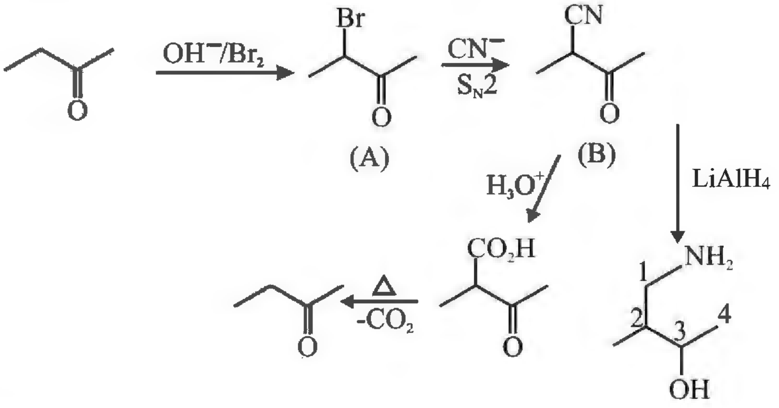


23.(A) Compound (P) has H and Br in axial trans locations while compound (Q) has no such arrangement.

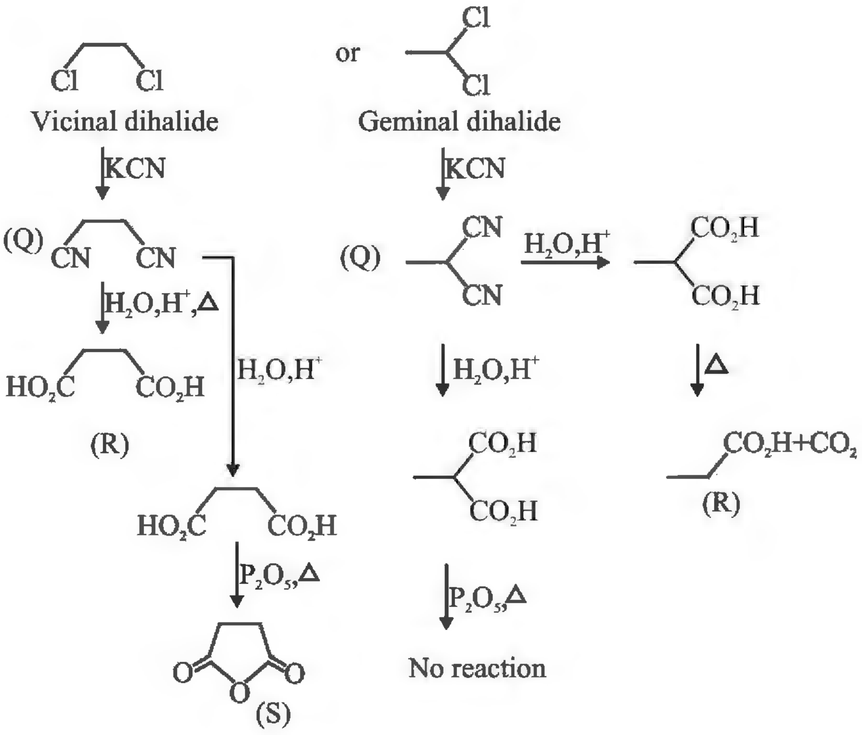
24.(B)



25.(D)



26.(ACD) (P) can be



27.(ABC) Ag^+ takes out the halide ion and speeds up the formation of carbocation. α - haloketones undergo reaction by S_N2 mechanism only but as carbocation is destabilized by electron withdrawing carbonyl group, it does not react by S_N1 mechanism. Acidic solution having H^+ helps in abstracting F^- ion from t-BuF, so its reaction becomes faster in acidic solution than in H_2O. S_N2 reaction on allylic substrates may undergo rearrangements.

28.(BC) The substrate is a 2° halide, so it can react by S_N1 and S_N2 pathways both. SCN^- is an ambidentate nucleophile with S atom as soft base and N atom as hard base. Hard base undergoes reaction via S_N1 pathway as carbocation is a hard acid while soft bases prefer to go via S_N2 route.

29.(A) Rate of Reaction = Rate due to S_N2 + Rate due to S_N1

$$= 3.2\times10^{-5}[2-\text{Bromobutane}] + 1.5\times10^{-6}[\text{2- bromobutane}] = [\text{2- bromobutane}]\ 3.35\times10^{-5}$$

$\therefore$ % of reaction occurring by S_N1 mechanism $= \dfrac{1.5\times10^{-6}[2-\text{Bromobutane}]}{3.35\times10^{-5}[2-\text{bromobutane}]}\times100 = 4.4\ \%$

$\therefore$ % of reaction occurring by S_N2 mechanism = 95.4%

% of racemization in the reaction = 4.4%

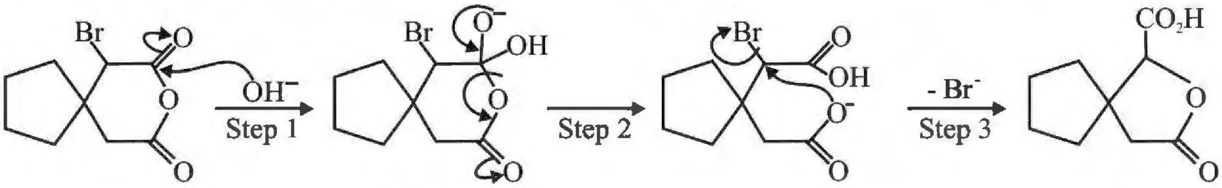
% of inversion product in the reaction = 95.4 + 2.2 = 97.6%.

30.(ABCD) Peroxide effect is shown by HBr only and other hydrogen halides even in the presence of peroxides follow polar mechanism.

31.(CD) Alcoholic $AgNO_3$ will give immediate while ppt. of AgCl with $CH_2 = CH - CH_2Cl$ while $CH_3CH_2CH_2 - Cl$ will give only on warming.

$CH_2 = CH - CH_2Cl$ will decolorize cold aq. $KMnO_4$ while there is no decolorization by $CH_3CH_2CH_2Cl$.

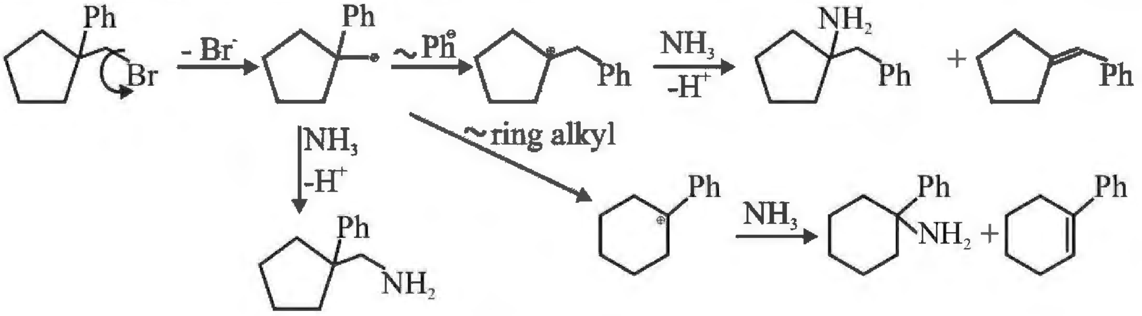
32.(ABD)



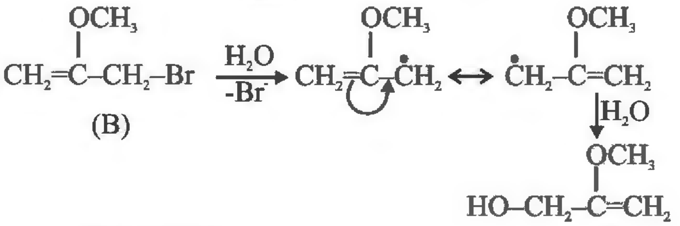
Step 1 and Step 2 involves nucleophilic addition on acyl carbon followed by elimination of CO_2^- group but overall reaction in referred as nucleophilic substitution at acyl carbon.

Step 3 involves nucleophilic substitution at alkyl carbon.

33.(ABD) As the substrate has 2 β- substitutes, so it can not react by S_N2 mode and NH_3 being a polar solvent, the reaction occur by S_N1 mode.



34.(ACD)



$$CH_2{=}\overset{\displaystyle OCH_3}{\overset{|}{C}}{-}CH_2{-}Br \xrightarrow[-Br^-]{H_2O} CH_2{=}\overset{\displaystyle OCH_3}{\overset{|}{C}}{-}\overset{\bullet}{C}H_2 \leftrightarrow \overset{\bullet}{C}H_2{-}\overset{\displaystyle OCH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow{H_2O} HO{-}CH_2{-}\overset{\displaystyle OCH_3}{\overset{|}{C}}{=}CH_2$$

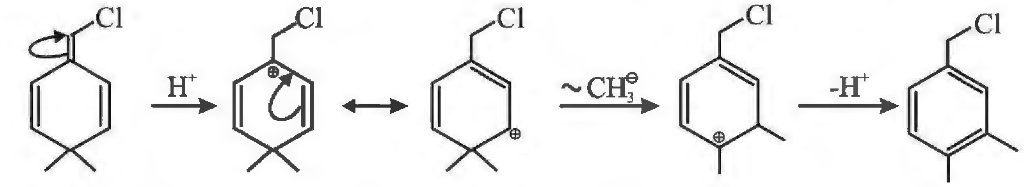
(B)

-I effect of OCH_3 will dispense the e^- density in the transition state of compound (B) more than that of compound (A) in S_N2 reaction.

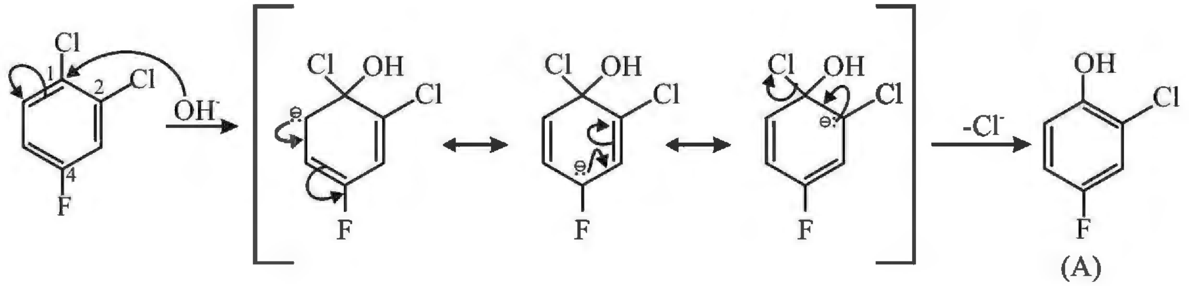
Compound (A) gives rearranged and non-rearranged product when reacted by via S_N1 as well as S_N2 pathways.

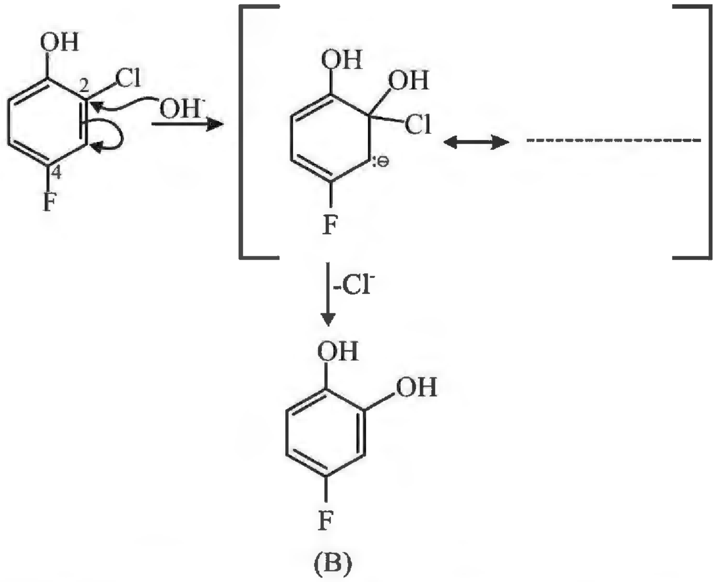
35.(ABC) $CH_3CH_2O^-$ is a strong nucleophile, so it prefers S_N2 attack in reaction (A). NH_3 is a strong nucleophile , so it reacts by S_N2 mode in reaction (B). CH_3O^- is a strong nucleophile, so undergoes S_N2 reaction in (C). CH_3OH is a weak nucleophile.

36.(ABD)



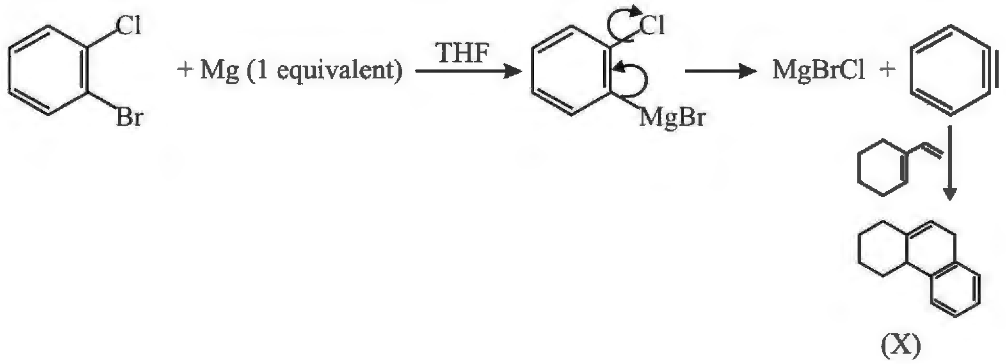
37.(AC)



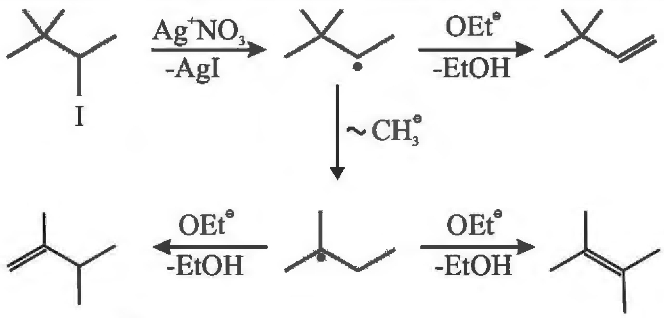


-I effect of OH group in (A) makes Cl at 2 more electrophilic than F at position 4.

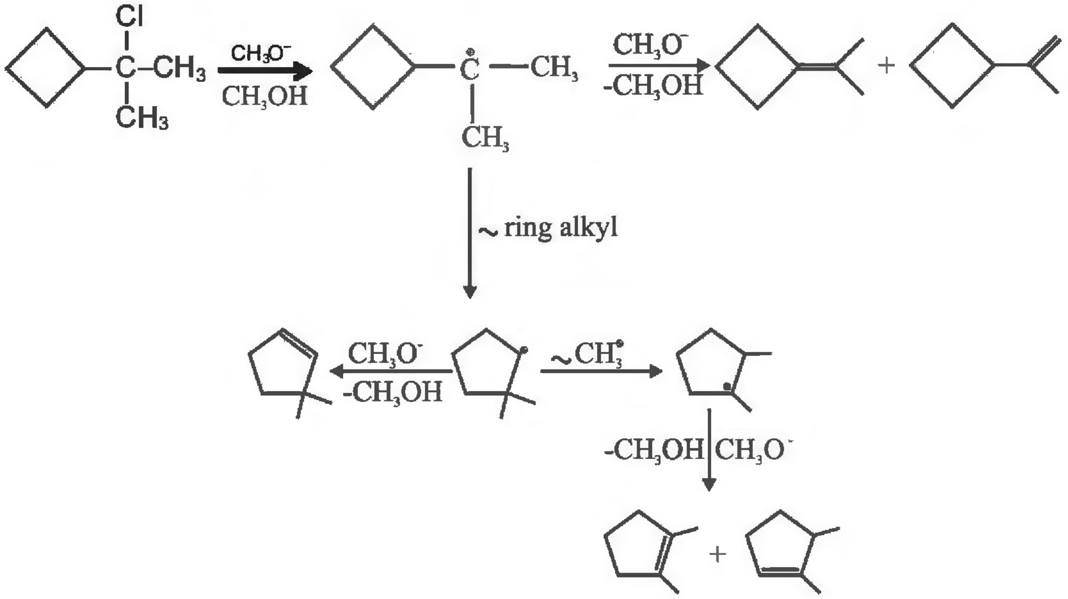
38.(ABCD)



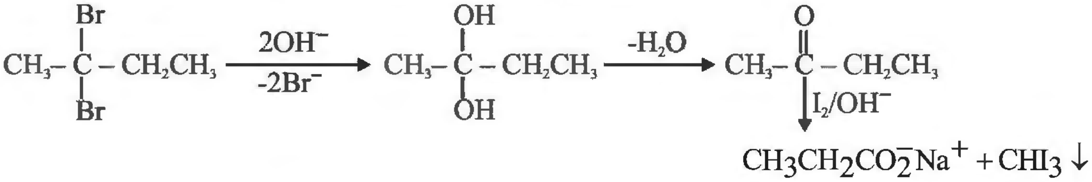
39.(ABC)



40.(ABCD)



41.(ABD) Compounds containing $CH_3-\overset{O}{\overset{\|}{C}}-$ unit or $CH_3-\overset{OH}{\overset{|}{C}H}-$ unit or any compound that can be converted into these units under the reaction condition gives iodoform test.



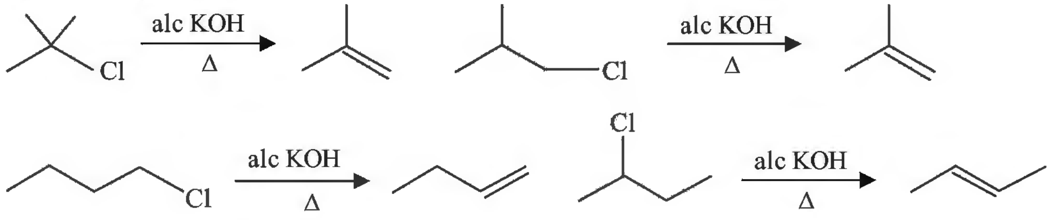
$$CH_3-\underset{Br}{\overset{Br}{C}}-CH_2CH_3 \xrightarrow[-2Br^-]{2OH^-} CH_3-\underset{OH}{\overset{OH}{C}}-CH_2CH_3 \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3 \xrightarrow{I_2/OH^-} CH_3CH_2CO_2^-Na^+ + CHI_3\downarrow$$

42.(ABC) $CaOCl_2 + H_2O \rightleftharpoons Ca(OH)_2 + Cl_2$

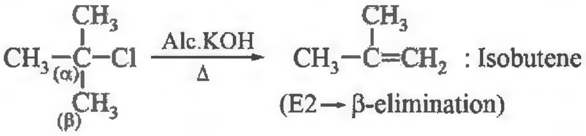
$Cl_2 + OH^- \rightleftharpoons OCl^- + Cl^-$

Bleaching powder provides Cl_2 (Chlorinating agent), OCl^- (oxidizing agent) and OH^- (hydrolyzing agent).

43.(ABD) With AgCN, the major product is alkyl isocyanide.
With NaCN, the major product is alkyl cyanide. With $NaNO_2$, the major product is alkyl nitrite and with $AgNO_2$, it is nitro alkane.

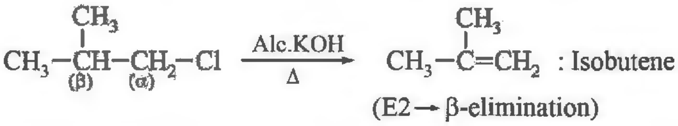


44.(AB)



$$CH_3-\underset{\underset{(\beta)}{CH_3}}{\overset{CH_3}{\underset{(\alpha)}{C}}}-Cl \xrightarrow[\Delta]{Alc.KOH} CH_3-\overset{CH_3}{C}=CH_2 \text{ : Isobutene}$$

(E2 → β-elimination)

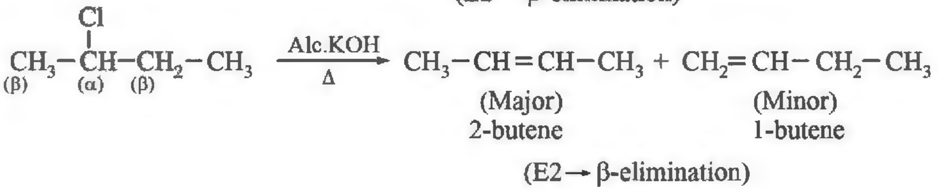


$$CH_3-\underset{(\beta)}{\overset{CH_3}{CH}}-\underset{(\alpha)}{CH_2}-Cl \xrightarrow[\Delta]{Alc.KOH} CH_3-\overset{CH_3}{C}=CH_2 \text{ : Isobutene}$$

(E2 → β-elimination)

$$CH_3-CH_2-\underset{(\beta)}{CH_2}-\underset{(\alpha)}{CH_2}\,Cl \xrightarrow[\Delta]{Alc.KOH} CH_3-CH_2-CH=CH_2 \text{ : 1-butene}$$

(E2 → β-elimination)



$$\underset{(\beta)}{CH_3}-\underset{(\alpha)}{\overset{Cl}{CH}}-\underset{(\beta)}{CH_2}-CH_3 \xrightarrow[\Delta]{Alc.KOH} \underset{\substack{\text{(Major)}\\\text{2-butene}}}{CH_3-CH=CH-CH_3} + \underset{\substack{\text{(Minor)}\\\text{1-butene}}}{CH_2=CH-CH_2-CH_3}$$

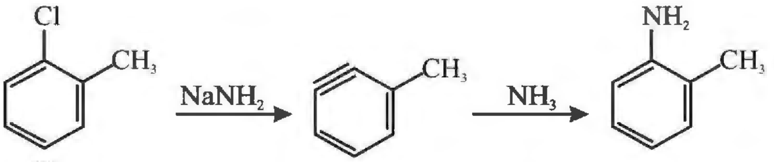
(E2 → β-elimination)

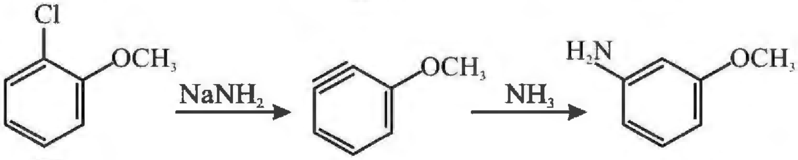
45.(BC) Reactivity order (a) 1° > 2° > 3° R in RCO_2Ag.

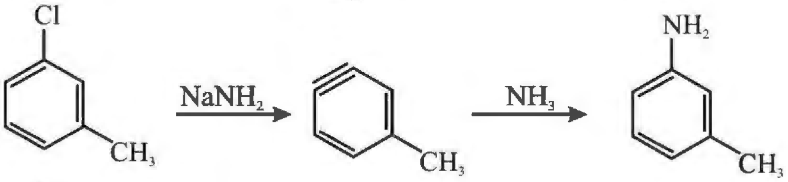
(b) $Br_2 > Cl_2$

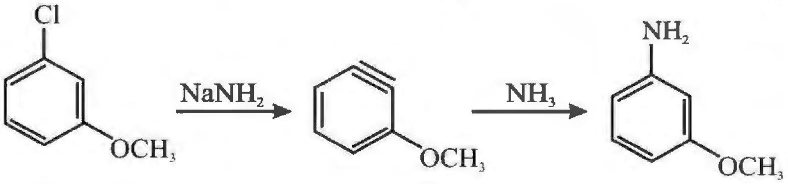
In case X = I Simmonini reaction happens : $2R-COOAg \xrightarrow[CCl_4]{I_2} RCOOR + 2AgI + CO_2$

46.(BCD)

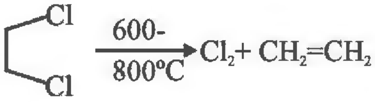




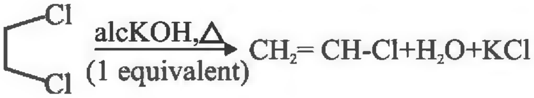




47.(BC)

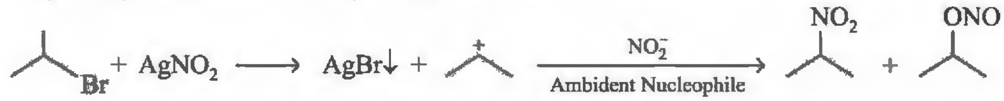


$HC \equiv CH \xrightarrow[Hg^{2+},\ 65°C]{HCl} CH_2 = CH-Cl$



$CH_3-CH_3+Cl_2 \xrightarrow{400°C} CH_3-CH_2-Cl+H-Cl$

48.(CD)



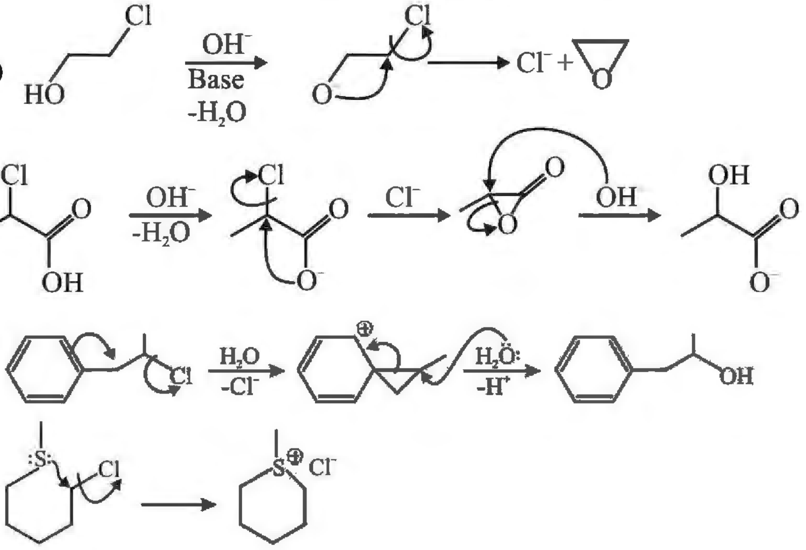
49.(AB) Rate of S_N1 reaction

(a) $R-I>R-Br>R-Cl>R-F$

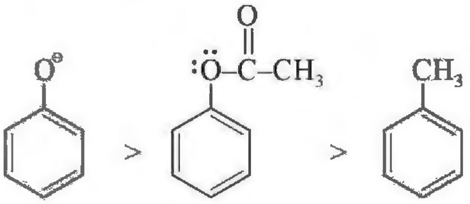
(b) $H_2O>CH_3OH>CH_3SH$ (decreasing polarity of solvent)

(c) Greater the steric crowding in the substrate, greater is the rate (Steric acceleration)

50.(ABCD)



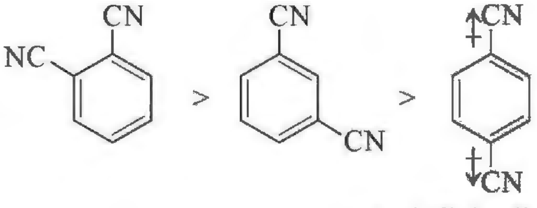
51.(AD)



show +M effect

show +M effect but lone pair of oxygen atom is also in delocalisation with carbonyl center (–C(=O)–)

show +H effect

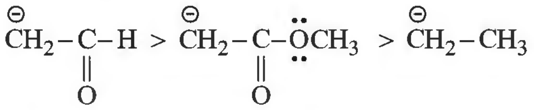


cancel all the dipole moment

52.(ABCD)

(A) II > III > I → More stronger is the $\overline{e}$ withdrawing group, more stable is the –ve charge.

(B)

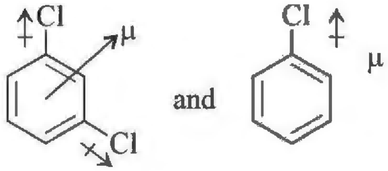


$$\overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-H > \overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-\ddot{O}CH_3 > \overset{\ominus}{C}H_2-CH_3$$

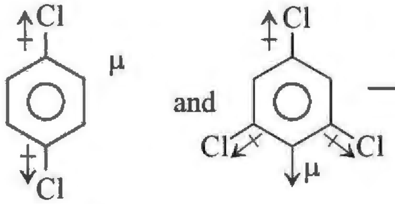
(C) I > II > III → More is the conjugation, more is the stability of –ve charge

(D) $\overset{\ominus}{C}H_3 > \overset{\ominus}{C}D_3$ More +I effect of D destabilize carbanion.

53.(C) (A)



(C)

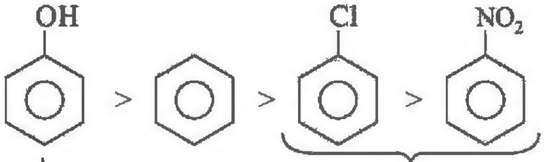


μ = 0

⟶ cancel all dipole moment μ = 0

54.(ABC)

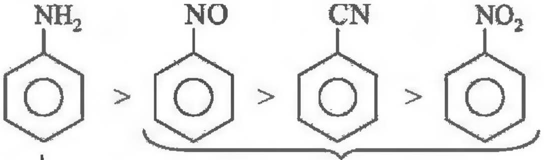
(A)



$\bar{e}$ donating group showing +M effect

$\bar{e}$ withdrawing group.Showing –M effect – NO_2 > – Cl withdraw greater $\bar{e}$ density

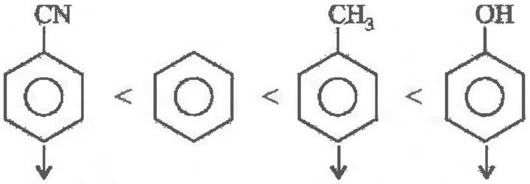
(B)



$\bar{e}$ donating group showing +M effect

$\bar{e}$ withdrawing group. Showing –M effect – NO_2 > – CN > – NO

(B)



show –M effect ↓ withdraw $\bar{e}$ density by mesomeric effect

showing +H effect ↓ donate $\bar{e}$ density by hyperconjugation

showing +M effect ↓ donate $\bar{e}$ density by mesomeric effect

→ Mesomeric effect is stronger than Hyperconjugation

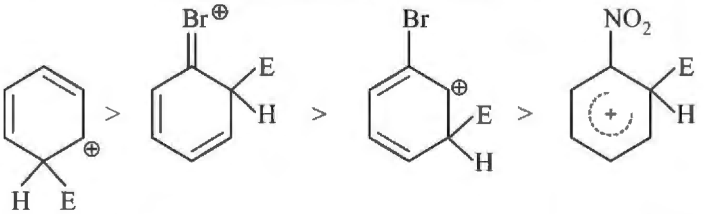
55.(BCD) $\overset{\ominus}{O} \rightleftharpoons P(CH_3)_2$ donating of –ve charge into vacant orbital of phosphorus

$\overset{\ominus}{O}-\overset{\oplus}{P}(CH_3)_3 \longleftrightarrow O = P(CH_3)_3$

$\overset{\ominus}{O} \rightleftharpoons B(CH_3)_2$ donating of –ve charge into vacant orbital of Boron

56. (BD) It is free radical substitution reaction. Intermediate of this reaction is free radical. It is planar intermediale having unpaired electron in p-orbital.

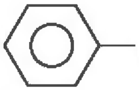
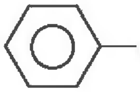
57. (ABCD) Order of energy of intermediate arenuim ion is:



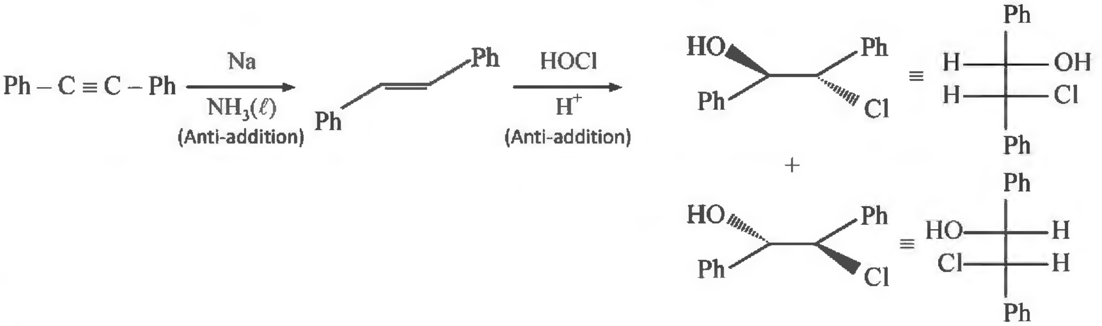
Br and NO_2 are electron withdrawing groups and presence of electron withdrawing group decreases the stability of arenium ion.

58.(BD) Strongly deactivated substrates are not suitable for F.C. acylation. Phenolic compounds and aniline are also not suitable for F.C. reaction because these form complex with Lewis acid which is used as catalyst in F.C. reaction.

59.(BCD)

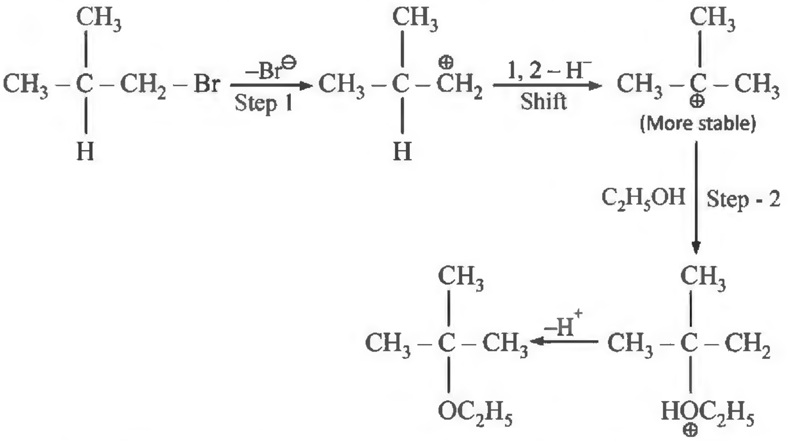
Left hand side phenyl ring of  $O-CH_2-Ph$ and  $NH-COPh$ is activated for electrophilic aromatic substitution reaction.

60.(BC)



61.(ABC)

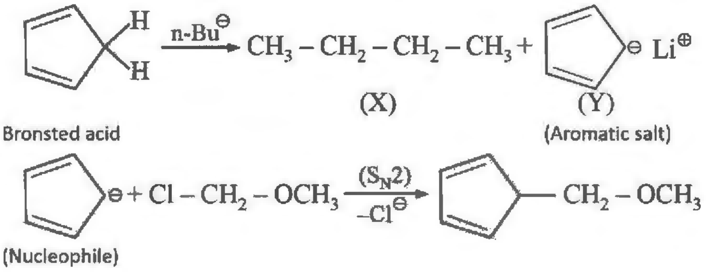
It is solvolysis reaction and proceed by S_N1 reaction mechanism.



$$CH_3-CH(CH_3)-CH_2-Br \xrightarrow[\text{Step 1}]{-Br^{\ominus}} CH_3-CH(CH_3)-\overset{\oplus}{C}H_2 \xrightarrow[\text{Shift}]{1,2-H^-} CH_3-\overset{\oplus}{C}(CH_3)-CH_3 \xrightarrow[\text{Step - 2}]{C_2H_5OH} CH_3-C(CH_3)(\overset{\oplus}{O}HC_2H_5)-CH_3 \xrightarrow{-H^+} CH_3-C(CH_3)(OC_2H_5)-CH_3$$

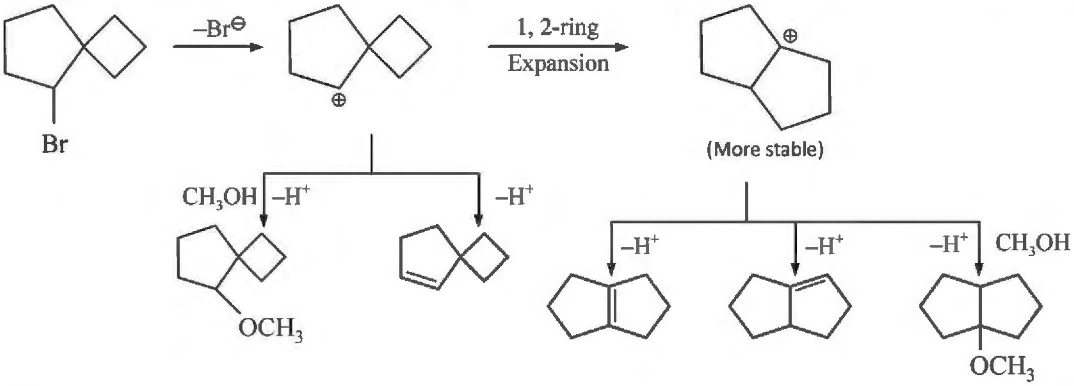
For S_N1, rate of reaction depends upon conc. of only alkyl halide.

62.(ABC)



63.(ABCD)

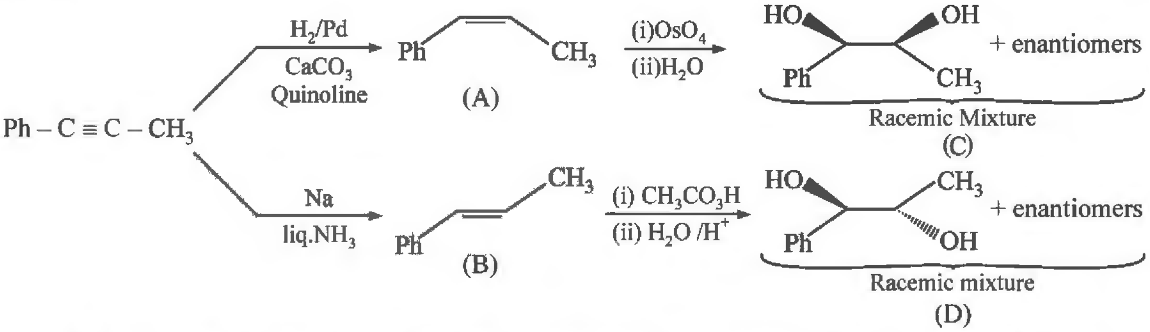
It is solvolysis reaction, takes place by formation of intermediate carbocation. Minor product is also formed through E1 elimination reaction mechanism



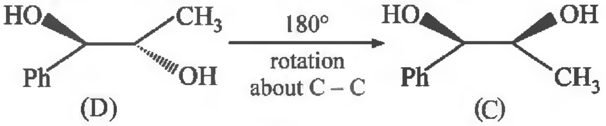
64.(ABCD)

Primary organic halide undergoes nucleophilic substitution by S_N2 reaction mechanism.

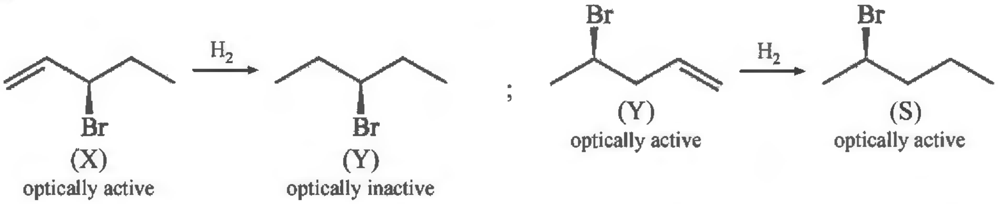
65.(ABC)



Product (C) and (D) are identical and can't be separated by fractional distillation. (A) and (B) are diastereomers and gives same product on catalytic hydrogenation.



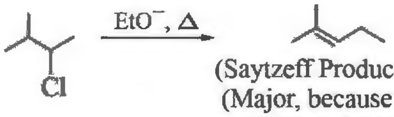
66.(ABD)



67.(B) (P)

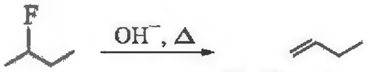
(Saytzeff Product-E2 mechanism
(Major, because more
substituted alkene)

(Q)



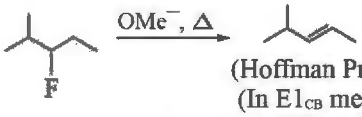
(Saytzeff Product-E2 mechanism
(Major, because more
substituted alkene)

(R)



(Hoffman Product-E1_{CB} mechanism
(In E1_{CB} mechanism, carbanion
stability plays dominant role)

(S)

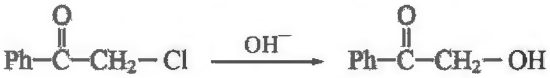


(Hoffman Product-E1_{CB} mechanism
(In E1_{CB} mechanism, carbanion
stability plays dominant role)

68.(A) (P)

In presence of strong base like EtO^-
and presence of β-hydrogen, E_2
elimination takes place

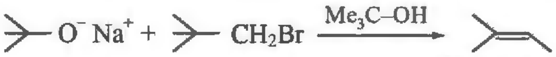
(Q)



$$Ph-\overset{O}{\overset{\|}{C}}-CH_2-Cl \xrightarrow{OH^-} Ph-\overset{O}{\overset{\|}{C}}-CH_2-OH$$

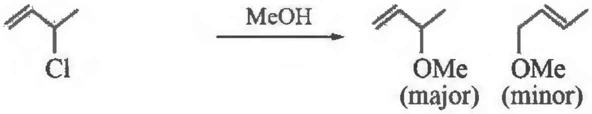
Because of absence of β-hydrogen,
and Cl being a good leaving group, S_N2
substitution takes place

(R)



Because of absence of β-hydrogen,
and presence of α–3° methyl group,
E1 elimination takes place.
(Proved by rearrangement)

(R)

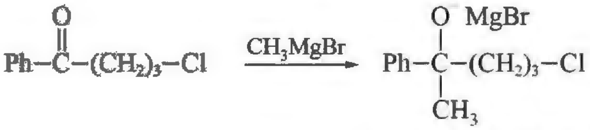


Because of stability of allylic carbocation
and Cl being a good leaving group,
S_N1 substitution takes place

69.(C) (P)

Because of 1°-halide group,
Nucleophillic substitution through S_N2
mechanism take place

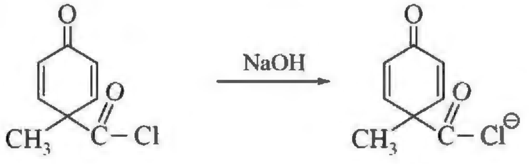
(Q)



$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-(CH_2)_3-Cl \xrightarrow{CH_3MgBr} Ph-\underset{\underset{CH_3}{|}}{\overset{\overset{O\ MgBr}{|}}{C}}-(CH_2)_3-Cl}$

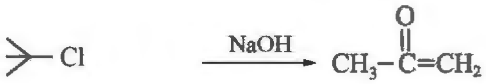
Nucleophillic addition of
Grignard reagent across a
carbonyl group

(R)



Nucleophillic acyl substitution of
acid chloride, in presence of base

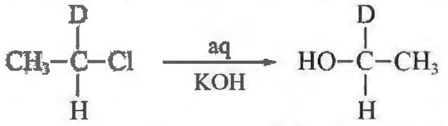
(S)



Because of 3° halide group,
Cl is a good leaving group, E1
elimination takes place via a 3°-carbocation

70. **[P – A, E] → [Q – B] → [R – C, E] → [S – D, E]**

(P)

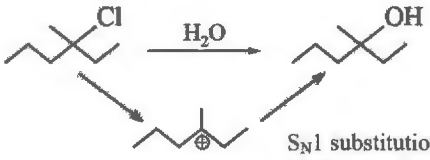


$\mathrm{CH_3-\underset{\underset{H}{|}}{\overset{\overset{D}{|}}{C}}-Cl \xrightarrow[KOH]{aq} HO-\underset{\underset{H}{|}}{\overset{\overset{D}{|}}{C}}-CH_3}$

S_N2 substitution, Inversion
because of Back-side attack

So, P → A, E

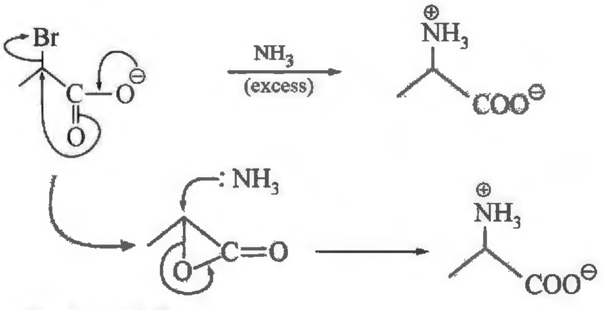
(Q)



S_N1 substitution, through
3°-Carbocation, which is planar.
So, Recemization takes place.

So, Q → B

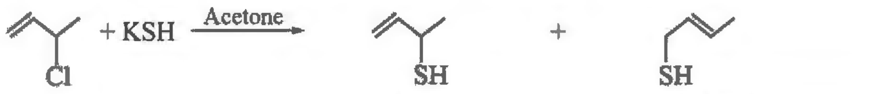
(R)



S_N2 substitution, through
NGP mechanism.
So, retention of configuration

So, R → C, E

(S)

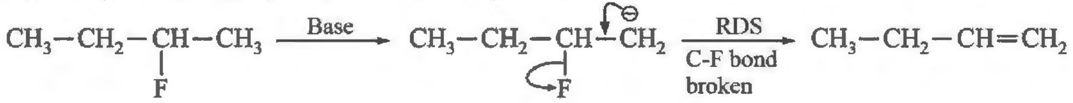


(Inversion product, through S_N2 mechanism) (Optically inactive product, because of allylic rearrangement)

So, S → D, E

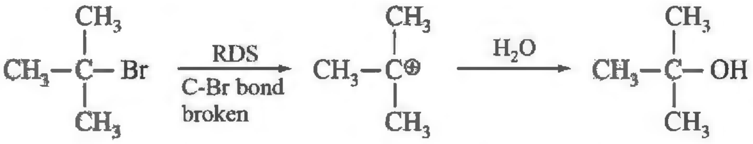
71. **[P – A, B, C, D] → [Q – C, D] → [R – A, B, C, E] → [S – A]**

(P)



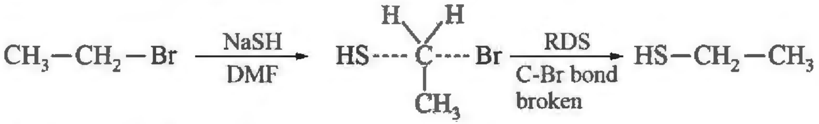
$$CH_3-CH_2-\underset{F}{CH}-CH_3 \xrightarrow{Base} CH_3-CH_2-\underset{F}{CH}-\overset{\ominus}{C}H_2 \xrightarrow[\text{C-F bond broken}]{RDS} CH_3-CH_2-CH=CH_2$$

S_N1 mechanism :



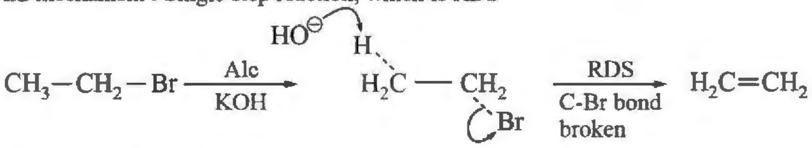
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[\text{C-Br bond broken}]{RDS} CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

S_N2 mechanism : Single step reaction, which is RDS



$$CH_3-CH_2-Br \xrightarrow[DMF]{NaSH} HS\cdots\underset{CH_3}{\overset{H\ \ H}{C}}\cdots Br \xrightarrow[\text{C-Br bond broken}]{RDS} HS-CH_2-CH_3$$

E2 mechanism : Single step reaction, which is RDS



$$CH_3-CH_2-Br \xrightarrow[KOH]{Alc} \overset{HO^{\ominus}\ \ H}{H_2C}-\underset{Br}{CH_2} \xrightarrow[\text{C-Br bond broken}]{RDS} H_2C=CH_2$$

So, P → A, B, C, D

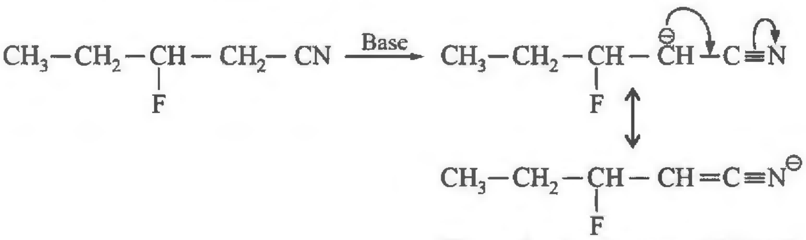
(Q) Due to EWG at β-position, in case of E2 mechanism, $\beta-H$ becomes more acidic and incase of S_N2 mechanism, it makes $\alpha-C$ more electrophilic So, $Q \rightarrow C, D$

(R) $\frac{K_H}{K_D}=1$, when C–H bond is not breaking in the RDS step. In such cases, kinetic Isotope effect is absent.

In El_{CB} mechanism, S_N2 mechanism → no. C–H bond breaks in RDS step, but in E2 mechanism α C – H bond breaks in RDS step.

In S_N1 mechanism no C–H bond breaking in RDS step. So, $\frac{K_H}{K_D} \approx 1$ So, $R \rightarrow$ A, B, C, E

(S) In El_{CB} mechanism,

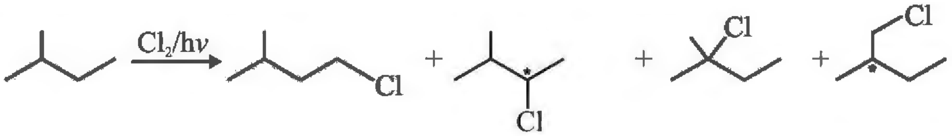


$$CH_3-CH_2-\underset{F}{CH}-CH_2-CN \xrightarrow{Base} CH_3-CH_2-\underset{F}{CH}-\overset{\ominus}{C}H-C\equiv N \leftrightarrow CH_3-CH_2-\underset{F}{CH}-CH=C\equiv N^{\ominus}$$

(So, carbanion is more stabilized)

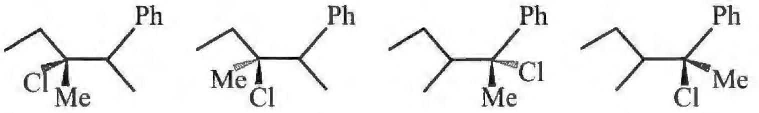
So, formation of carbanion in step – I is highly favored, which favors product formation in El_{CB} mechanism

72.(4)



(d + *l*) (optically active) (d + *l*) (optically active)

73.(4)

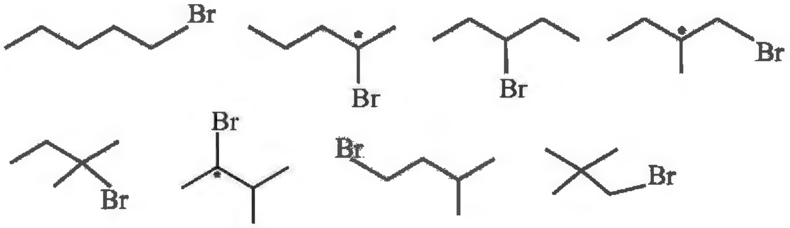


74.(9) Compounds 1, 2, 5, 6, 8, 9, 10, 11 and 12 will undergo reaction by S_N2 pathway.

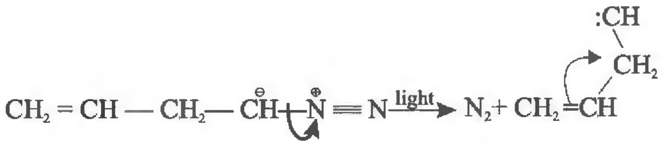
1° allylic, 1° benzylic halides and $\alpha-$halo ketones undergo reaction by S_N2 mode.

75.(6) Aryl halides with more electron withdrawing groups at ortho and para positions are more susceptible to bimolecular S_NAr reaction. Therefore, compound 6 is most reactive.

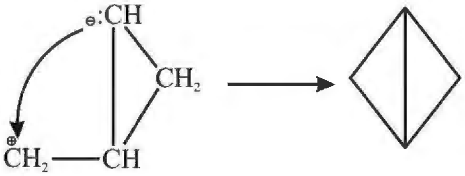
76.(6)



77.(9)



$CH_2=CH-CH_2-\overset{\ominus}{C}H-\overset{\oplus}{N}\equiv N \xrightarrow{\text{light}} N_2 + CH_2=CH-CH_2-\ddot{C}H$



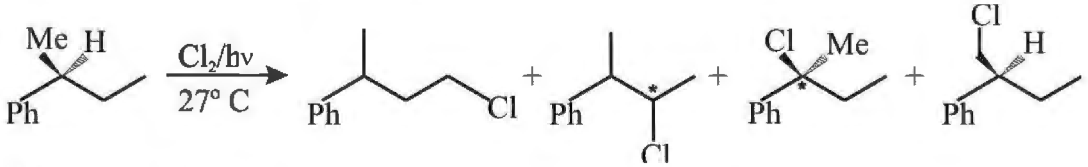
Molar mass = 54

$\therefore \quad x+y=5+4=9$

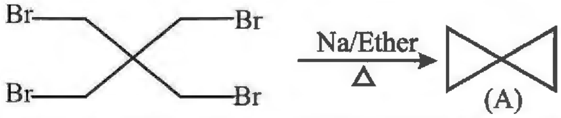
78.(6) Compounds 5, 8, 9 form same products by S_N1 and S_N2 mechanism while compound 11 reacts by S_N2 mechanism only, 6, 7 react by S_N1 only.

79.(5) In reaction no. 1, 2, 5, 8, and 10, the rate of reaction increases with increase in concentration of nucleophile.

80.(6)

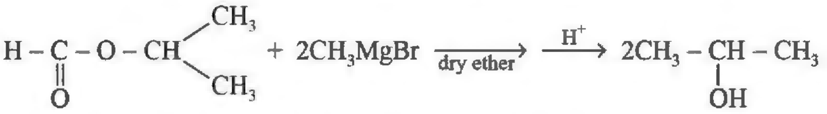


81.(2)



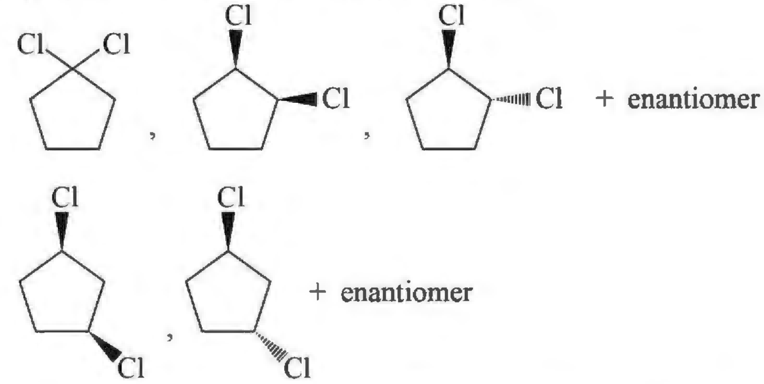
The product has 2 rings, so degree of unsaturation in (A) is 2.

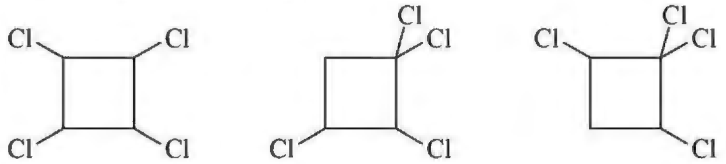
82.(8) $CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$

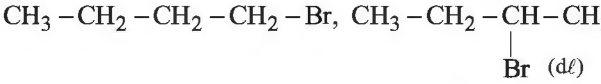
83.(1) 

$$\mathrm{H-\underset{\underset{O}{\|}}{C}-O-CH\begin{matrix}CH_3\\CH_3\end{matrix} + 2CH_3MgBr \xrightarrow[\text{dry ether}]{} \xrightarrow{H^+} 2CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$

Principal chain of ester contains only one carbon atom.

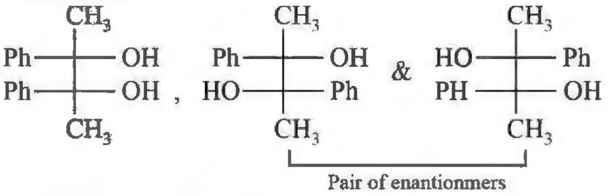
84.(7) 

85.(3) 

86.(3) 

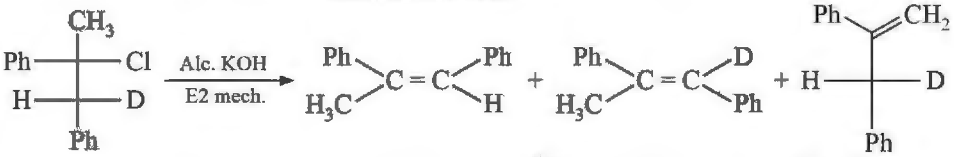
$$\mathrm{CH_3-CH_2-CH_2-CH_2-Br,\ CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3}\ (d\ell)$$

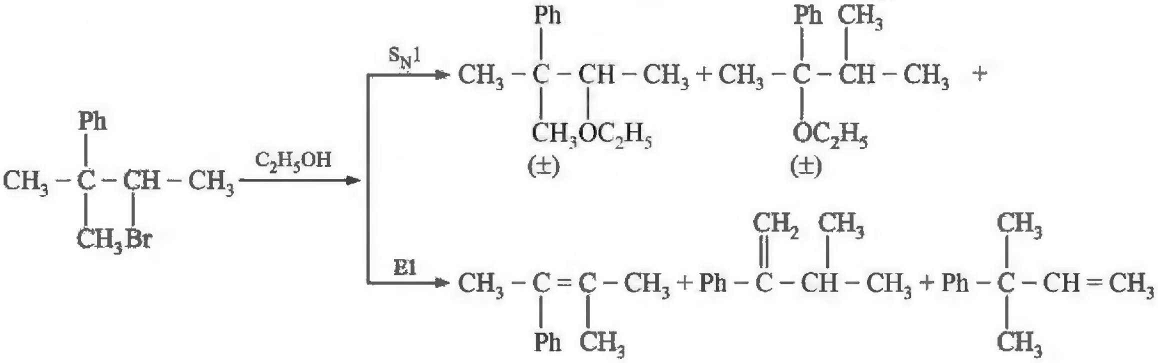
87.(9) Intermediate is tert-butyl carbocation $(CH_3)_3\overset{+}{C}$ and total nine hyperconjugative H-atoms are present in this intermediate.

88.(32) 

Total number of products = 3

Total number of fractions = 2

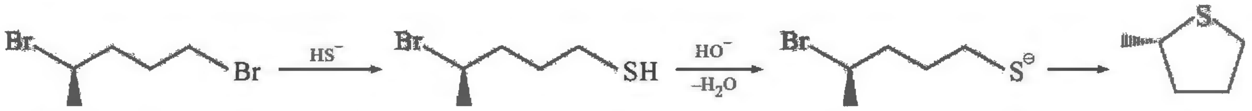
89.(3) 

90.(43) 

91.(31)

92.(8)

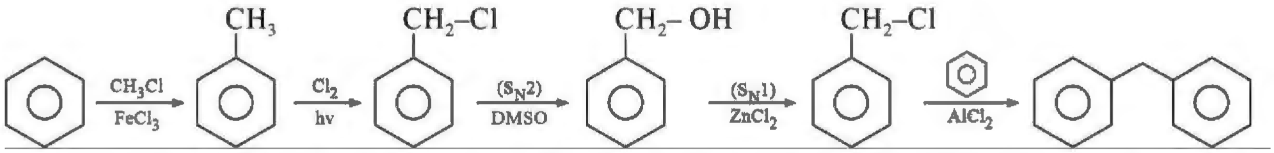
93.(31.37%)



94.(8) All these reactions are correct with respect to product and mechanism of reaction.

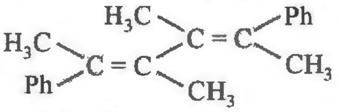
95.(4) 1, 4, 7, 9 proceed by S_N1 pathway. **96.(8)** All are correct. **97.(8)** All are correct.

98.(2)



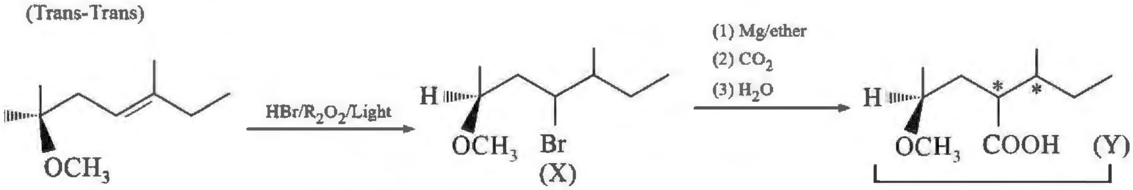
99.(3) Rearrangement of carbon skeleton of substrate is possible when carbocation intermediate is formed. This is possible in. Electrophilic addition on alkenes, S_N1, E1

100.(1) Only one product (single stereoisomers)



(Trans-Trans)

101.(4)

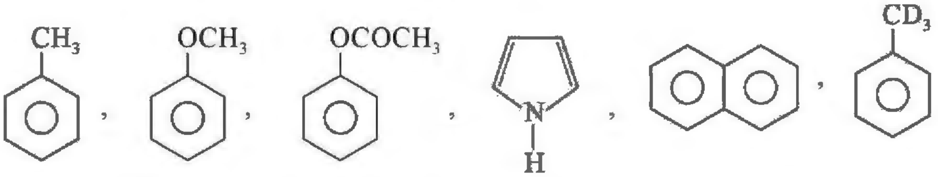


$Z = 4 \xleftarrow{\text{fractional distillation}}$

S R R
S R S
S S R
S S S

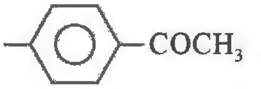
All diastereomers

102.(6)



are more reactive than benzene towards nitration.

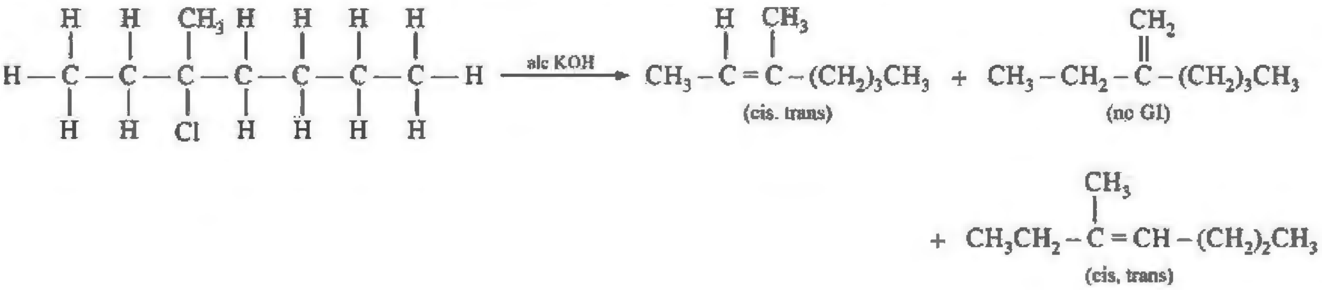
103.(6)



, $-\overset{O}{\overset{\|}{C}}-O-CH_3$, $-CN$, $-NO_2$, $-\overset{\oplus}{N}\equiv N:$, $-CH=CH-CHO$ show –M effect.

104.(3) **105.(5)** 5(i, iii, iv, v, vii)

106.(4) Presence of electron releasing group activate alkene for electrophilic addition reaction. **107.(5)**

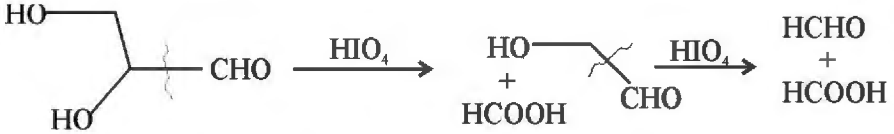


$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-(CH_2)_4CH_3 \xrightarrow{\text{alc KOH}} CH_3-\overset{H}{C}=\overset{CH_3}{C}-(CH_2)_3CH_3 + CH_3-CH_2-\overset{CH_2}{\overset{\|}{C}}-(CH_2)_3CH_3 + CH_3CH_2-\overset{CH_3}{C}=CH-(CH_2)_2CH_3$$

Oxygen Containing Organic Compounds-I

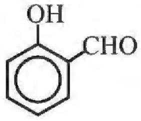
1.(A) Conjugated isomer is more stable than the non-conjugated; out of these trans isomer is more stable. Hence option (a) is the major product.

2.(A)



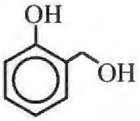
3.(D) At every step with one mole HIO_4 carry out cleavage of carbon-carbon bond with one step up oxidation.

4.(C) X =

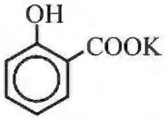


Reimer-Tiemann product

Y =

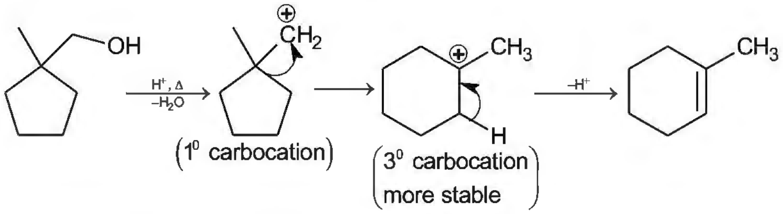


Z =



Cannizzaro reaction product

5.(C)

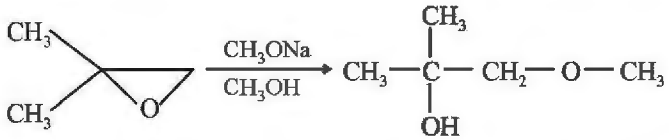


6.(C) Here the oxygen containing ring act as a –OR group. It activates the benzene ring thereby the positions ortho and para w.r.t. O are more electron rich than the position meta w.r.t. O. Hence both ortho & para w.r.t. O would attacked by electrophile.

7.(B) It is S_N2 reaction

$$(CH_3)CO^- + C_6H_5-\overset{+\delta}{C}H_2-\overset{-\delta}{Cl} \rightarrow (CH_3)_3CO-CH_2C_6H_5$$

8.(A)



In base catalyzed ring opening nucleophile attacks on less substituted carbon.

9.(D) Iodoform reaction.

10.(ABD) $C_2H_5Br \xrightarrow{KOH} C_2H_5OH \xrightarrow{X_2} CH_3-CHO \xrightarrow[OH^-]{X_2} CX_3-CHO \xrightarrow{OH^-} CX_3^- +$

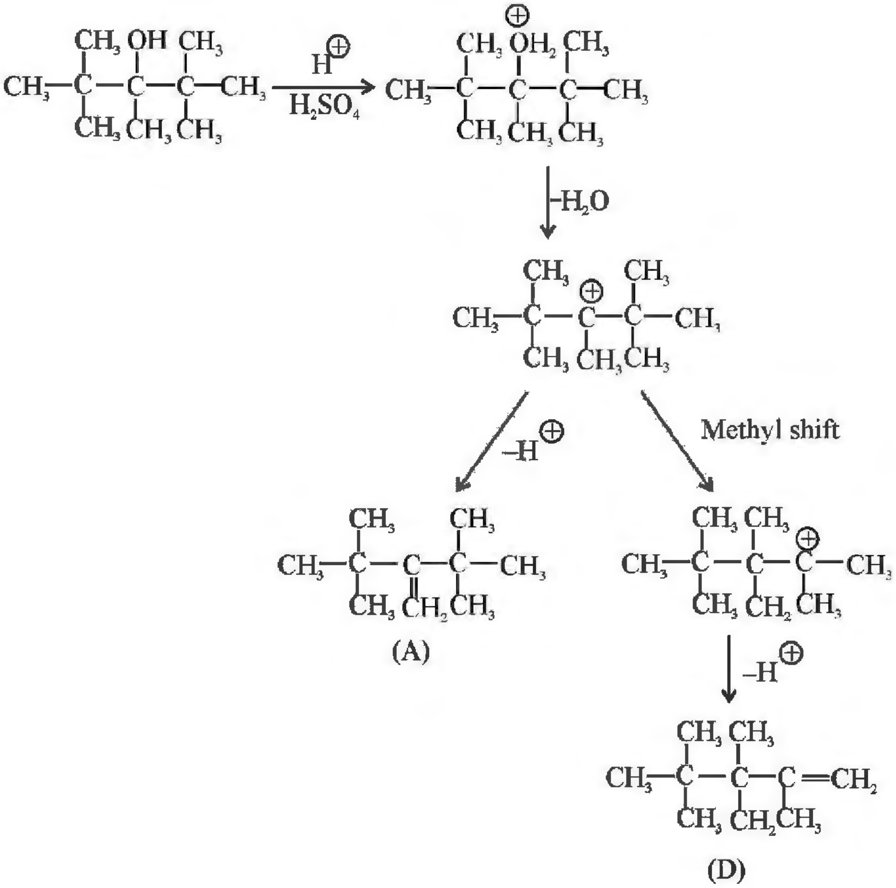
$+HCOOH \longrightarrow CHX_3 + HCOO^-$

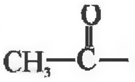
A, B, D ⟶ also gives haloform reaction

11.(AC) Tert. alkyl halides and aryl halides do not undergo Williamson synthesis

12.(ABC) Aryl halides do not undergo nucleophilic substitution.

13.(AD)



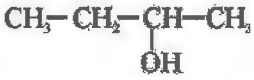
14.(ABCD) All compounds with  $CH_3-\overset{O}{\overset{\|}{C}}-$ group give haloform test.

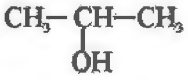
15.(CD) Alkyl halides give elimination reaction

16.(ABC) $FeCl_3$ solution is used to test phenol.

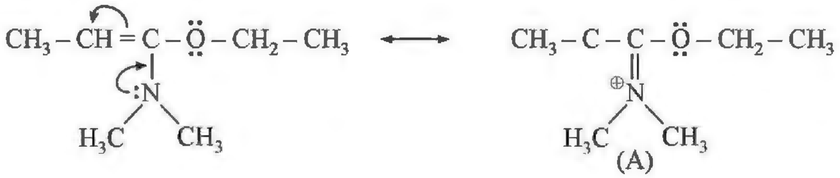
17.(AB) In option (C) and (D) ethene is formed as the major product.

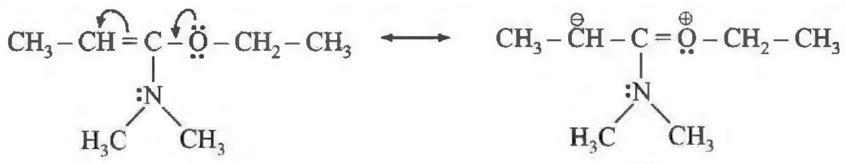
18.(CD) (A) and (B) carry out syn-hydroxylation, (C) and (D) carry out anti hydroxylation.

19.(AB) (C) forms  $CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

(D) forms  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$

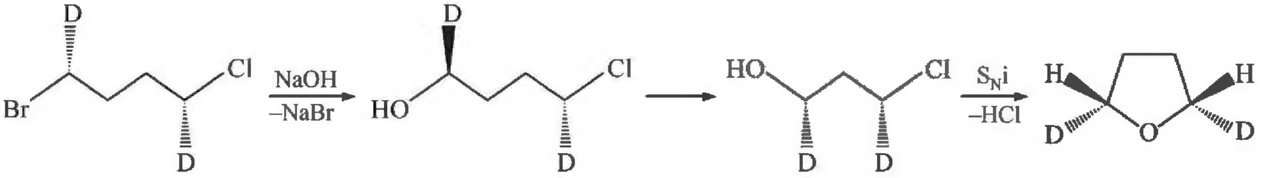
20.(AB)



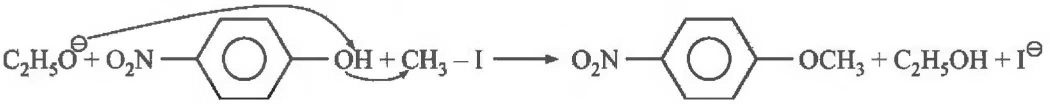


(B)

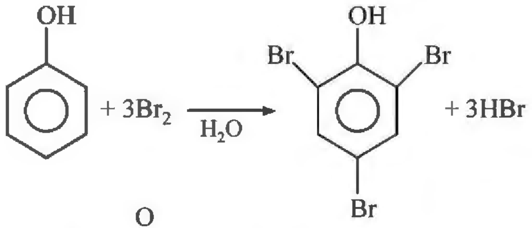
21.(BC) Bromide ion is better leaving group than chloride ion. Compound X is formed by S_N2 reaction mechanism while Y is formed by intramolecular S_N2 reaction mechanism.

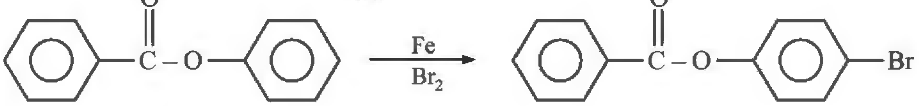


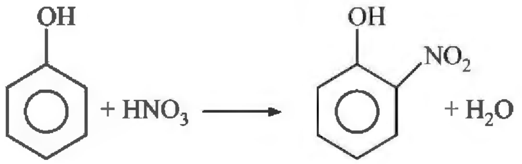
22.(AB) $C_2H_5O^{\ominus} + CH_3I \longrightarrow C_2H_5OCH_3 + I^{\ominus}$



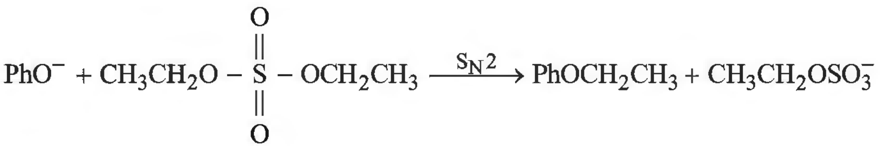
23.(ABD)







PhOH + NaOH ⟶ PhONa



$$PhO^- + CH_3CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OCH_2CH_3 \xrightarrow{S_N2} PhOCH_2CH_3 + CH_3CH_2OSO_3^-$$

24.(ABCD)

(A) Electrophilic attack of D^+ on strongly activated benzene

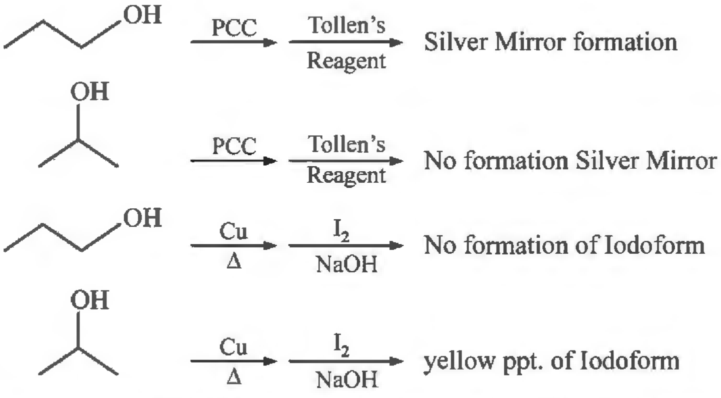
(B) It is diazocoupling reaction and it is an example of electrophilic substitution reaction.

(C) Desulphonation is also an electrophilic substitution reaction. In this reaction attacking electrophile is H^+ ion and leaving group is SO_3

(D) CO_2 acts as electrophile. Kolbe – Schmidt reaction of sodium phenoxide with CO_2 is an electrophilic substitution reaction.

25.(AD) X and Y are monosubstituted benzene containing chiral carbon atom. Also contain primary or secondary alcoholic OH group.

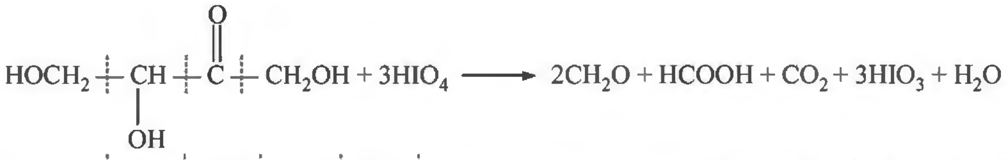
26.(BC)



Both 1-propanol and 2-propanol are oxidized by $KMnO_4$. Reaction with conc. H_2SO_4 form 1-propene and further there is no reaction of propene with Fehling's solution.

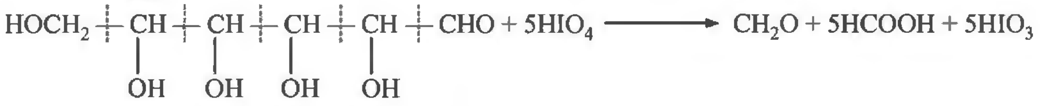
27.(ACD)

(A)



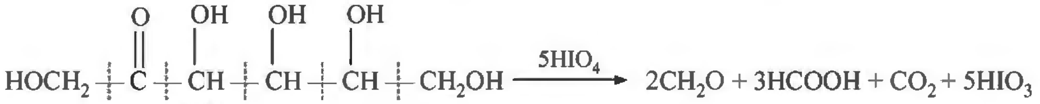
$$HOCH_2-\underset{OH}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2OH + 3HIO_4 \longrightarrow 2CH_2O + HCOOH + CO_2 + 3HIO_3 + H_2O$$

(B)



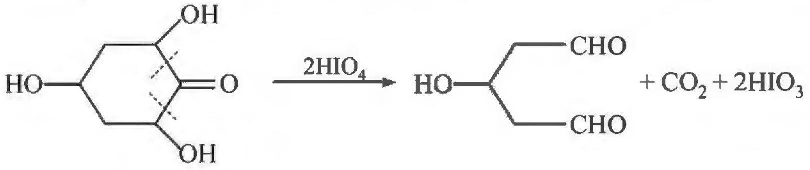
$$HOCH_2-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CHO + 5HIO_4 \longrightarrow CH_2O + 5HCOOH + 5HIO_3$$

(C)

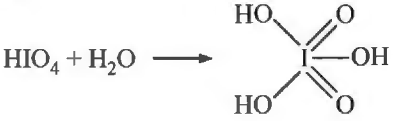


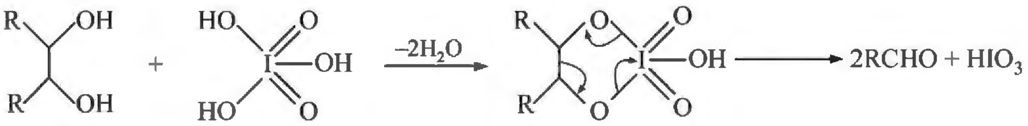
$$HOCH_2-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-CH_2OH \xrightarrow{5HIO_4} 2CH_2O + 3HCOOH + CO_2 + 5HIO_3$$

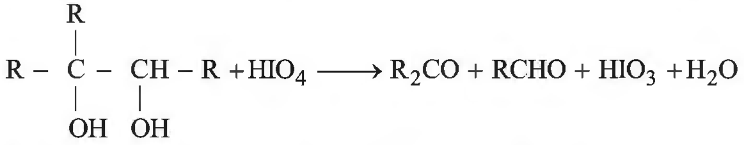
(D)



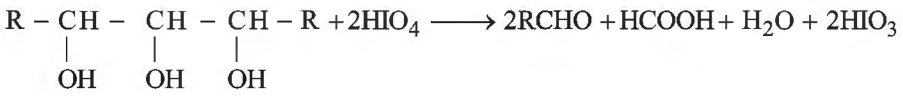
28.(ABCD)







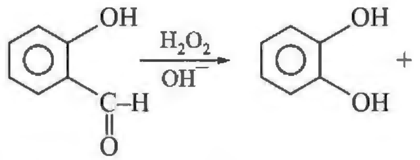
$$R-\underset{OH}{\underset{|}{\overset{R}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-R + HIO_4 \longrightarrow R_2CO + RCHO + HIO_3 + H_2O$$



$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R + 2HIO_4 \longrightarrow 2RCHO + HCOOH + H_2O + 2HIO_3$$

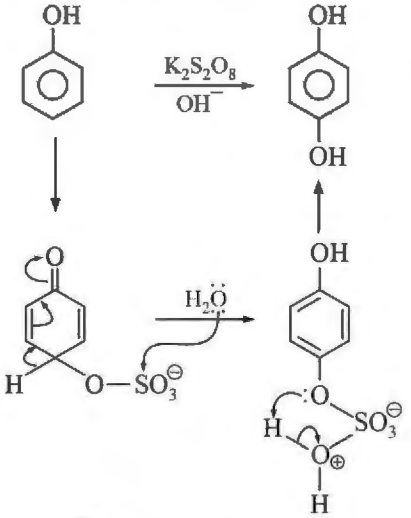
29. **[A-p] → [B-r] → [C-s] → [D-q]**

(A)



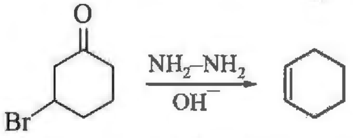
+ $HCOO^-$: Dakin Oxidation

(B)



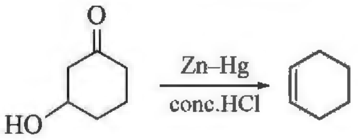
: Elb's: Persulphate Oxidation

(C)



This involves Wolf-kishner reduction along with dehydrohalogenation in presence of base

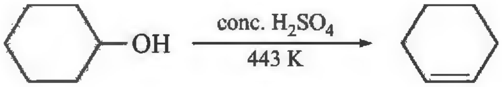
(D)



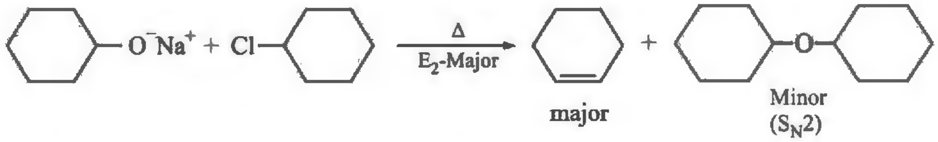
This reaction involves Clemmensen reduction along with dehydration in presence of concentrated hydrochloric acid.

30. **[A-r] → [B-r, q] → [C-p] → [D-s]**

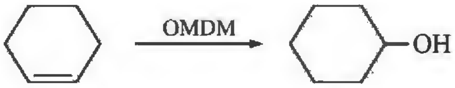
(A)



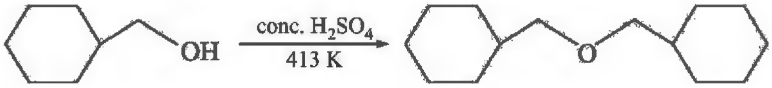
(B)



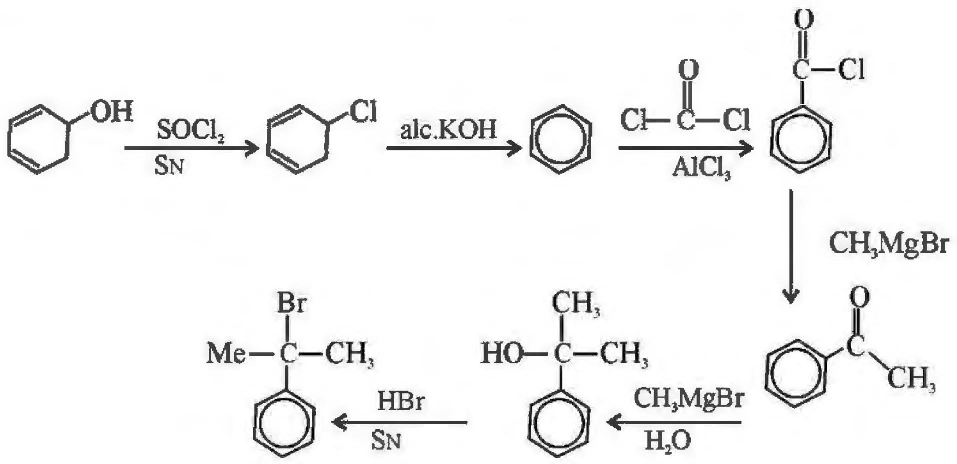
(C)



(D)

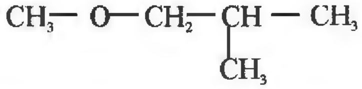


31.(3)

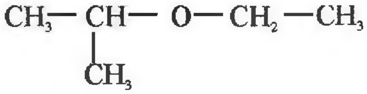


32.(6)

$CH_3-CH_2-CH_2-CH_2-O-CH_3$

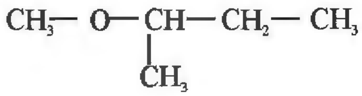


$CH_3-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

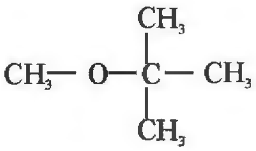


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_2-CH_3$

$CH_3-CH_2-CH_2-O-CH_2-CH_3$



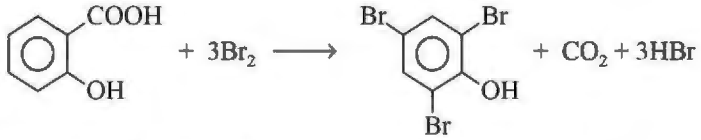
$CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$



$CH_3-O-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

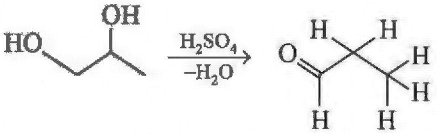
33.(9) It is Reimer-Tiemann reaction and attacking reactive species of this reaction is dichloro carbene, $CCl_2\left(:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}-\overset{\cdot\cdot}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\right)$. It is electron deficient having three electron pairs on each atom.

34.(9) Salicylic acid on reaction with Br_2 water undergo bromination cum decarboxylation. Product [P] is 2, 4, 6-tribromophenol.



Mole of Br_2 used = $3\times$ moles of salicylic acid taken.

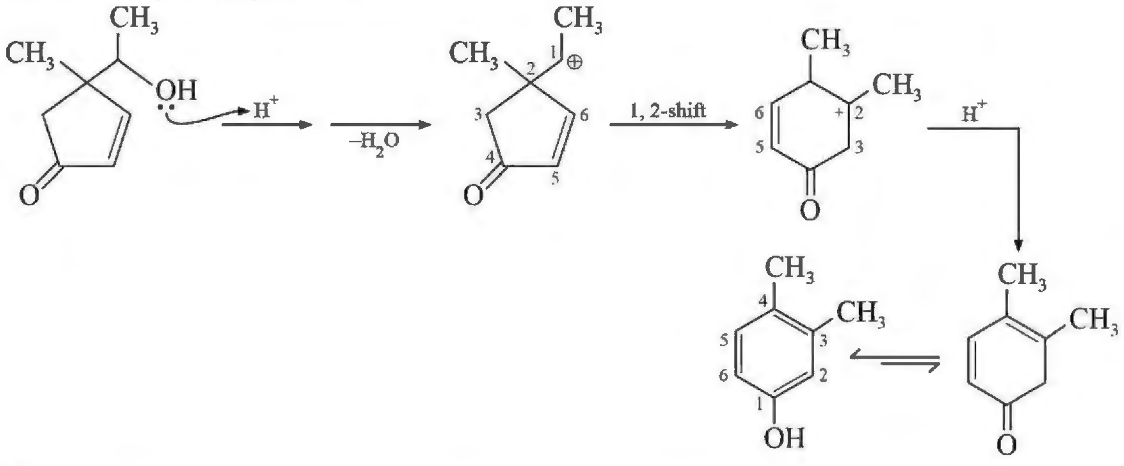
35.(9) It is pinacol-pinacolone type rearrangement



C – H σ-bonds = 6
C – C σ-bonds = 2
C – O σ-bonds = 1

36.(1) PCC can oxidise only primary and secondary alcohols. It can't oxidise tertiary alcohol. Only one tertiary alcohol is possible for molecular formula $C_5H_{12}O$ i.e., 

37.(8) It is acid catalyzed dehydration of alcohol.

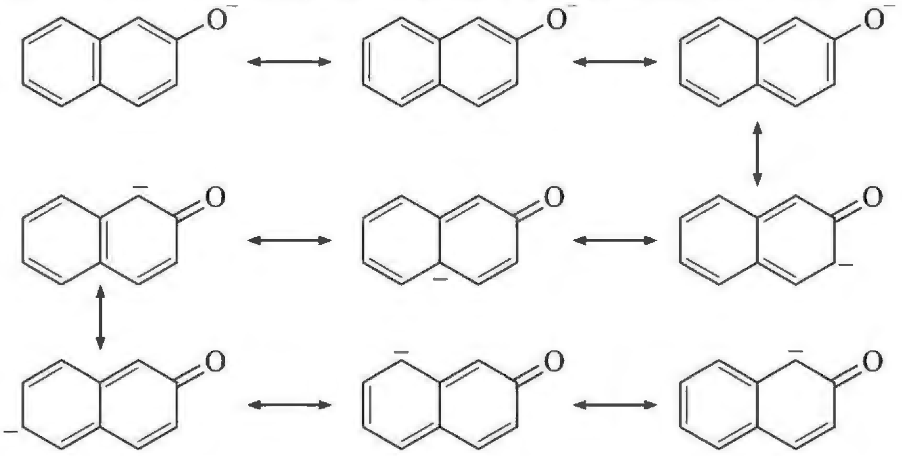


Note:

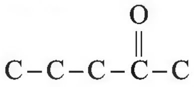
(1) Migratory aptitude of vinyl group is more than that of methyl.

(2) Enolic form having aromatic character is more stable than keto form.

38.(9)

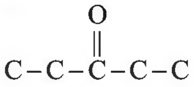


39.(3) **(i)**



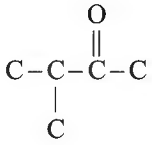
$\mathrm{C-C-C-\overset{O}{\overset{\|}{C}}-C}$

(ii)



$\mathrm{C-C-\overset{O}{\overset{\|}{C}}-C-C}$

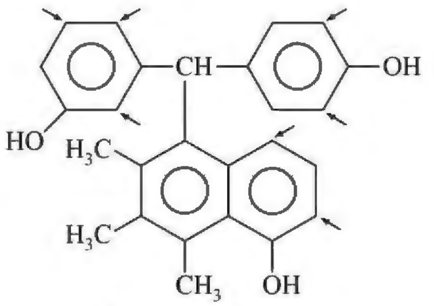
(iii)



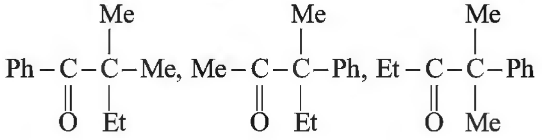
$\mathrm{C-\underset{C}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-C}$

40.(2) (p & v)

41.(7)

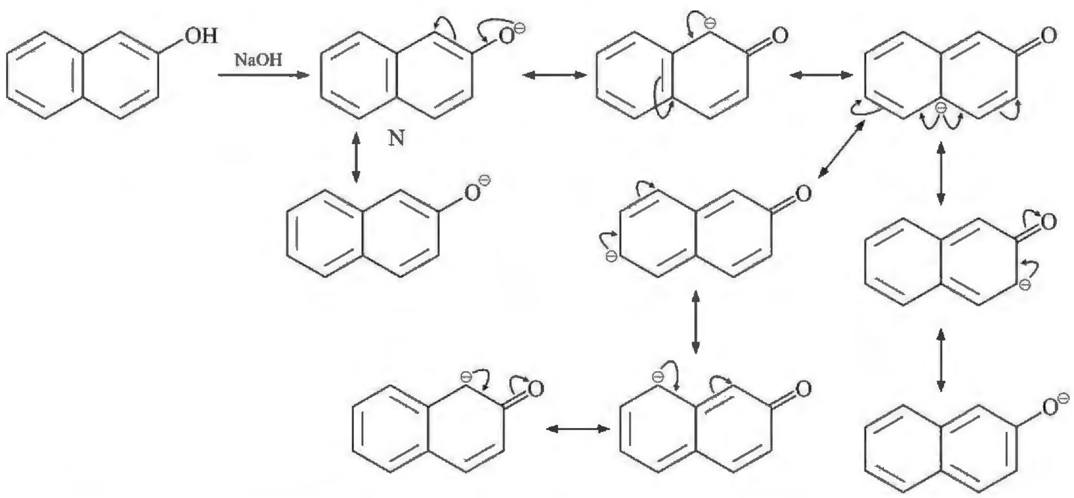


42.(3)

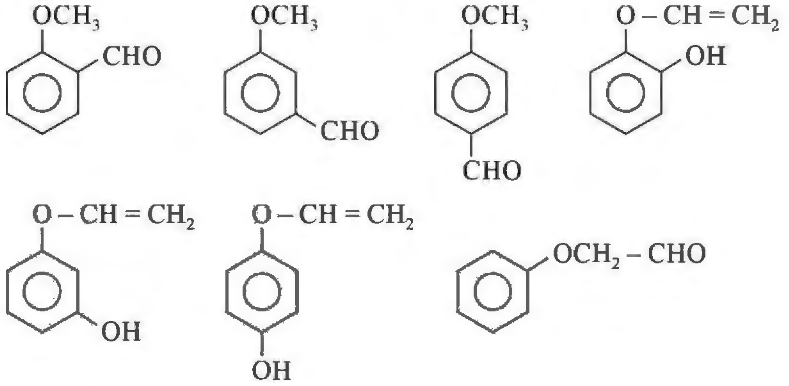


$\mathrm{Ph-\underset{O}{\underset{\|}{C}}-\overset{Me}{\overset{|}{\underset{Et}{\underset{|}{C}}}}-Me,\ Me-\underset{O}{\underset{\|}{C}}-\overset{Me}{\overset{|}{\underset{Et}{\underset{|}{C}}}}-Ph,\ Et-\underset{O}{\underset{\|}{C}}-\overset{Me}{\overset{|}{\underset{Me}{\underset{|}{C}}}}-Ph}$

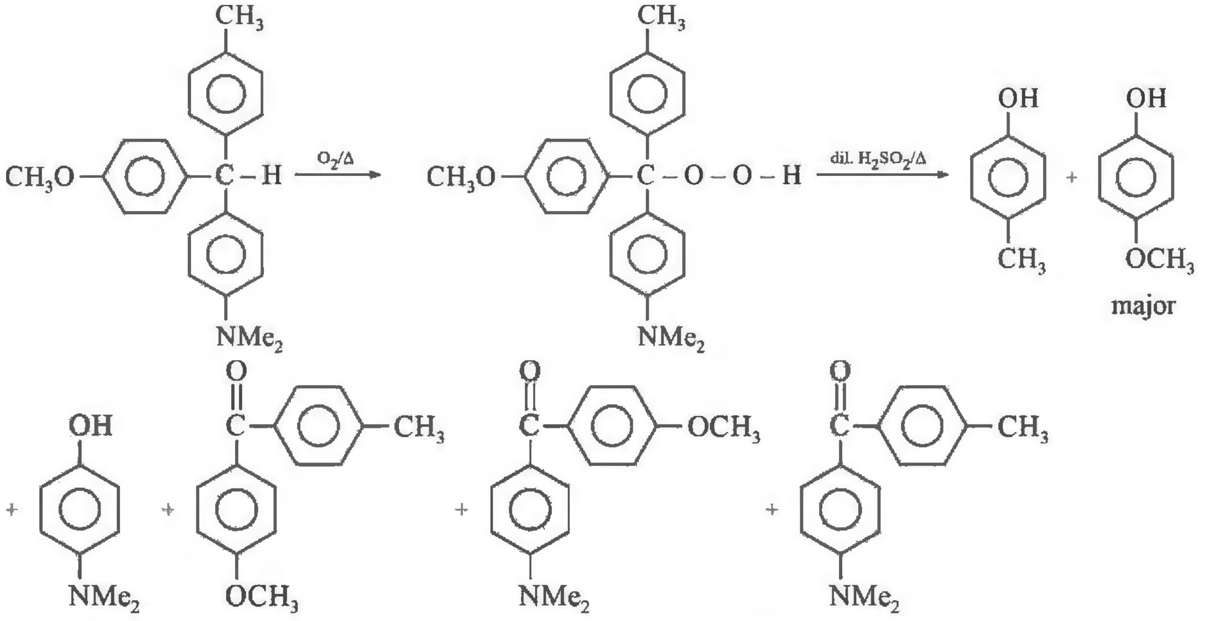
43.(9)



44.(16)



45.(06)



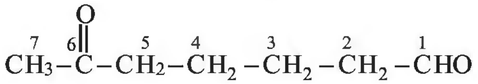
[Total product 6]

46.(05) $R-\underset{\underset{O}{\|}}{C}-O$ produces red coloration with neutral $FeCl_3$ (tested in inorganic Qual. Analysis as well) while phenolic

^-OH group produces violet coloration with neutral $FeCl_3$

Oxygen Containing Organic Compounds-II

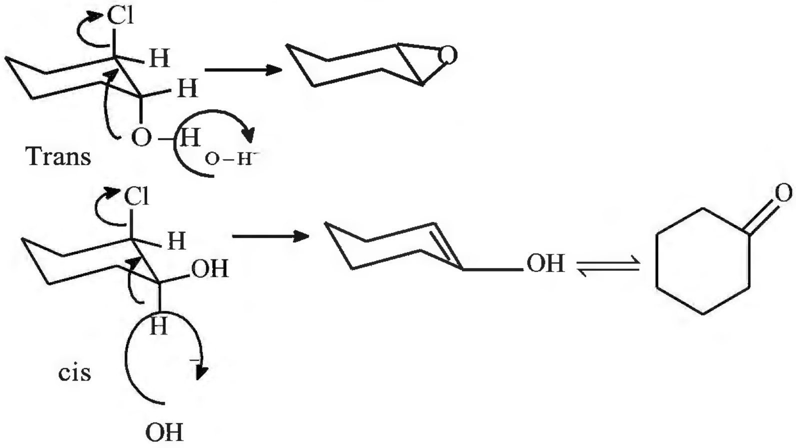
1.(D)



$$\overset{7}{C}H_3-\overset{6}{\overset{O}{\overset{\|}{C}}}-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}HO$$

During addition of NaOH, firstly carbanion is generated from the said compound, and that will attack $-C=O$ group internally. Carbanion from C–2 can attack carbonyl group at C–6 to give option (A). Similarly carbanion from C–7 and C–5 can attack carbonyl group of C–1 to give option (B) and (C) respectively. So (D) cannot be formed.

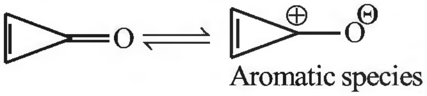
2.(A)



3.(D) Use stoichiometry of reaction.

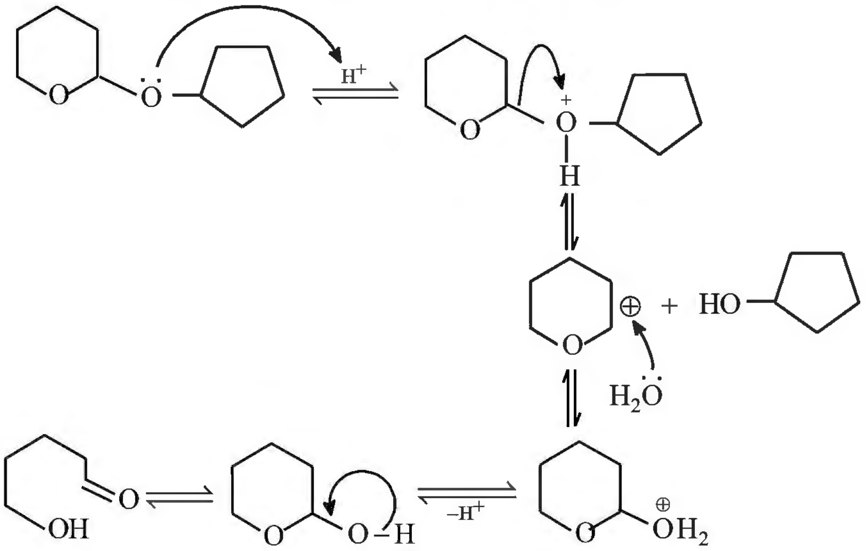
4.(B) Sterically hindered ketonic group cannot react with glycol.

5.(A) Since (A) exist as aromatic species so would have highest dipole moment.

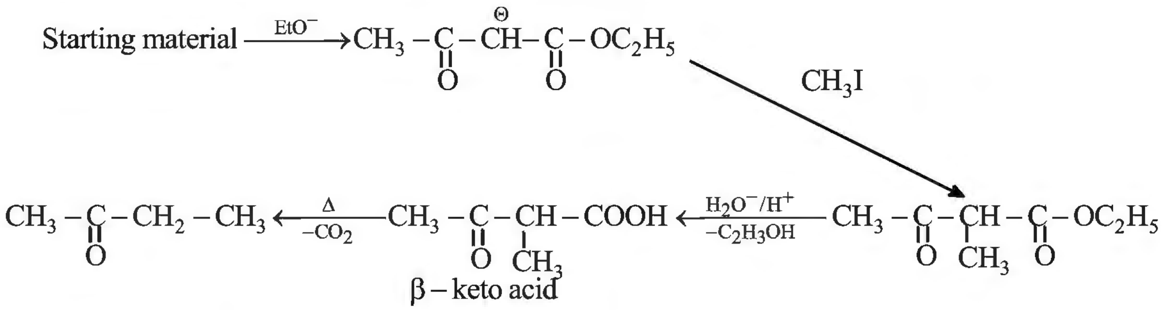


6.(A) Hydrolysis of (I) will give $CH_2=\overset{OH}{\overset{|}{C}}-CH_3$ which on tautomerism give CH_3COCH_3 whereas hydrolysis of (II) will give CH_3-CH_2-CHO. Acetone and propanal can be distinguished by Fehling, Benedict and Tollen's reagent whereas Brady's reagent react with both.

7.(C) Starting compound is acetal which on hydrolysis will give aldehyde or ketone

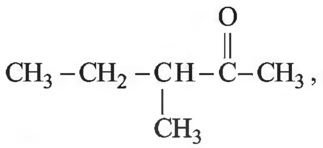


8.(A)



$$\text{Starting material} \xrightarrow{EtO^-} CH_3-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{C}H-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{CH_3I} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}H-\underset{\underset{O}{\|}}{C}-OC_2H_5$$

$$\xrightarrow[-C_2H_5OH]{H_3O^+/H^+} \underset{\beta-\text{keto acid}}{CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}H-COOH} \xrightarrow[-CO_2]{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$



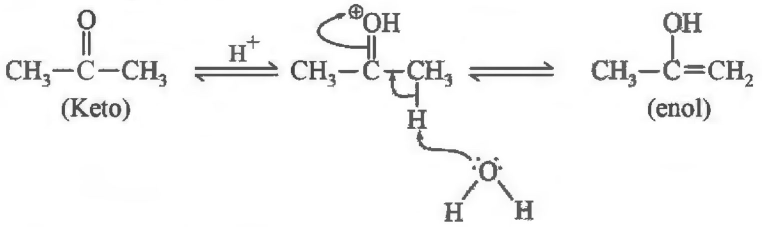
9.(B) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{O}{\|}}{C}-CH_3$, gives iodoform test and hydrazine test. In dil.alkaline medium, it would first make carbanion which on abstraction of proton will generate racemic mixture.

10.(B) Except (D), all compounds are optically active as they have one chiral carbon in them. (A) is ketone so wont give tollen test. Out of (B) and (C), (C) would undergo racemisation as α-H is attached to chiral carbon, which deprotonates first and then on protonation it result in racemisation So compound in bottle (Y) is B.

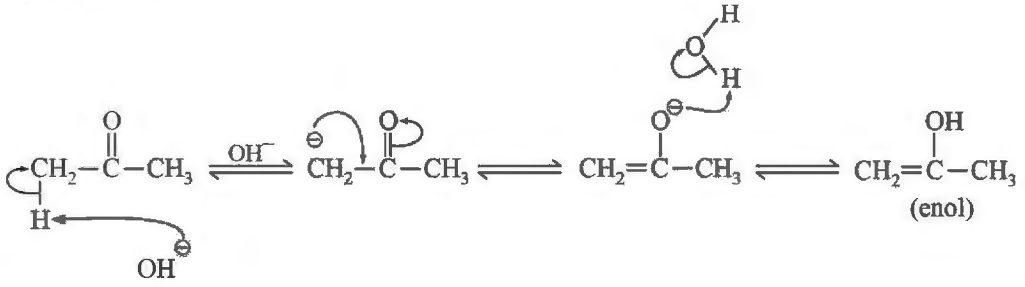
11.(ABCD) All are correct Statements.

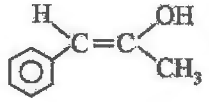
Generally enol is less stable than keto because $C=O$ bond energy is 799 kJ/mol, as against $C=C$ bond energy is 622 kJ/mol. So, $C=O$ bond is stronger then $C=C$ bond.

- Acid catalyzed tautomerism:

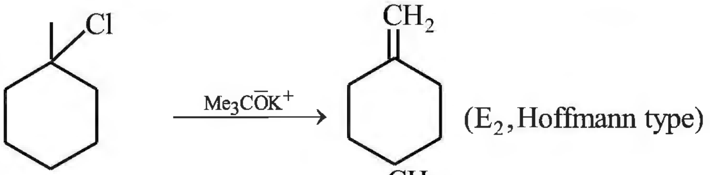


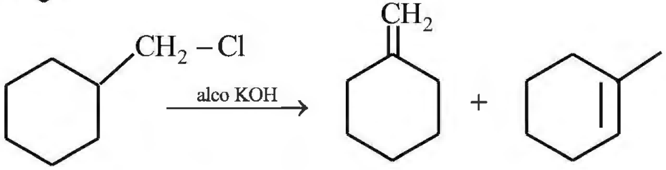
- Base catalyzed tautomerism:

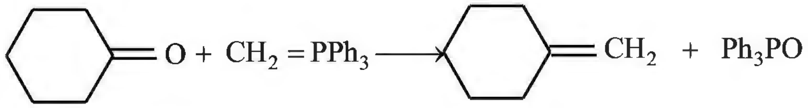


-  is stabilized by extended conjugation with Benzene ring.

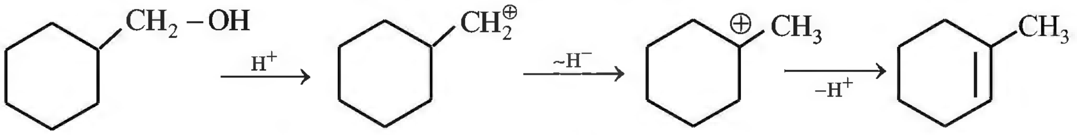
12.(ABC)



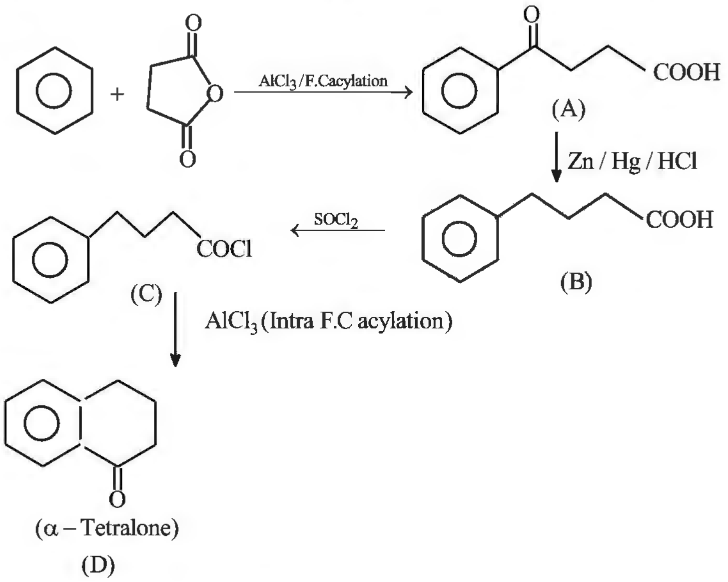




It is a wittig reaction



13.(ABCD)

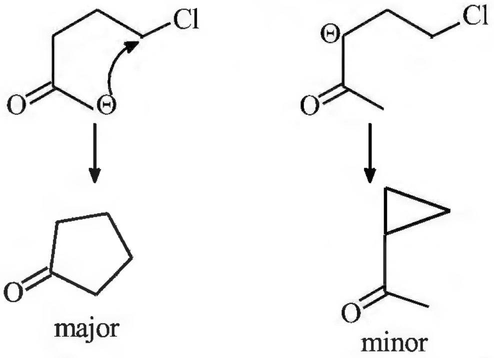


14.(ABC)

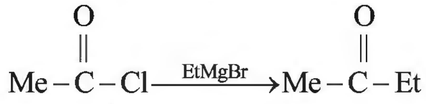
(A) $CH_3COCH_2CH_3$ in basic medium undergo kinetically controlled enolisation whereas in acidic medium it undergo thermodynamically controlled enolation.

(B) Perkin condensation

(C)



15.(BCD) All are correct statements:

- C–Mg bond is 35% Ionic, whereas C–Cu bond is 21% Ionic and C–Cd bond is 18% Ionic
- The reactivity of EtMgBr (Grignard Reagent) is more than Et_2Cd and Et_2CuLi (Gilman Reagent)
- 

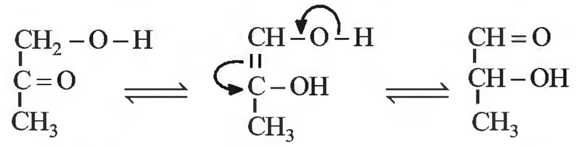
  $Me-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{EtMgBr} Me-\overset{O}{\overset{\|}{C}}-Et$: Nucleophillic Addition Elimination Reaction because Cl is a good leaving group.
- 

  $Me-\overset{O}{\overset{\|}{C}}-Et \xrightarrow{EtMgBr} Me-\underset{Et}{\overset{OMgBr}{C}}-Et$

  Nucleophillic Addition only because, alkyl is not good leaving group
- Ketones further react with RMgx to give 3° alcohols because they do not contain suitable leaving groups. So, they undergo Nucleophillic Addition rather than Nucleophillic substitution. [Although, it is true that ketones are more reactive to nucleophile than acid chlorides]

16.(ABC) $CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O$

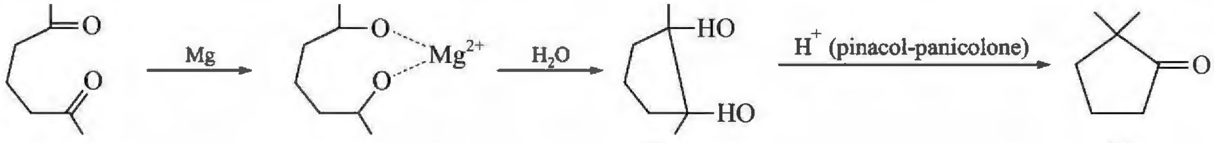
α- hydroxyl aldehyde undergo Tollen reagent test, as it rearranges to aldehyde as shown below:



α – hydroxy aldehyde

17.(AC) Carbonyl group of (A) is more electrophilic so $\overline{O}H$ will attack (A) rather than carbonyl group of (B). Therefore (A) would be hydride ion donar.

18.(BD)



(B) (C)

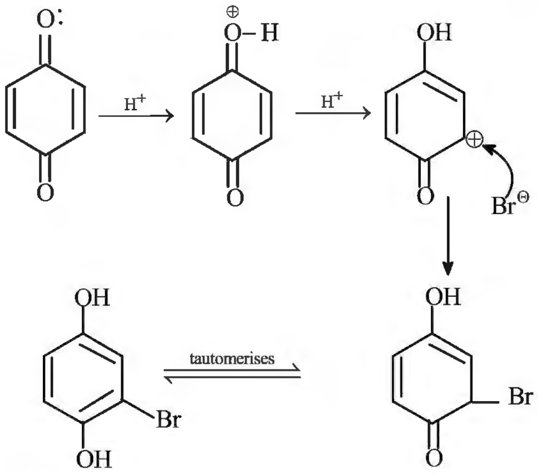
19.(ABCD) **(A)** Iodoform Reaction

(B) $HCOOH + 2Cu^{2+} + 4OH^- \rightarrow Cu_2O + CO_2\uparrow + 3H_2O$.

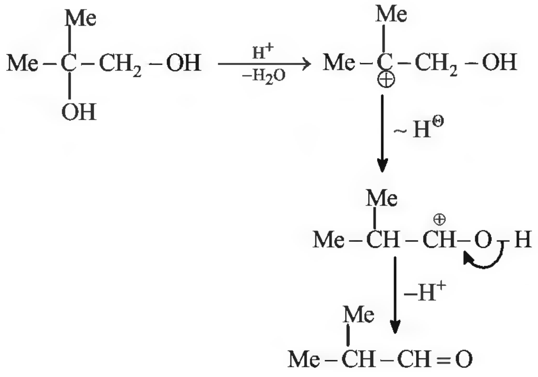
(C) and (D): SeO_2 convert methylene or methyl group adjacent to carbonyl group to carbonyl group and this reagent may be used for oxidation of allyllic carbon to carbonyl group.

20.(CD) Aldehyde give test with Tollen's regent where as ketones wont.DNP test is given by both aldehydes and ketones CH_3CO^- give iodoform test.

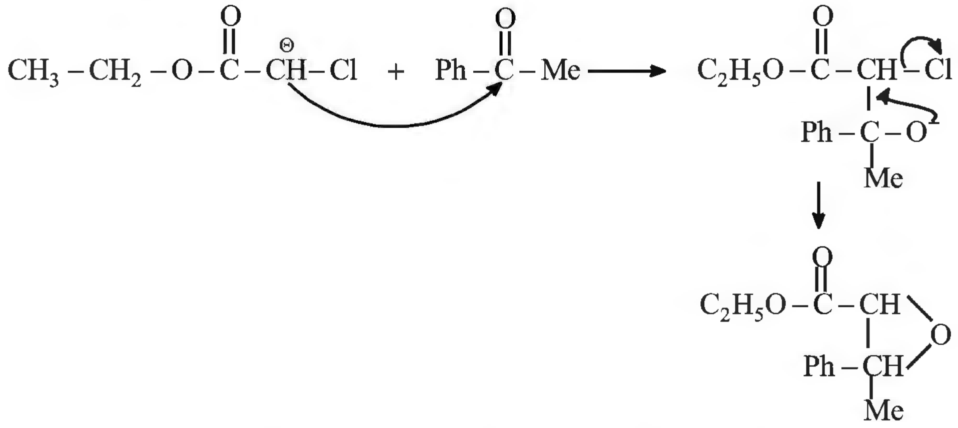
21.(ABC)



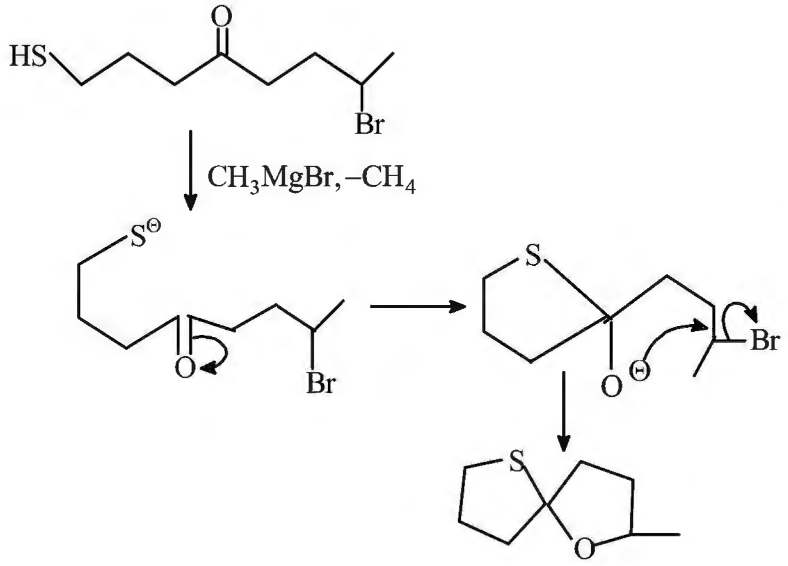
(B)

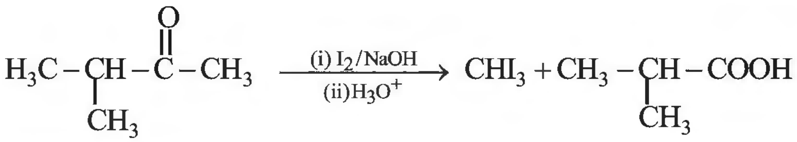


(C)



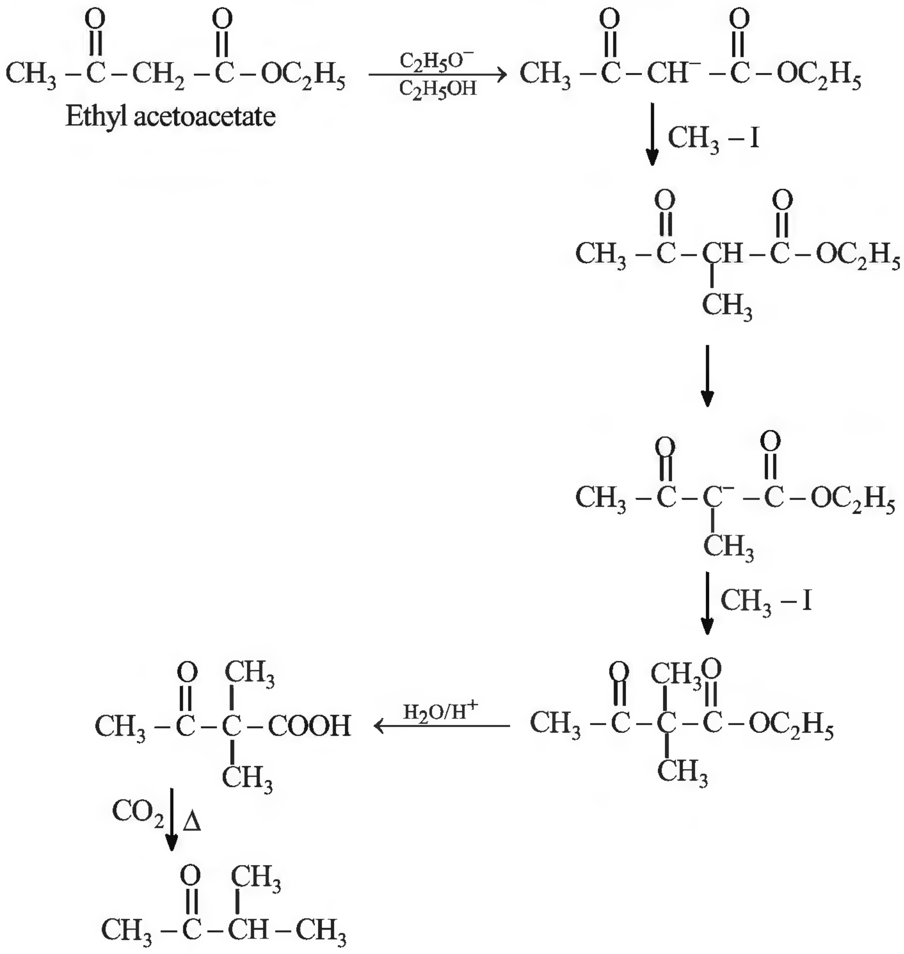
22.(BCD) It is Claisen condensation in which ester having α–H undergo self condensation in presence of strong base



23.(ABD) 

$$H_3C-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{(ii)}H_3O^+]{\text{(i) }I_2/NaOH} CHI_3+CH_3-\underset{CH_3}{CH}-COOH$$

(C) option is incorrect



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5O^-} CH_3-\overset{O}{\overset{\|}{C}}-CH^- -\overset{O}{\overset{\|}{C}}-OC_2H_5$$

Ethyl acetoacetate

$$\downarrow CH_3-I$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

$$\downarrow$$

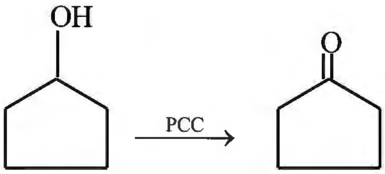
$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{C^-}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

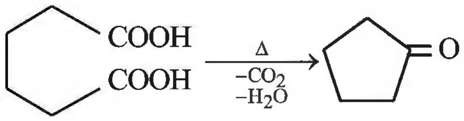
$$\downarrow CH_3-I$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{H_2O/H^+} CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-COOH$$

$$\downarrow CO_2\ \Delta$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{CH}-CH_3$$

24.(AB) (A) 

(B) 

(C) It is Rosenmumd's Reduction which give Pentanal

(D) It will give cyclopentylmethanol

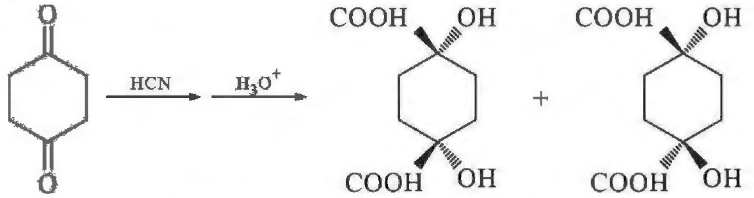
25.(BC) $HCHO \xrightarrow{NH_3} \text{Urotropine}$

$CH_3CHO \xrightarrow{NH_3} \text{Acetaldimine}$

$C_6H_5CHO \xrightarrow{NH_3} \text{Hydrobenzamide}$

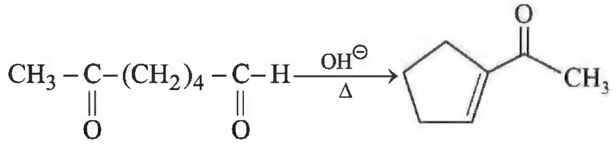
$\text{Acetone} \xrightarrow{NH_3} \text{Acetonediamine}$

26.(ABD)

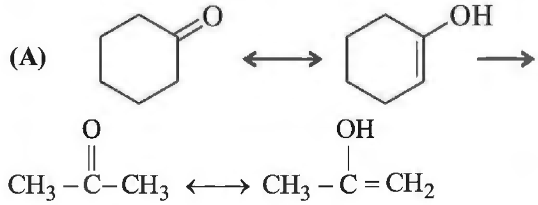


The products are optically inactive due to presence of plane of symmetry and G.I. (diastereomers) of the molecules exist.

27.(ABC)

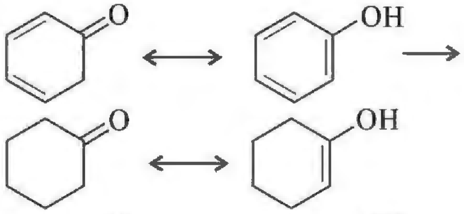


28.(ACD) (A)



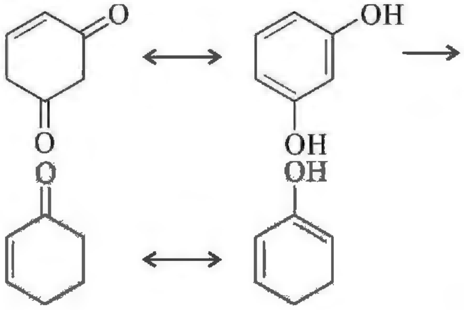
⟶ will form more substituted double bond so having mere enol content

(C)



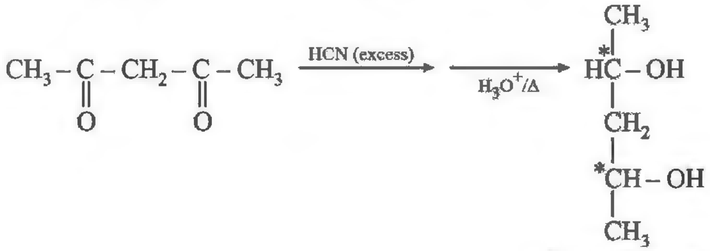
⟶ Benzene ring is more stable

(D)



⟶ Benzene ring is more stable

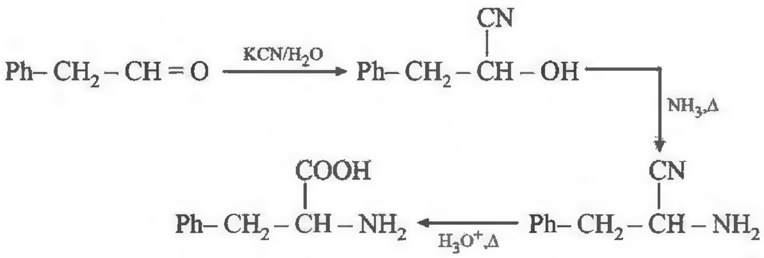
29.(BCD)



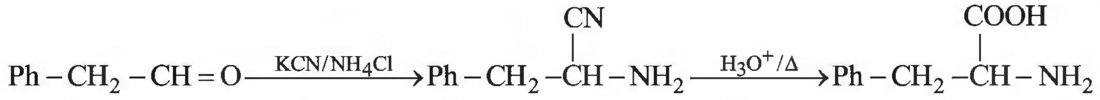
2 enantiomers + 1 meso

30.(ABC)

(A)

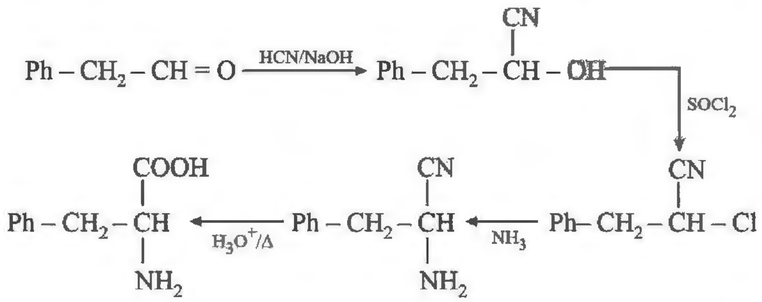


(B)



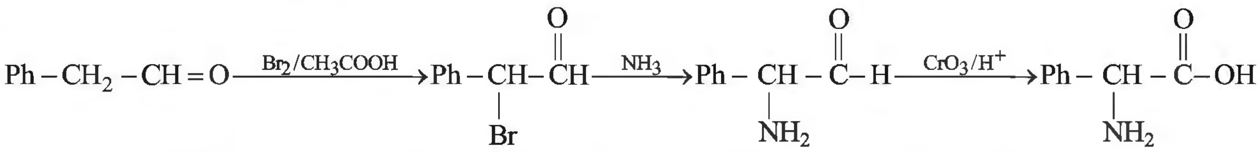
$$Ph-CH_2-CH=O\xrightarrow{KCN/NH_4Cl}Ph-CH_2-\overset{\overset{\large CN}{|}}{C}H-NH_2\xrightarrow{H_3O^+/\Delta}Ph-CH_2-\overset{\overset{\large COOH}{|}}{C}H-NH_2$$

(C)



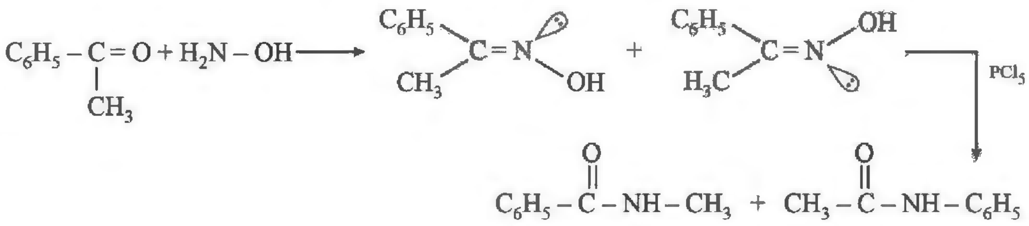
$$Ph-CH_2-CH=O\xrightarrow{HCN/NaOH}Ph-CH_2-\overset{\overset{\large CN}{|}}{C}H-OH\xrightarrow{SOCl_2}Ph-CH_2-\overset{\overset{\large CN}{|}}{C}H-Cl\xrightarrow{NH_3}Ph-CH_2-\underset{\underset{\large NH_2}{|}}{\overset{\overset{\large CN}{|}}{C}H}\xrightarrow{H_3O^+/\Delta}Ph-CH_2-\underset{\underset{\large NH_2}{|}}{\overset{\overset{\large COOH}{|}}{C}H}$$

(D)



$$Ph-CH_2-CH=O\xrightarrow{Br_2/CH_3COOH}Ph-\underset{\underset{\large Br}{|}}{C}H-\overset{\overset{\large O}{||}}{C}H\xrightarrow{NH_3}Ph-\underset{\underset{\large NH_2}{|}}{C}H-\overset{\overset{\large O}{||}}{C}-H\xrightarrow{CrO_3/H^+}Ph-\underset{\underset{\large NH_2}{|}}{C}H-\overset{\overset{\large O}{||}}{C}-OH$$

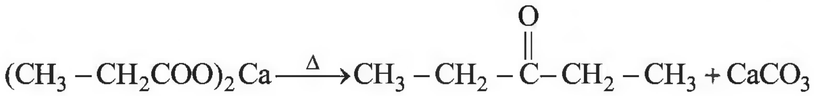
31.(ABCD)



$$C_6H_5-\underset{\underset{\large CH_3}{|}}{C}=O+H_2N-OH\longrightarrow$$

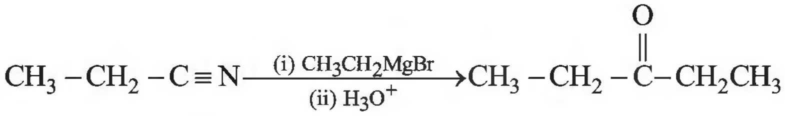
$$C_6H_5-\overset{\overset{\large O}{||}}{C}-NH-CH_3+CH_3-\overset{\overset{\large O}{||}}{C}-NH-C_6H_5$$

32.(ABD) (A)



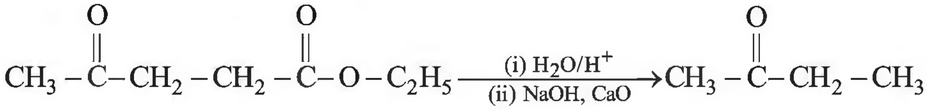
$$(CH_3-CH_2COO)_2Ca\xrightarrow{\Delta}CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-CH_2-CH_3+CaCO_3$$

(B)



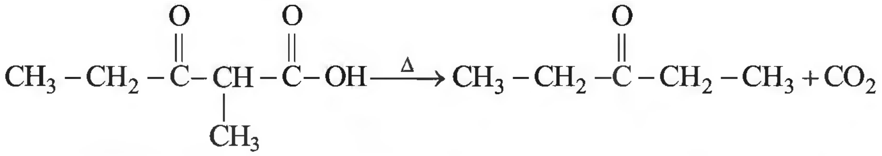
$$CH_3-CH_2-C\equiv N\xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }CH_3CH_2MgBr}CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-CH_2CH_3$$

(C)



$$CH_3-\overset{\overset{\large O}{||}}{C}-CH_2-CH_2-\overset{\overset{\large O}{||}}{C}-O-C_2H_5\xrightarrow[\text{(ii) NaOH, CaO}]{\text{(i) }H_2O/H^+}CH_3-\overset{\overset{\large O}{||}}{C}-CH_2-CH_3$$

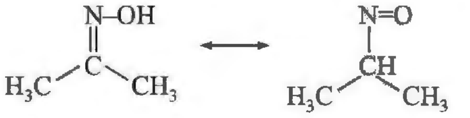
(D)



$$CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-\underset{\underset{\large CH_3}{|}}{C}H-\overset{\overset{\large O}{||}}{C}-OH\xrightarrow{\Delta}CH_3-CH_2-\overset{\overset{\large O}{||}}{C}-CH_2-CH_3+CO_2$$

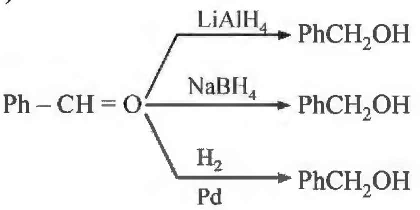
33.(AB)

(A)



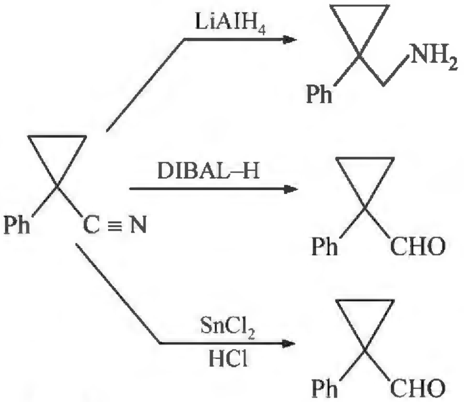
(B) $H_2C=CH-NH-CH_3 \longleftrightarrow H_3C-CH=N-CH_3$

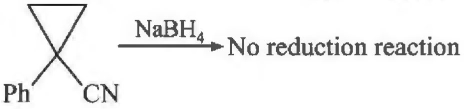
34.(ABD)



: $PH - CH = O \xrightarrow[\text{Red P}]{\text{HI}} Ph - CH_3$

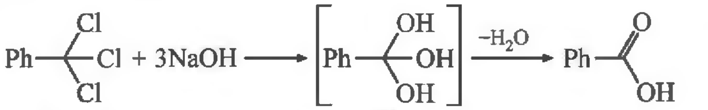
35.(CD)



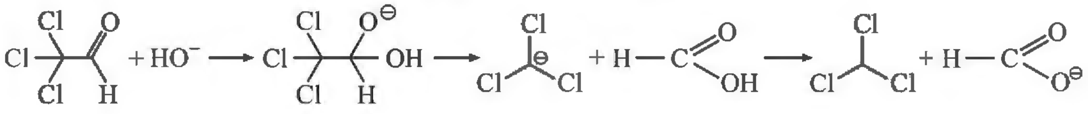


36.(ACD)

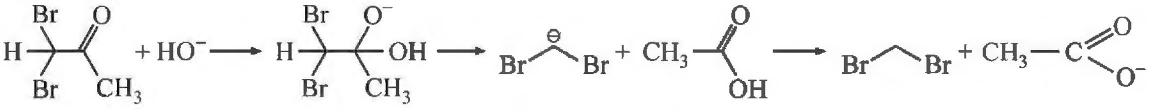
(A)



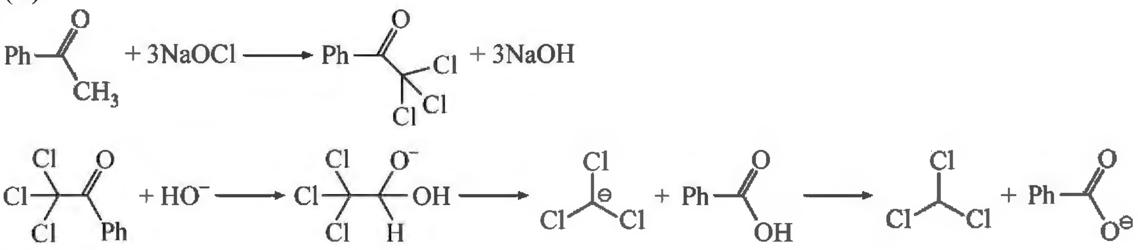
(B)



(C)



(D)



37.(ABCD)

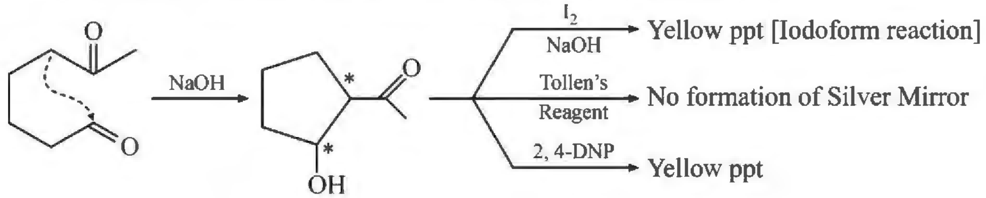
(A) $2HCHO + NaOD \longrightarrow CH_3OD + HCOONa$ [H^- transfer]

(B) $2HCDO + NaOEt \longrightarrow DCH_2ONa + DCOOEt$ [H^- transfer]

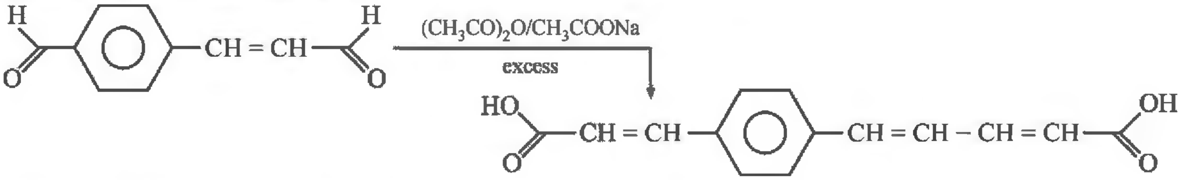
(C) $2HCDO + NaOH \longrightarrow DCH_2OH + DCOONa$ [H^- transfer]

(D) $D_2CO + NaOD \longrightarrow CD_3OD + DCOONa$ [D^- transfer]

38.(AC) Given compound undergoes intramolecular aldol reaction with aq. NaOH



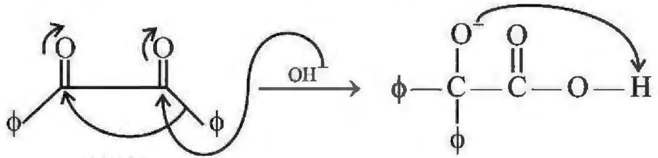
39.(B) Given reaction is Perkin reaction



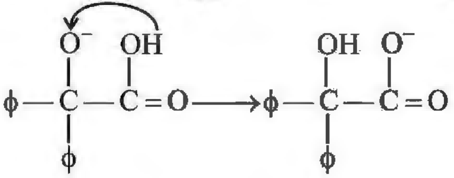
40.(AB) DIBAL-H selectively reduces ester and cyanide group to aldehyde group.

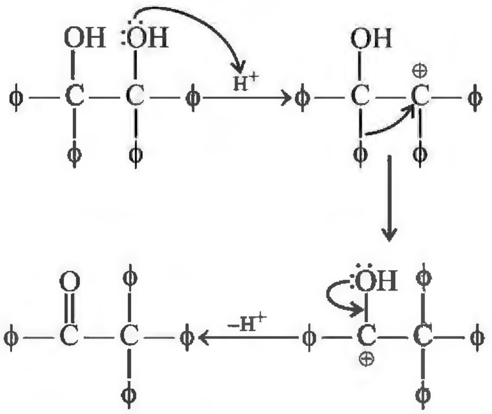
41. **[A-q, s] → [B-q, r, s] → [C-q, s] → [D-q, r, s]**

(A)

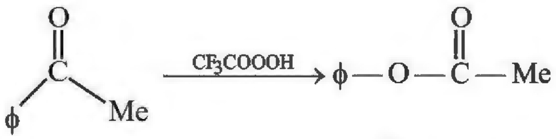


(B)



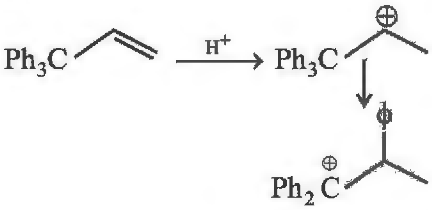


(C)

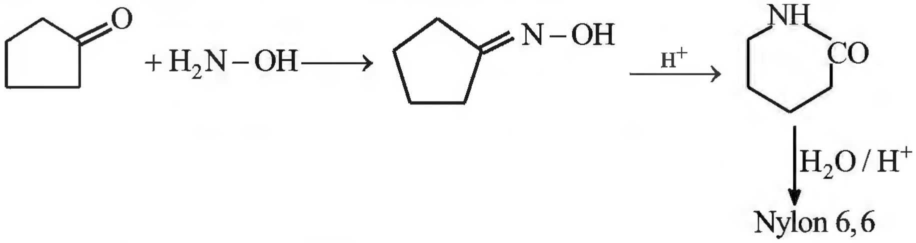


(Refer module Bayer Villiger oxidation)

(D)

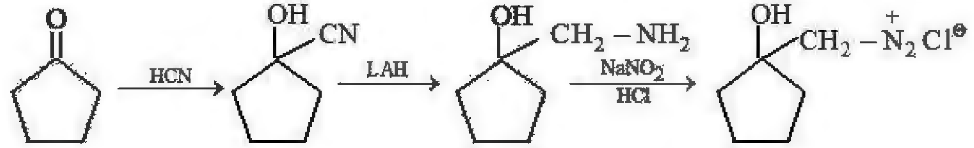


42.(D) **(P-2)**

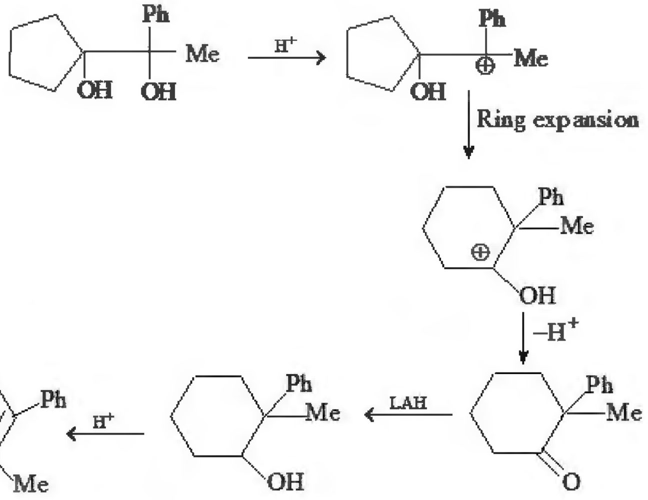


(Q-1) It is crossed intra aldol condensation

(R-4)



(S-3)

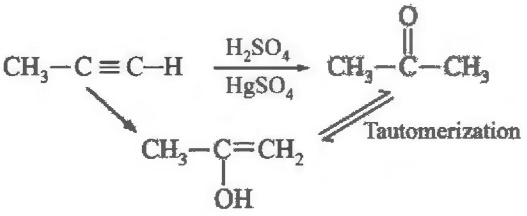


43.(C)

(P)

: Controlled Oxidation of alcohols

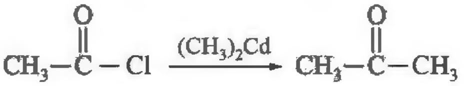
(Q)



$$CH_3-C\equiv C-H \xrightarrow[HgSO_4]{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$$CH_3-\underset{OH}{\underset{|}{C}}=CH_2 \rightleftharpoons \text{Tautomerization}$$

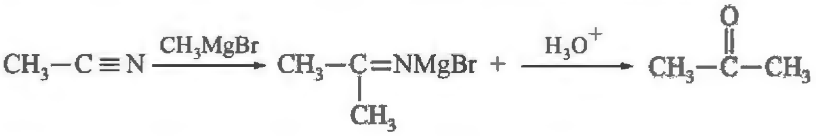
(R)



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{(CH_3)_2Cd} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

: Nucleophilic
Addition elimination reaction

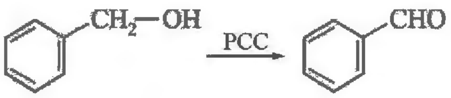
(S)



$$CH_3-C\equiv N \xrightarrow{CH_3MgBr} CH_3-\underset{CH_3}{\underset{|}{C}}=NMgBr + \xrightarrow{H_3O^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

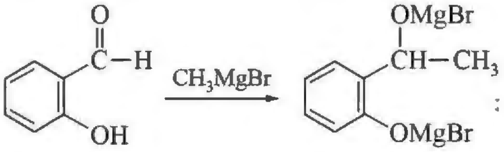
44.(C)

(P)



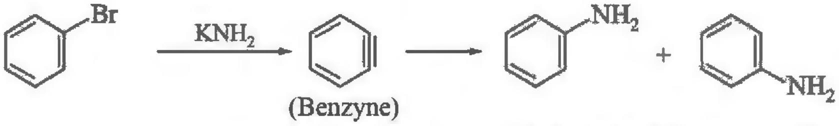
: Dehydrogenation

(Q)



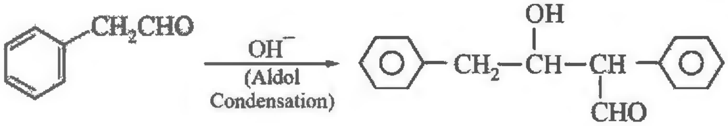
: Neucleophillic Addition and acid-base reaction

(R)



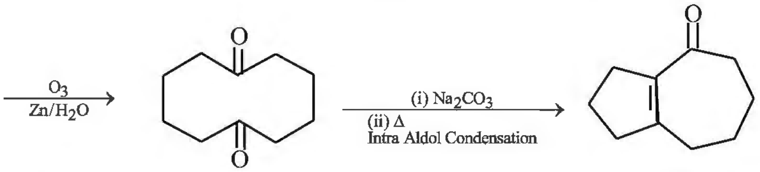
: Substitution by Benzyne Mechanism

(S)



: Self condensation in presence of alkali

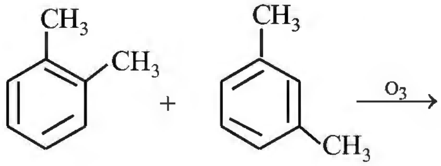
45.(2) Starting compound



(A) (B)

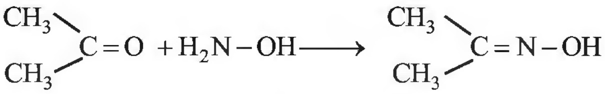
$$\frac{\text{DU in (B)}}{\pi-\text{bonds in (B)}}=\frac{4}{2}=2.$$

46.(8)

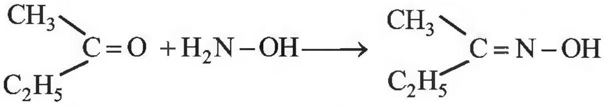


2 glyoxal + 4 methyl glyoxal

47.(3)



$$\begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>C=O+H_2N-OH\longrightarrow\begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>C=N-OH$$



$$\begin{matrix}CH_3\\ \\C_2H_5\end{matrix}\!\!>C=O+H_2N-OH\longrightarrow\begin{matrix}CH_3\\ \\C_2H_5\end{matrix}\!\!>C=N-OH$$

(This compound will have two geometrical isomers)

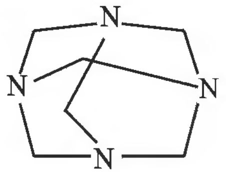
Total compound formed = 3

$CH_3-CO-CH_3\xrightarrow{OH^-}$ one self condensation product

$CH_3-CH_2-CO-CH_3\xrightarrow{OH^-}$ This can generate 2 type of carbanions so 2 self condensation products

48.(6) Crossed condensation product will be 3. Total products = 6

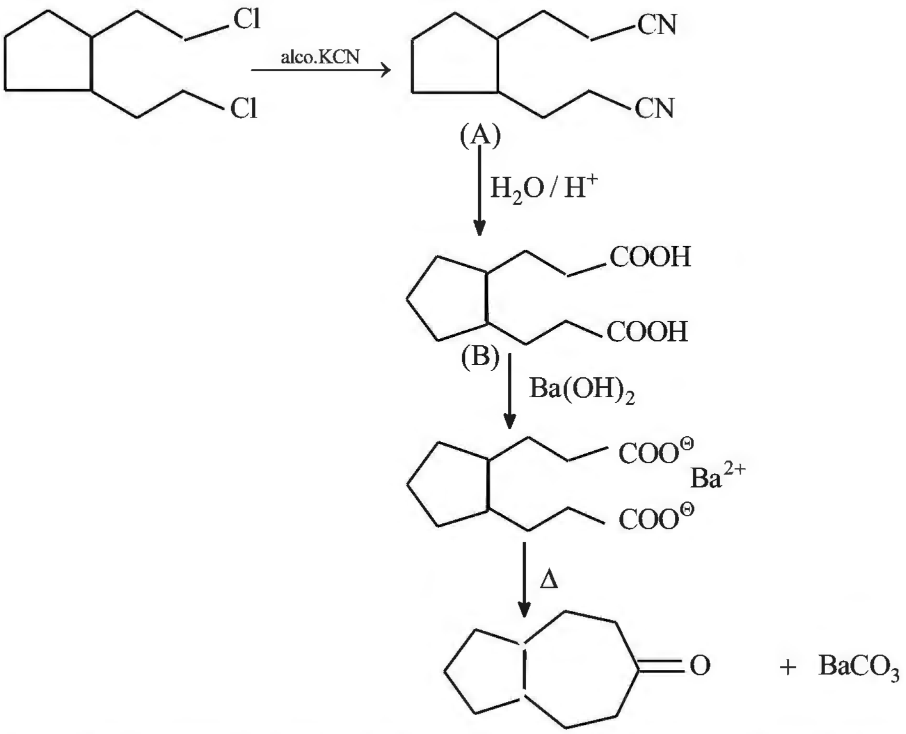
49.(6)



No of N–C–N bonds =6

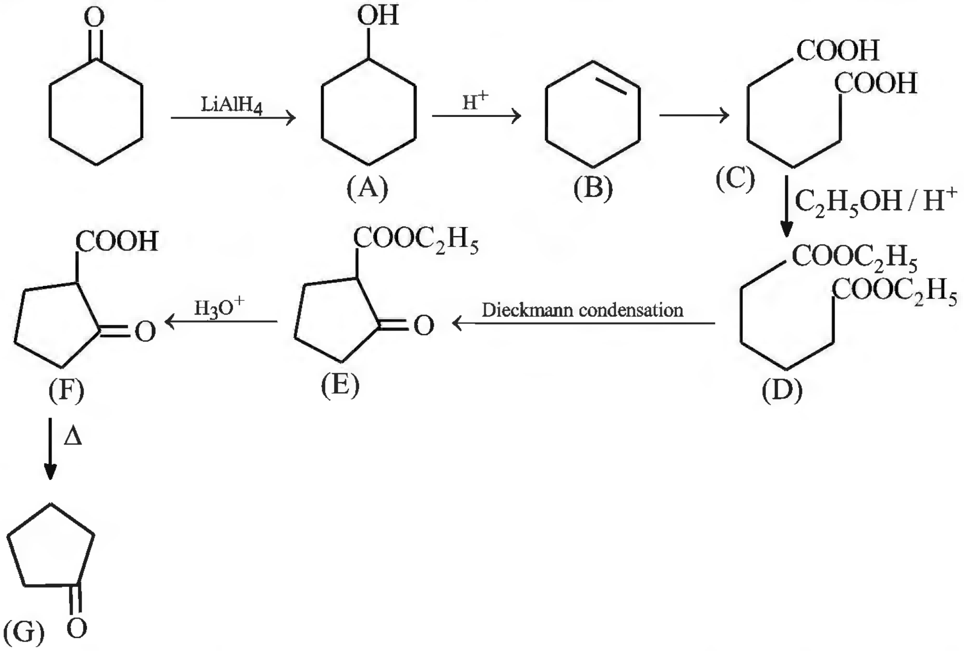
Urotropine is hexamethylene diamine $(CH_2)_6N_4$.

50.(3)

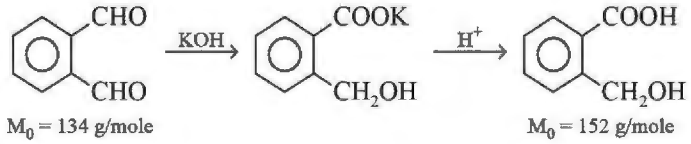


51.(8) Iodoform test is generally given by those compounds which have or can generate CH_3–CO– group in them.

52.(5)

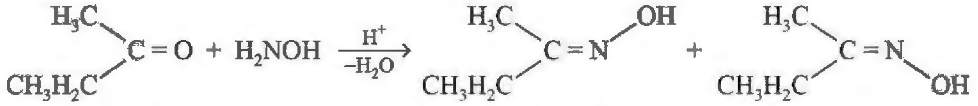


53.(9) It is intramolecular cannizzaro reaction. In this reaction molecular mass of reactant increases by 18 units.



$$\frac{152-134}{2}=\frac{18}{2}=9$$

54.(2) Carbonyl compounds on reaction with hydroxyl amine produce oximes. Oximes may shows geometrical isomerism.



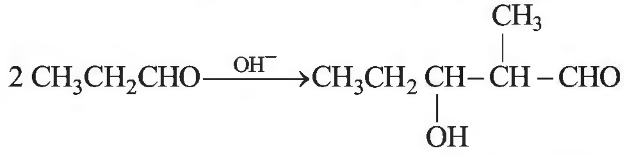
55.(3) Disproportionation reaction of formaldehyde with KOH is cannizzaro reaction. Cannizzaro reaction follows third order kinetics.

$$r = K[HCHO]^2[KOH]$$

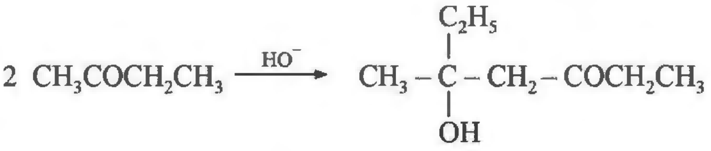
56.(10) Except (v) all other reactions are used to produce benzaldehyde. Vicinal disubstituted alkene on reaction with O_3/H_2O form carboxylic acid because it is oxidative ozonolysis reaction.

57.(9) Except (viii) all other reaction product is an aromatic compound.

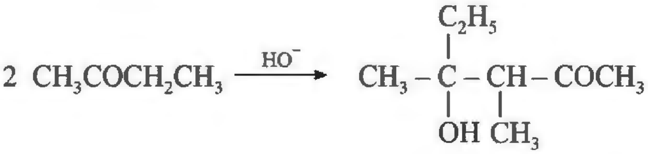
58.(6)



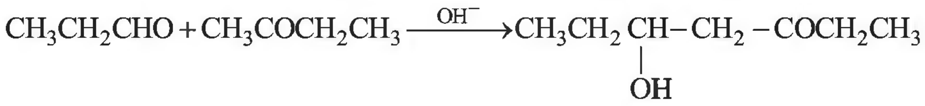
$$2\,CH_3CH_2CHO \xrightarrow{OH^-} CH_3CH_2\underset{\underset{OH}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CHO$$



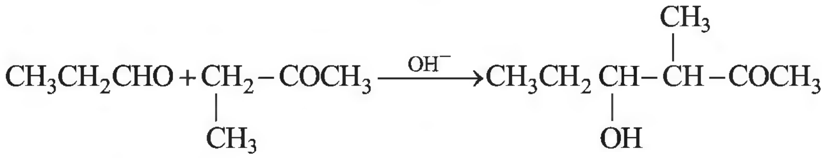
$$2\ CH_3COCH_2CH_3 \xrightarrow{HO^-} CH_3-\overset{\overset{C_2H_5}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-COCH_2CH_3$$



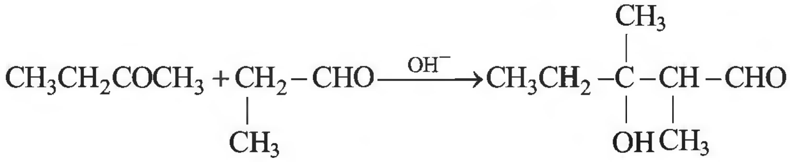
$$2\ CH_3COCH_2CH_3 \xrightarrow{HO^-} CH_3-\overset{\overset{C_2H_5}{|}}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-COCH_3$$



$$CH_3CH_2CHO+CH_3COCH_2CH_3 \xrightarrow{OH^-} CH_3CH_2\underset{\underset{OH}{|}}{CH}-CH_2-COCH_2CH_3$$

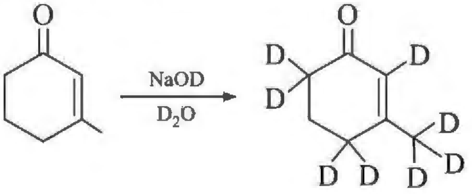


$$CH_3CH_2CHO+\underset{\underset{CH_3}{|}}{CH_2}-COCH_3 \xrightarrow{OH^-} CH_3CH_2\underset{\underset{OH}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-COCH_3$$



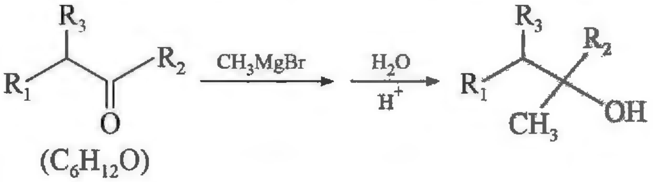
$$CH_3CH_2COCH_3+\underset{\underset{CH_3}{|}}{CH_2}-CHO \xrightarrow{OH^-} CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CHO$$

59.(8) All α and γ H atoms (in conjugation with C = O group) will be exchanged with D atoms.

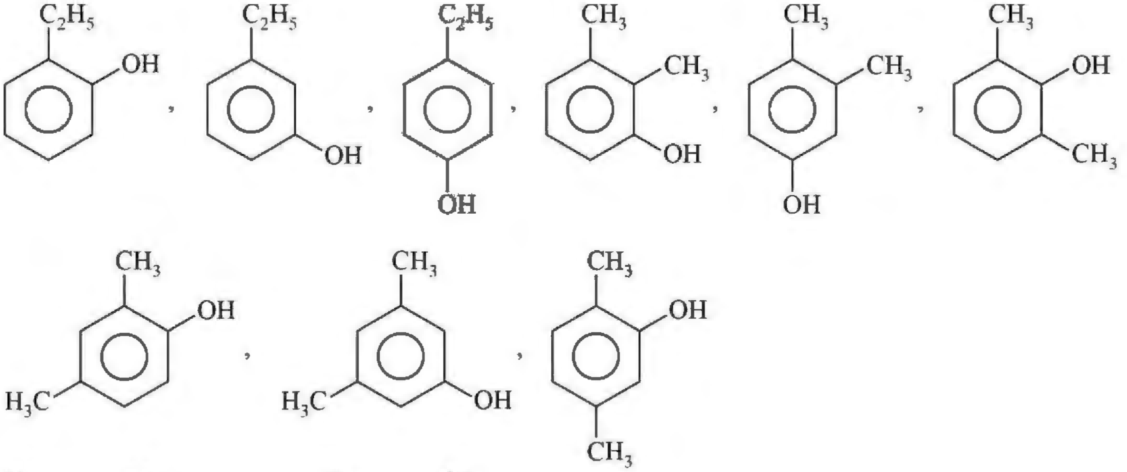


60.(5) Electron withdrawing group increases rate of nucleophilic addition reaction and aldehyde is more reactive than ketone.

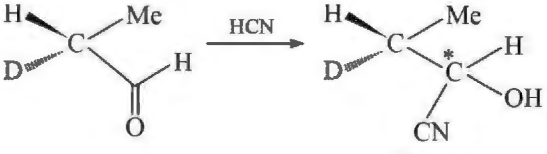
61.(0) Only racemic mixture or single stereo isomer is formed. Ketone is $C_6H_{12}O$.



62.(9)

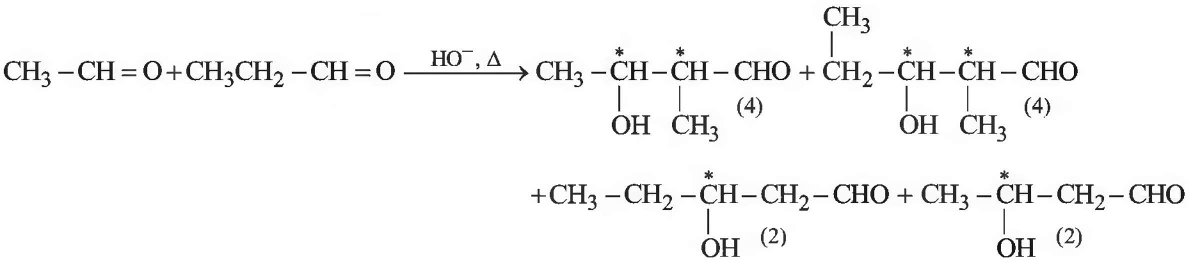


63.(2)



2-isomers
(Diastereomers)

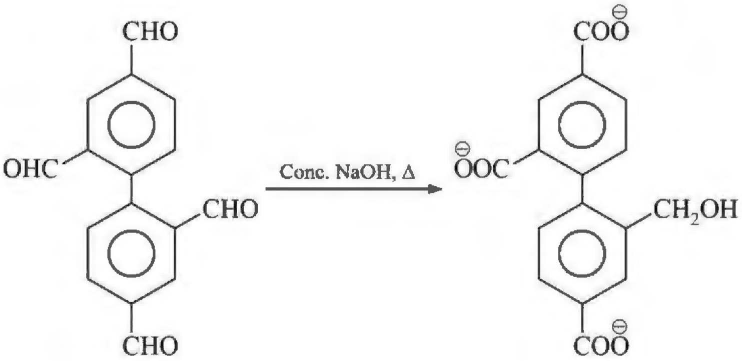
64.(12)

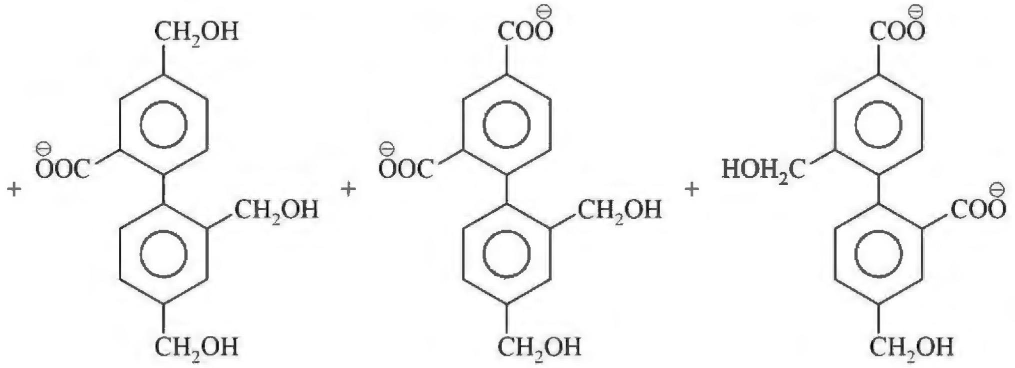


$$CH_3-CH=O+CH_3CH_2-CH=O\xrightarrow{HO^-,\Delta}CH_3-\underset{OH}{\overset{*}{C}H}-\underset{CH_3}{\overset{*}{C}H}-CHO\ ^{(4)}+\overset{CH_3}{C}H_2-\underset{OH}{\overset{*}{C}H}-\underset{CH_3}{\overset{*}{C}H}-CHO\ ^{(4)}$$

$$+CH_3-CH_2-\underset{OH}{\overset{*}{C}H}-CH_2-CHO\ ^{(2)}+CH_3-\underset{OH}{\overset{*}{C}H}-CH_2-CHO\ ^{(2)}$$

65.(4)

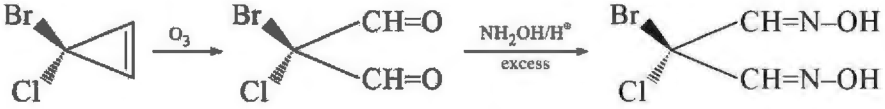




66.(3) 4, 5, 6

67.(12) X has 3 stereocentres with similar ends. Hence, 6 stereoisomers. $\mathrm{Y = CH_3-\underset{\underset{D}{|}}{C}H-CHO}$ has only one stereocentre, hence 2 stereoisomers. $\mathrm{Z = CH_3-\underset{\underset{D}{|}}{C}H-CH=NOH}$ has 2 stereocentre, hence 4 stereoisomers.

68.(04)



cis - cis
trans - trans
cis R trans
trans S cis

Total isomeric product = 4

69.(6)

$$\mathrm{HCHO + CH_3CHO + CH_3COCH_3 \xrightarrow{OH^{\ominus}} HOCH_2-CH_2-CHO + HOCH_2-CH_2COCH_3 +}$$

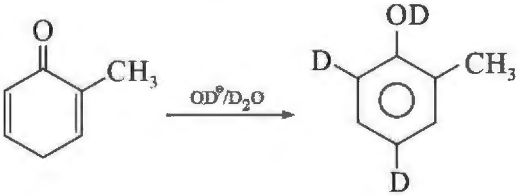
$$\mathrm{CH_3-\underset{\underset{OH}{|}}{C}H-CH_2-CHO + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-COCH_3 + CH_3-\underset{\underset{OH}{|}}{C}H-CH_2-COCH_3 + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CHO}$$

70.(7)

$$\mathrm{CH_2=\overset{\overset{OH}{|}}{C}-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3}\ ,\quad \underset{\text{cis \& trans}}{\mathrm{CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{||}}{C}-CH_2-CH_3}}\ ,$$

$$\underset{\text{cis \& trans}}{\mathrm{CH_3-\overset{\overset{O}{||}}{C}-CH=\overset{\overset{OH}{|}}{C}H-CH_2-CH_3}}\ ,\quad \underset{\text{cis \& trans}}{\mathrm{CH_3-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{OH}{|}}{C}H=CH-CH_3}}$$

71.(3)



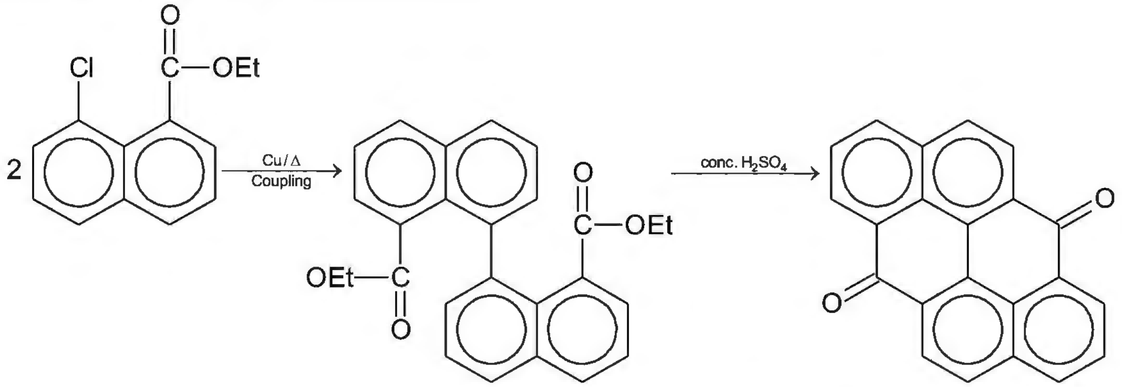
Oxygen Containing Organic Compound-III

1.(B) Elimination of CO takes place on heating α -keto acids.

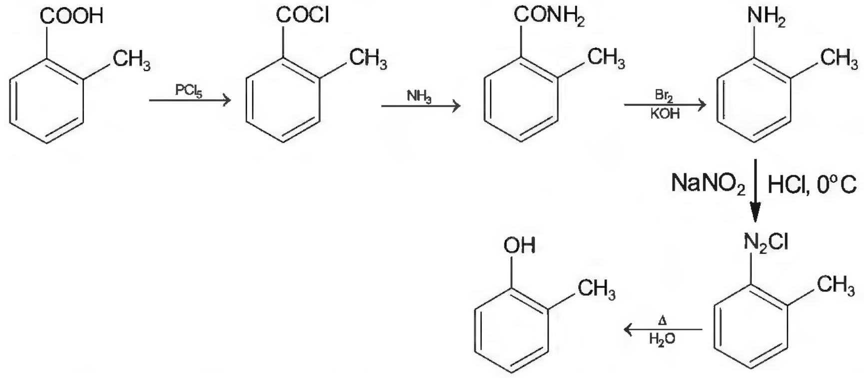
2.(B) Elimination of CO_2 takes place on heating β -keto acids.

3.(C) Option (C) is chiral and it does not decarboxylate.

4.(C)

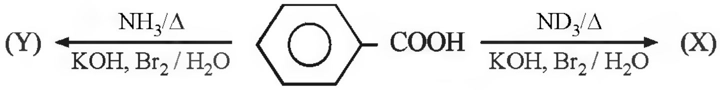


5.(A)

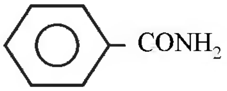


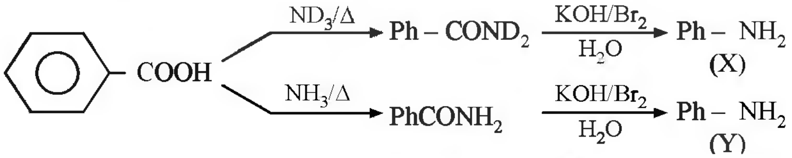
6.(B) Hoffmann Bromamide reaction takes place towards left end and Bromoform reaction takes place towards right end.

7.(D)

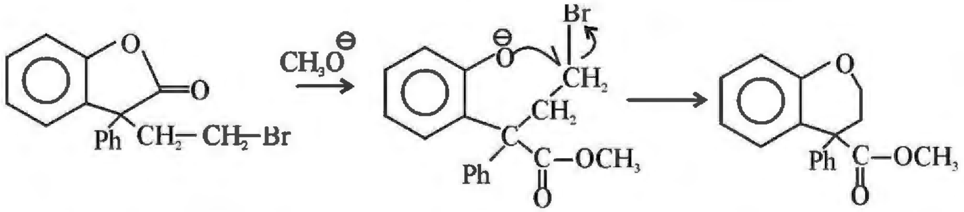


Both (X) and (Y) will be

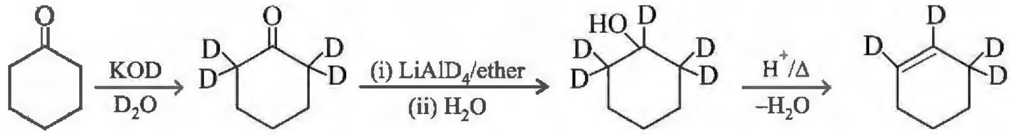




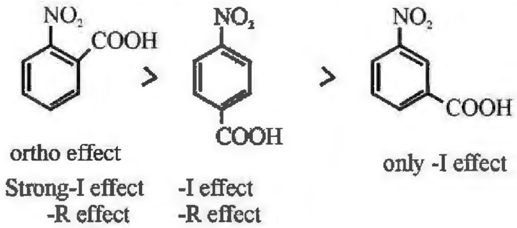
8.(B)



9.(A)



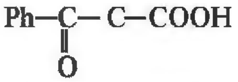
10.(D) **I.**



II. Higher the acidity of an acid lower the basicity of its conjugate base.

III. Higher the stability of an alkene lower the heat of hydrogenation.

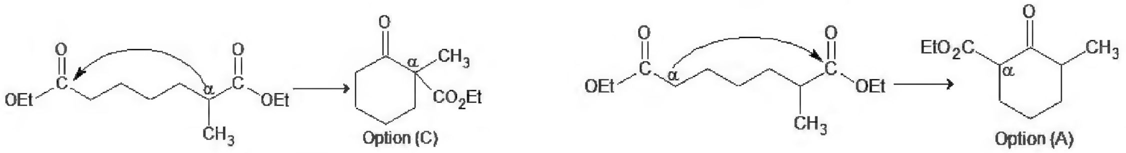
IV.



$Ph-\underset{\underset{O}{\|}}{C}-C-COOH$ is the β -keto acid so it would be having maximum ease for decarboxylation.

11.(B) This is an example of Cross – Cannizzaro reaction. The molecule first attacked is converted to sodium salt of benzoic acid in a Cannizzaro reaction. The presence of $-NO_2$ group activates the –CHO group towards nucleophilic attack. Therefore nitrobenzaldehyde is preferentially attacked.

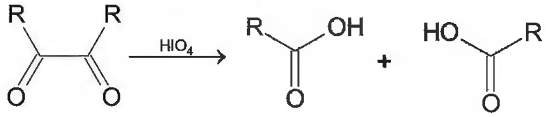
12.(A) The two probabilities are:



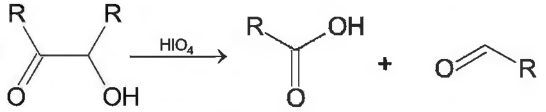
Option (C) lacks an acidic α - hydrogen, which is required to drive equilibrium of Dieckmann's reaction towards completion. Option (A) has an acidic hydrogen, so it is the correct answer.

13.(C)

(1)

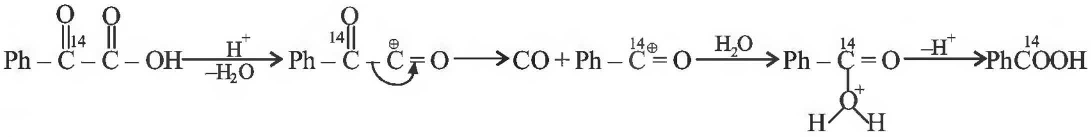


(2)



(4) $R-CHOH-CHOH-R \xrightarrow{HIO_4} R-CH=O + R-CH=O$

14.(A)



$Ph-\overset{\overset{O}{\|}}{\overset{14}{C}}-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-H_2O]{H^+} Ph-\overset{\overset{O}{\|}}{\overset{14}{C}}-\overset{\oplus}{C}=O \longrightarrow CO + Ph-\overset{14\oplus}{C}=O \xrightarrow{H_2O} Ph-\underset{\underset{H\quad H}{\overset{+}{O}}}{\overset{14}{C}}=O \xrightarrow{-H^+} Ph\overset{14}{C}OOH$

15.(ABCD)

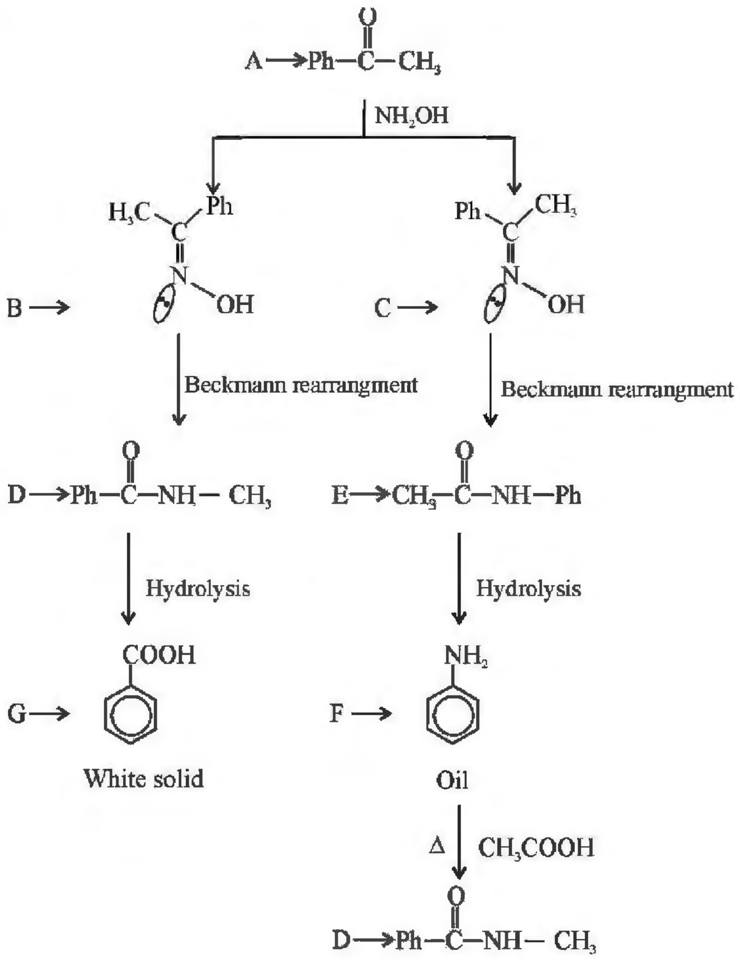
(A) $R-C\equiv N \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Sn+HCl}}$ Product (Stephen Reaction)

(B) $RCH_2OH \xrightarrow[CH_2Cl_2]{PCC}$ Product R-CHO

(C) $RCOCl \xrightarrow{LiAlH(OBu)_3}$ Product R – CHO due to bulky nature of $LiAlH(OBu)_3$
RCHO further does not react to form alcohol

(D) $RCOCl + H_2 \xrightarrow[\text{S or Quinoline}]{Pd-BaSO_4}$ Product (Rosenmund reaction all above reaction are used to form aldehyde only. Hence the (A, B, C, D)

16.(CD)



17.(AB) $CH_2 = CH - CHO \xrightarrow[\text{Fehling's Reagent}]{\text{Tollen's Reagent}} CH_2 = CH - COOH + Ag(\downarrow)/Cu_2O(\downarrow)$ (Silver mirror) (Reddish Brown)

$$CH_2 = CH - CHO \xrightarrow[\Delta]{KMnO_4/H^+} HCOOH + \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

In (C), MPV reaction cannot be used for this purpose, as it requires a secondary alcohol compound, and also it perform reduction of aldehyde, not oxidation. So, A and B are correct.

18.(ABC) A is isobutyric ester.

19.(BCD) The above reaction is Hoffmann Bromamide reaction.

20.(AC) (B) is long chain and (D) is trans isomer **21.(BC)** Baeyer Villiger followed by hydrolysis of ester

22.(ABCD) β -keto acid, gem-dicarboxylic acids, α-Nitro-carbocylic acid, β, γ-unsaturated carboxylic acid on heating decarboxylate to give CO_2

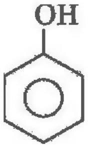
23.(AC) Esterification in (A) and amide formation in (C)

24.(ABC) Oxidation of side chain gives carboxylic acid. In option (D) O-atom attached cannot be oxidised to –COOH.

25.(ACD)(A) $\bar{e}$ withdrawing group increases the acidic strength $(-NO_2 > -F)$
$\bar{e}$ donating group decreases the acidic strength.

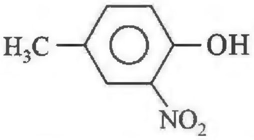
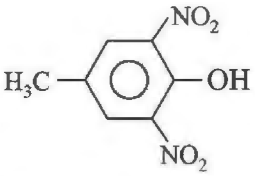
(C) $(-NO_2 > -F) \rightarrow -I$ effect

(D) $-CH_2CH_3$ show +I effect

26.(ACD) Carbolic acid → 

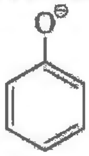
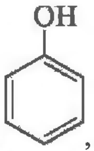
This is less acidic than

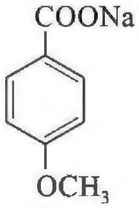
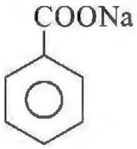
(A) CH_3COOH

(C)  **(D)** 

ē withdrawing group increases the acidic strength

27.(BC) It is ascorbic acid and H_b is more acidic because after deprotonation, O^- will show delocalization which will stabalise the molecule.

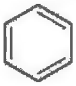
28.(BD) (B)  more stable than , Because in phenoxide ion, carbon will acquire –ve charge and in phenol, oxygen will acquire +ve charge which make molecule less stable.

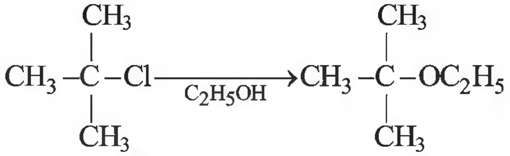
(D)  less stable than 

Because $-OCH_3$ group shows +M effect which will destabalise the -COO group.

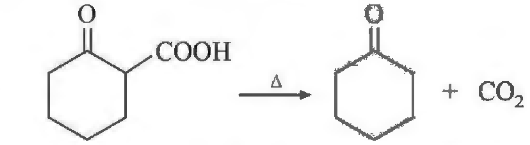
29.(AC) (A) $CH_3COOK \xrightarrow{\text{electrolysis}} CH_3-CH_3$

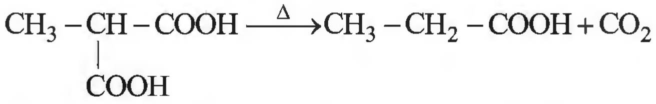
(B) $CH_3COOAg \xrightarrow{Br_2/CCl_4} CH_3Br + CO_2 + AgBr$

(C) $Ph-COOH \xrightarrow[CaO,\ \Delta]{NaOH}$ 

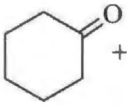
(D) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl \xrightarrow[C_2H_5OH]{} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OC_2H_5$$

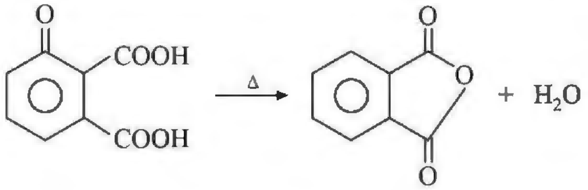
30.(ABC) **(A)** 

(B) 

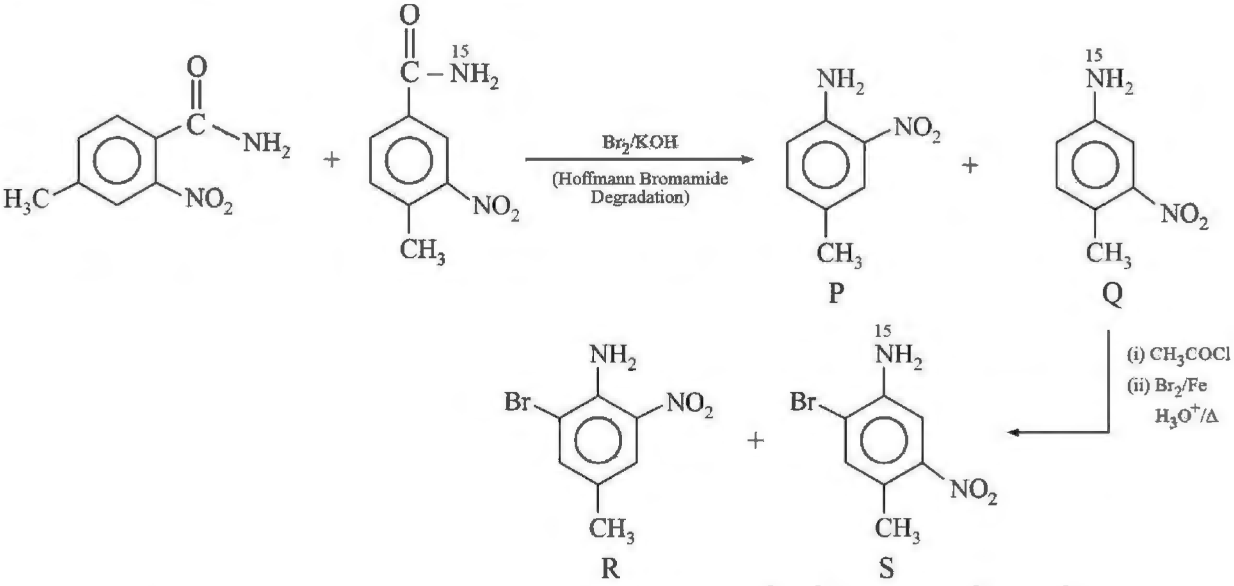
$$CH_3-\underset{COOH}{\underset{|}{CH}}-COOH \xrightarrow{\Delta} CH_3-CH_2-COOH + CO_2$$

(C) $HOOC-(CH_2)_5-COOH \xrightarrow{Ca(OH)_2/\Delta}$  + CO_2

(D)



31.(BC)

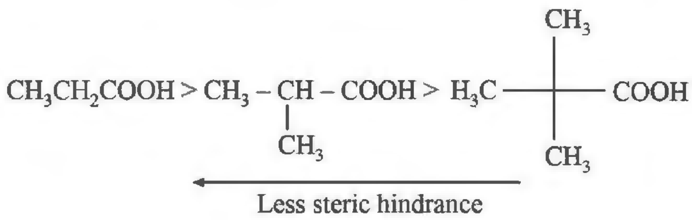


32.(AB) (A)

$$CH_3COCl > (CH_3CO)_2O > CH_3COOEt > CH_3CONH_2 > Cl^{\ominus} > {}^{\ominus}O\underset{\underset{O}{\|}}{C}-CH_3 > {}^{\ominus}OEt > {}^{\ominus}NH_2$$

$$\xleftarrow[\text{order of leaving group}]{}$$

(B)



$$CH_3CH_2COOH > CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH > H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-COOH$$

$$\xleftarrow[\text{Less steric hindrance}]{}$$

33.(ABCD)

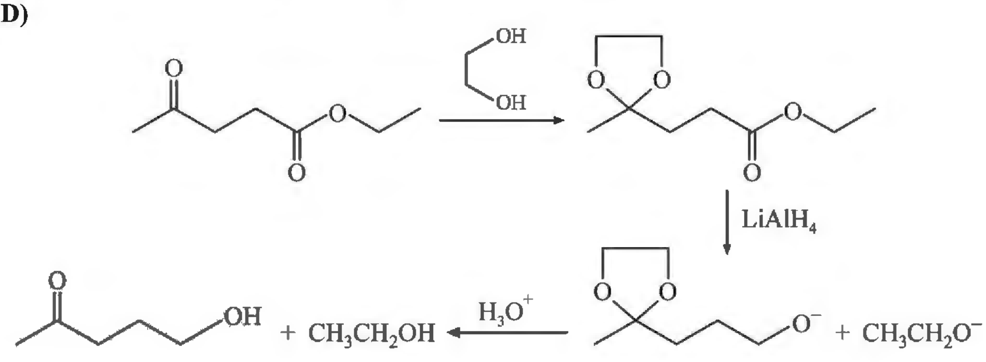
(A) $LiAlH_4 \Rightarrow$ Reduce Ester, Acid, Amide, Ketone & Nitro

(B) $NaBH_4 \Rightarrow$ Reduce only Ketone

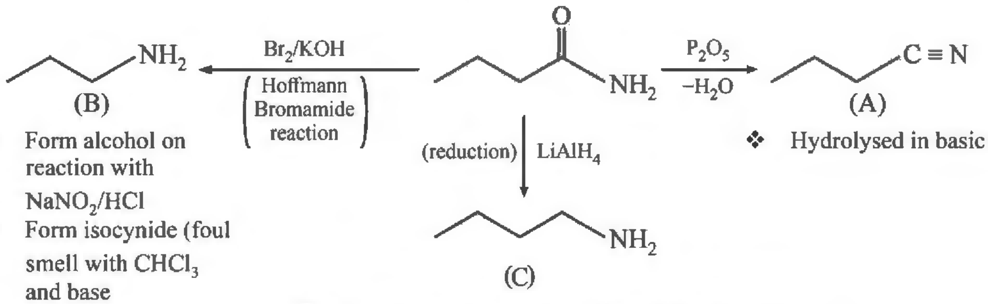
(C) $Na / C_2H_5OH \Rightarrow$ Reduce Ester and Ketone

(D) MPV reduction is only for Ketone

34.(ACD)

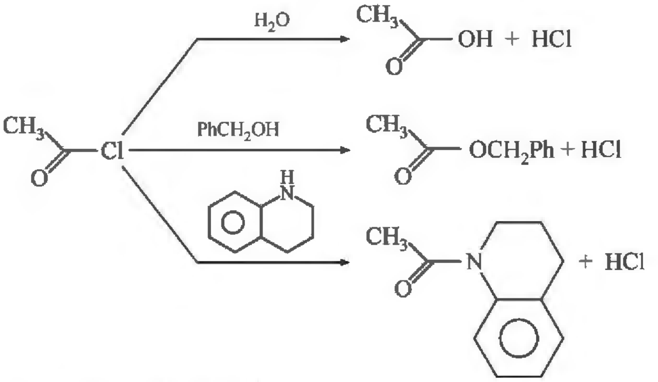


35.(ABC)



- ❖ Form alcohol on reaction with $NaNO_2/HCl$
- ❖ Form isocynide (foul smell with $CHCl_3$ and base
- ❖ Hydrolysed in basic medium
- ❖ Form isocynide (foul smell with $CHCl_3$ and base)

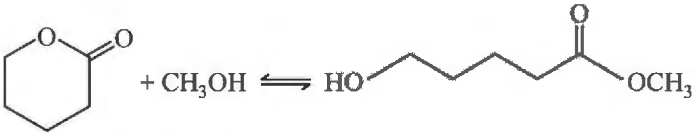
36.(D)



No reaction with 3° amine

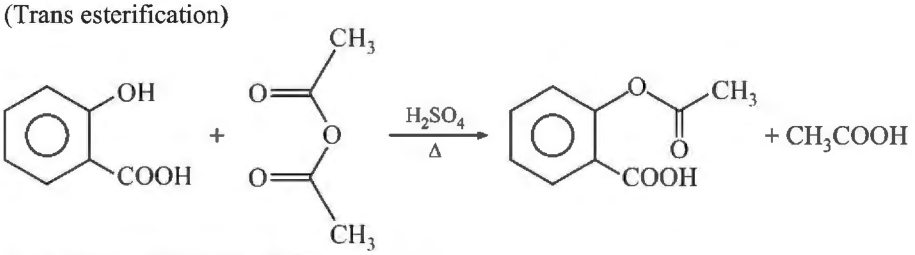
37.(ABD)

(A)



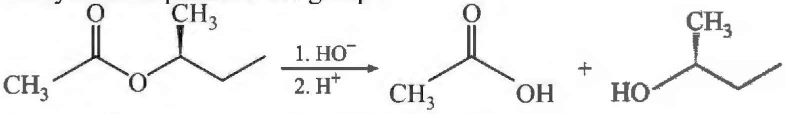
(Trans esterification)

(B)



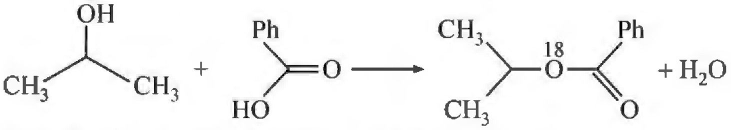
Acetylation of phenolic OH group

(C)



Hydrolysis of ester involving alkyl-O-cleavage

(D)



Esterification reaction involving acyl-O-cleavage

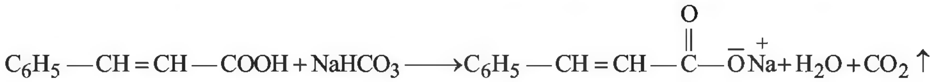
38.(ABCD)

$LiAlH_4$ can reduce ketone, cyanide, ester and anhydride groups. $NaBH_4$ can reduced only ketone.

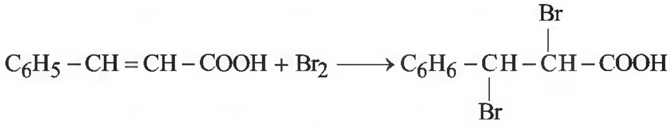
39. **[A-p, r] [B-p, q, r] [C-p, r, s] [D-p, r]**

(A) $CH_3COOH + FeCl_3 \longrightarrow \underset{\text{(Red)}}{(CH_3COO)_3Fe} + HCl$

(B)

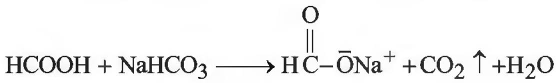


$C_6H_5-CH=CH-COOH + NaHCO_3 \longrightarrow C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na} + H_2O + CO_2\uparrow$



$C_6H_5-CH=CH-COOH + Br_2 \longrightarrow C_6H_6-\underset{\underset{Br}{|}}{C}H-\overset{\overset{Br}{|}}{C}H-COOH$

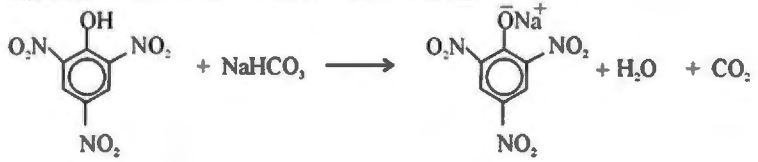
(C)



$HCOOH + NaHCO_3 \longrightarrow H\overset{\overset{O}{\|}}{C}-\bar{O}Na^+ + CO_2\uparrow + H_2O$

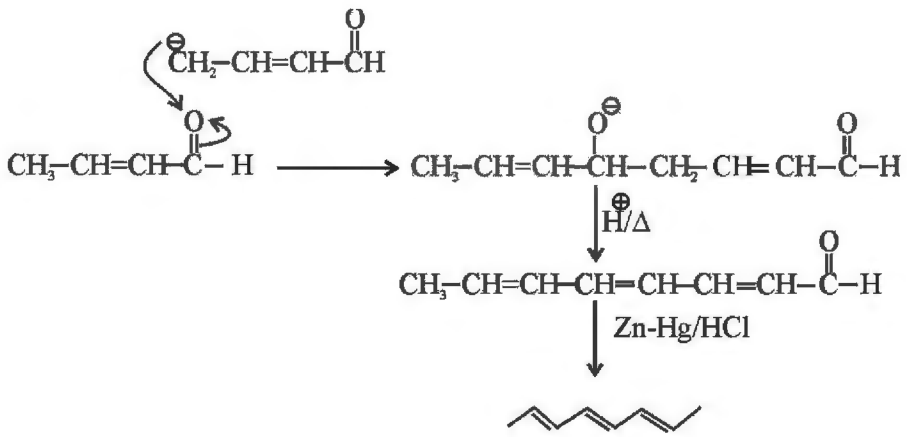
$HCOOH + 2Ag + 2\bar{OH} \rightarrow CO_2 + Ag\downarrow + 2H_2O$

(D)



40. **[A→r; B→s ; C→q; D→p]**

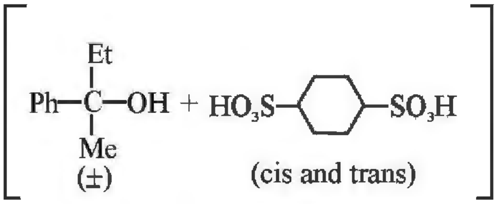
41.(6)



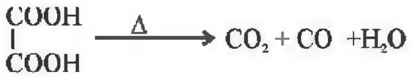
No. of stereo isomers are

cis, cis, cis
cis, cis, trans
cis, trans, cis
cis, trans, trans
trans, cis, trans
trans, trans, trans

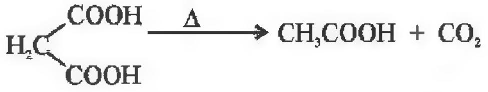
42.(4)



43.(3)



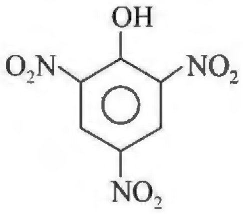
$$HOOC-COOH \xrightarrow{\Delta} CO_2 + CO + H_2O$$



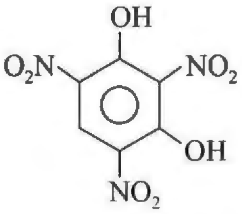
$$H_2C(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

$$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + CO_2$$

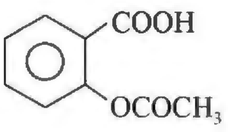
44.(4) Aspirin, Penicillin, Valeric acid and Anthranilic acid contain carboxylic acid functional group.



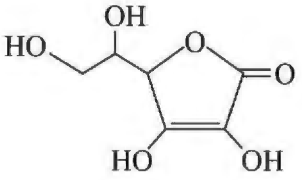
Picric acid



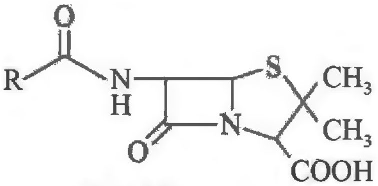
Styphnic acid



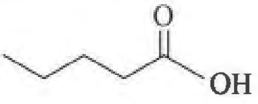
Aspirin



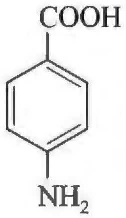
Ascorbic acid



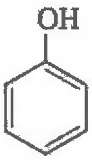
Penicillin



Valeric acid



Anthranilic acid



Carbolic acid

45.(22)

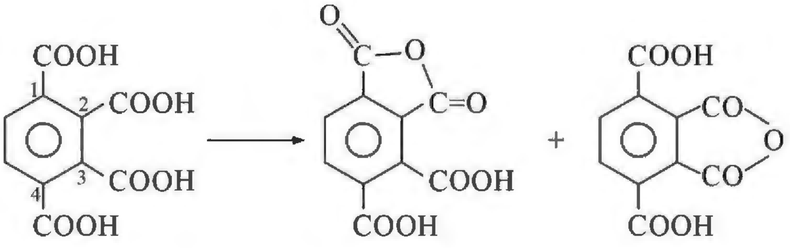
46.(21)

47.(4) $CH_3CH_2CH=CH(CH_2)_2COOCH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} CH_3CH_2CHO + OHCCH_2CH_2COOCH_3 \xrightarrow[H_2O]{LiAlH_4}$

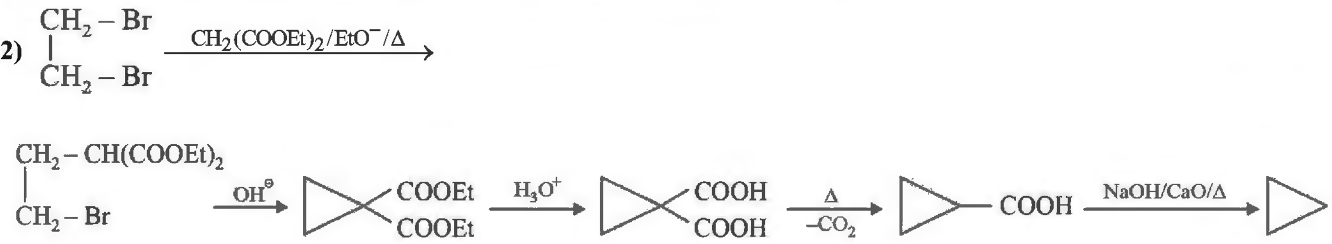
$CH_3CH_2CH_2OH + HOCH_2CH_2CH_2CH_2OH + CH_3OH \xrightarrow{CH_3COOH}$ 4 moles are required

48.(5) 5, 1, 3, 8 only.

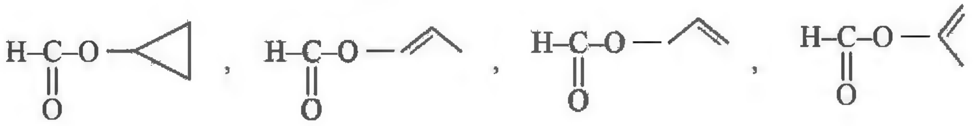
49.(10)

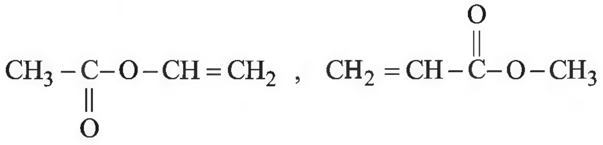


50.(42)



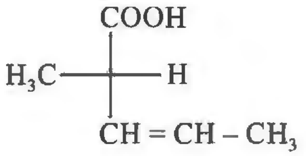
51.(9)





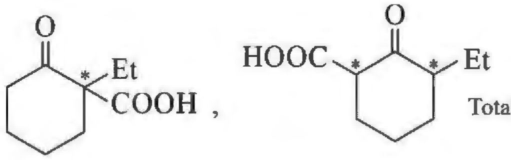
$CH_3-\underset{\underset{O}{\|}}{C}-O-CH=CH_2$, $CH_2=CH-\overset{\overset{O}{\|}}{C}-O-CH_3$

52.(6) The smallest optically active alkenoic acid which can also show geometrical isomerism can be written as



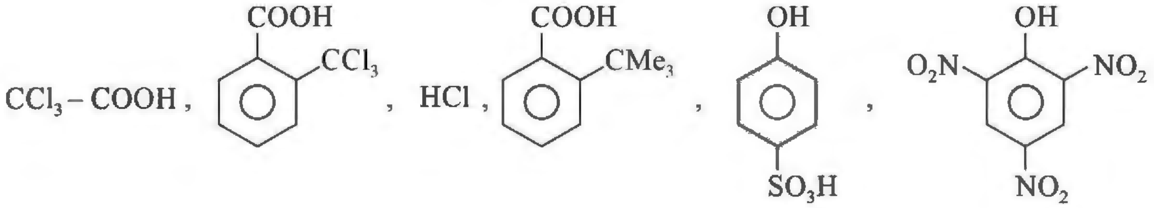
Hence its molecular formula is $C_6H_{10}O_2$.

53.(6)



Total = 2 + 4 = 6

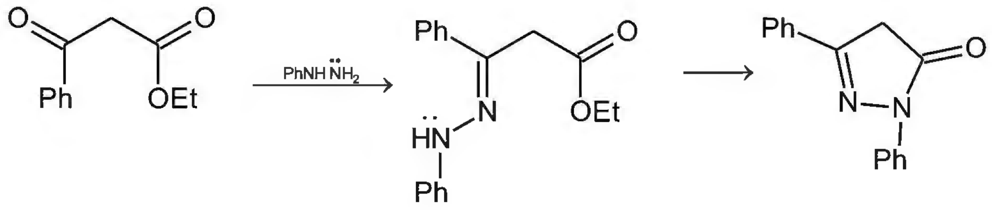
54.(6)



Nitrogen Containing Organic Compound

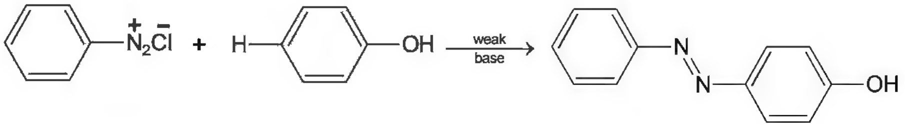
1.(B) Diazotization coupling takes place at most activated position of ring.

2.(B)

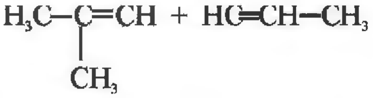


3.(C) Beckmann's rearrangement

4.(B)



5.(C) Product mixture:



$H_3C-\underset{CH_3}{\underset{|}{C}}=CH + HC\equiv CH-CH_3$

6.(B)

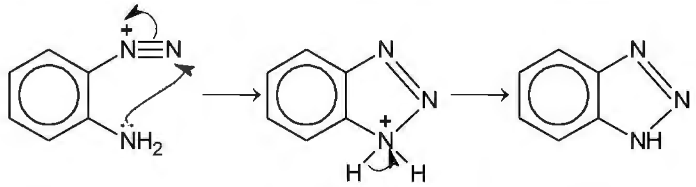
$(CH_3)_3\overset{+}{N}-\overset{-}{B}(CH_3)_3$

$CH_2=\overset{+}{N}=\overset{-}{N}$ } All have coordinate bonds

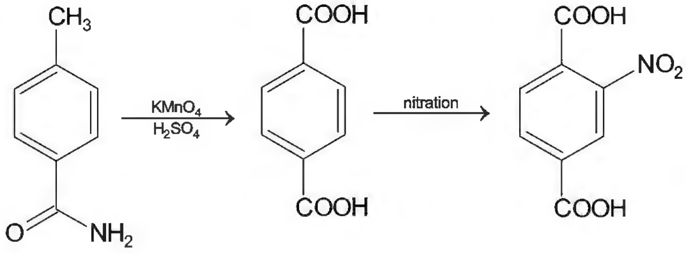
In (F $(CH_3)_3\overset{+}{N}-\overset{-}{O}$

7.(D) N^2 is pyrrole and is least basic due to conjugation while N^3 is most basic due to being amine and +I effect.

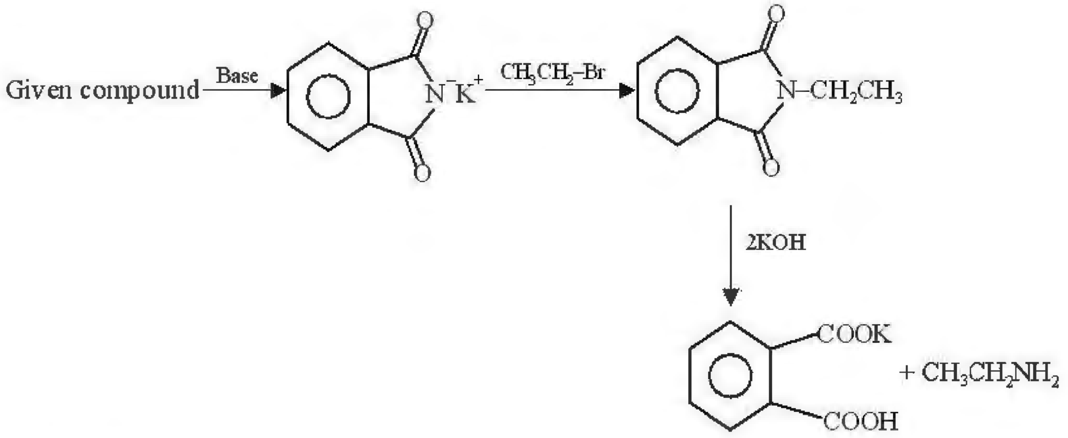
8.(C)



9.(A)



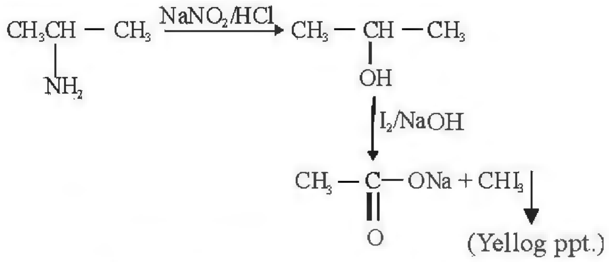
10.(A)



11.(B) $PhNH_2 + CHCl_3 \xrightarrow{\Delta} PhNC + 3KCl + 3H_2O$ $PhNC \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} Ph-NH-CH_3$

12.(A)

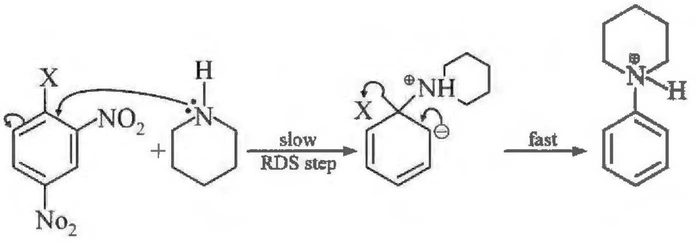
$$\begin{tikzcd}
CH_3CH_2CH_2NH_2 \arrow[r, "NaNO_2/HCl"] & CH_3CH_2CH_2OH + N_2 \arrow[d, "I_2/NaOH"] \\
& \text{No iodoform test}
\end{tikzcd}$$



$$\underset{\displaystyle NH_2}{CH_3CH} - CH_3 \xrightarrow{NaNO_2/HCl} CH_3-\underset{\displaystyle OH}{CH}-CH_3 \xrightarrow{I_2/NaOH} CH_3-\underset{\displaystyle O}{\overset{\|}{C}}-ONa + CHI_3\downarrow$$

(Yellog ppt.)

13(BCD) This is a nucleophilic substitution reaction on aromatic compound, whose EWG $-NO_2$ at ortho and para position increases the rate of reaction, by increasing the electrophilicity of the ring.



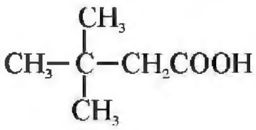
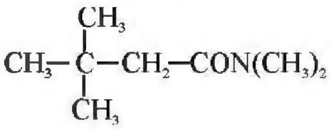
Here, RDS step is step-I because here aromaticity is lost. Order of reactivity is $F > Cl > Br > I$, because exceptionally high electronegativity of F increase electrophilicity and so, the rate of nucleophilic attack is maximum with X = F. So, the correct choice are B, C, D.

14.(BCD) (A) on reduction form secondary amines

15.(A) Amides are less basic than amines.

16.(BCD) Aliphatic 1° amine released N_2 on treatment with HNO_2.

17.(CD) Substituted aryl amines do not give this reaction.

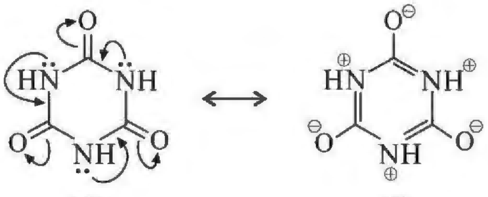
18.(AD) Compound (A) is 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2COOH$
Compound (C) is 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CON(CH_3)_2$

19.(BC) In reaction 1, elimination product is governed by Hoffmann's rule.
In reaction 2, elimination product is governed by Saytzeff's rule.

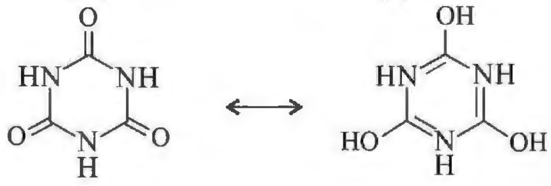
20.(CD) N-nitroso amine is formed by 2°-amine.

21.(ACD) Tollen's test is given by aldehydes.

22.(ABCD)



(R) **(S)**

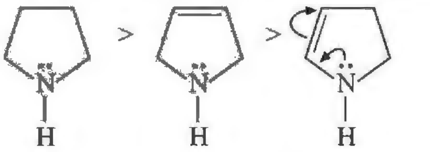


(R) **(P)**

Show both resonance and toutomerism

23.(BD) (B) (I = V) → Kekule structure
(II = IV) → same structure
(I = V) > (II = IV) → Neutral molecule is more stable than charged molecule.
(D) (II = IV) > III → Opposite charge at less distance is more stable

24.(BCD) (B) More +I effect, more basic strength,
(C) less delocalization, more basic strength
(D)



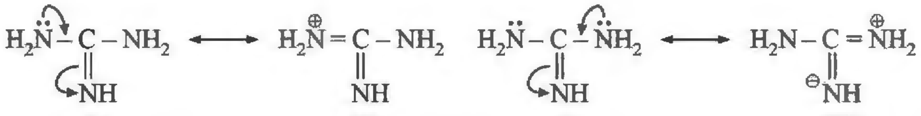
lone pair is
in conjugation

25.(ABCD)

(A) Both nitrogen of pyrimidine having same basic strength because both are sp^2 hybridized and having No delocalization.
(B) N-3 having no delocalization, So it's lone pair are more available for protonation.
(C) Only N-9 is able to delocalize
(D) All molecules are aromatic.

26.(ABCD)

(A)



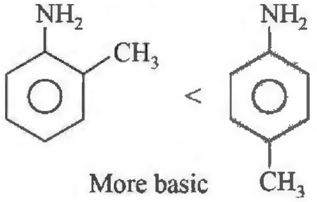
$H_2\ddot{N}-\underset{\underset{NH}{||}}{C}-NH_2 \longleftrightarrow H_2\overset{\oplus}{N}=\underset{\underset{NH}{||}}{C}-NH_2 \quad H_2N-\underset{\underset{NH}{||}}{C}-\ddot{N}H_2 \longleftrightarrow H_2N-\underset{\underset{^{\ominus}NH}{||}}{C}=\overset{\oplus}{N}H_2$

(I) (II) (I) (III)

Both II and III having equal contributing resonating structure.

(B) Diethyl amine will have more H-bonding.

(C)



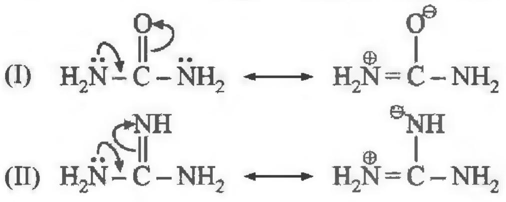
More basic

(D) Because of +I effect of methyl groups

27.(ABCD)

(A) Lone pair on the bridged nitrogen is easy to protonate

(B)



$(I)\ H_2\ddot{N}-\overset{\overset{O}{||}}{C}-\ddot{N}H_2 \longleftrightarrow H_2\overset{\oplus}{N}=\overset{\overset{O^{\ominus}}{|}}{C}-NH_2$

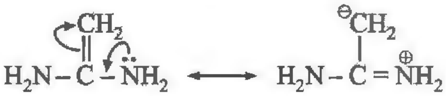
$(II)\ H_2\ddot{N}-\overset{\overset{NH}{||}}{C}-NH_2 \longleftrightarrow H_2\overset{\oplus}{N}=\overset{\overset{^{\ominus}NH}{|}}{C}-NH_2$ (N is more electron donor)

Secondary amine is more basic than primary amine

28.(BCD)

(B) CH_3COOH is more acidic than $Ph-OH$

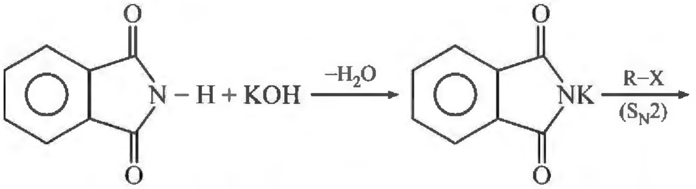
(C)



$H_2N-\overset{\overset{CH_2}{||}}{C}-\ddot{N}H_2 \longleftrightarrow H_2N-\overset{\overset{^{\ominus}CH_2}{|}}{C}=\overset{\oplus}{N}H_2$

(D) Lone pair of Nitrogen is in conjugation. So it will not be available for protonation.

29.(CD)



Reactivity order for S_N2

$1°\ R-X > 2°\ R-X$

Alkylhalide > Aryl halide

1° Allyl halide > 1° Alkyl halide

30.(AB)

$CH_3-Br+NH_3 \xrightarrow{S_N2} CH_3NH_2+HBr$

Excess (Nucleophile)

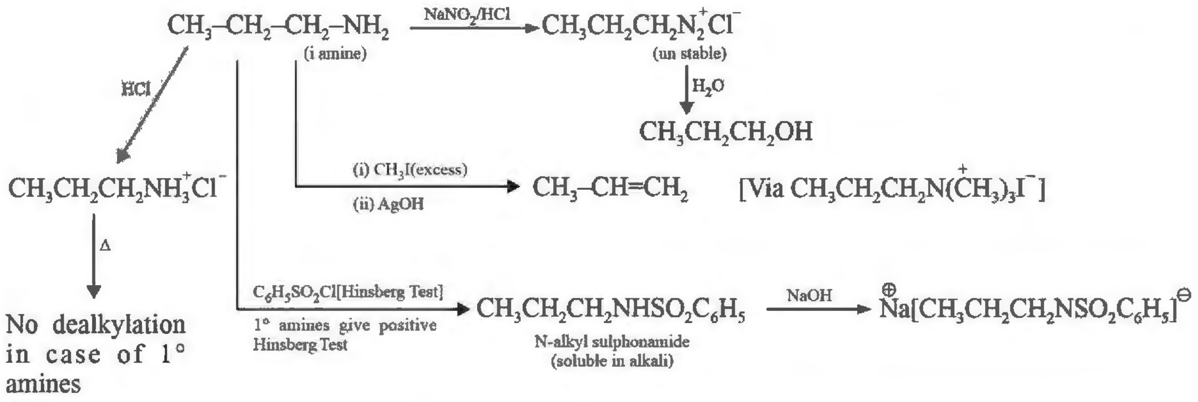
$CH_3Br+CH_3NH_2 \longrightarrow CH_3NHCH_3+HBr$

$CH_3Br+(CH_3)_2NH \longrightarrow (CH_3)_3N+HBr$

$CH_3Br+(CH_3)_3N \longrightarrow (CH_3)_4NBr$

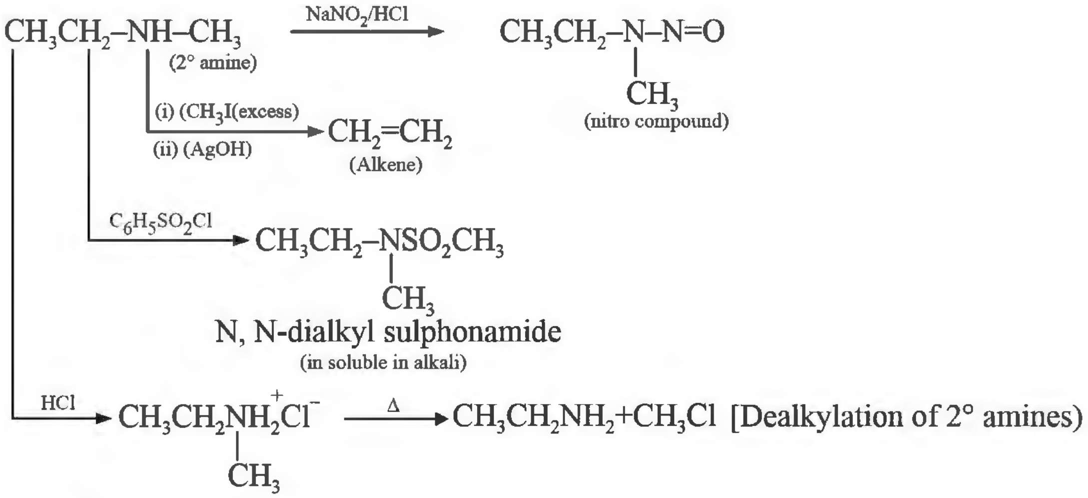
31. **A $\rightarrow$ r,s,t; B $\rightarrow$ p, r, s; C $\rightarrow$ s; D $\rightarrow$ q, t**

(A)



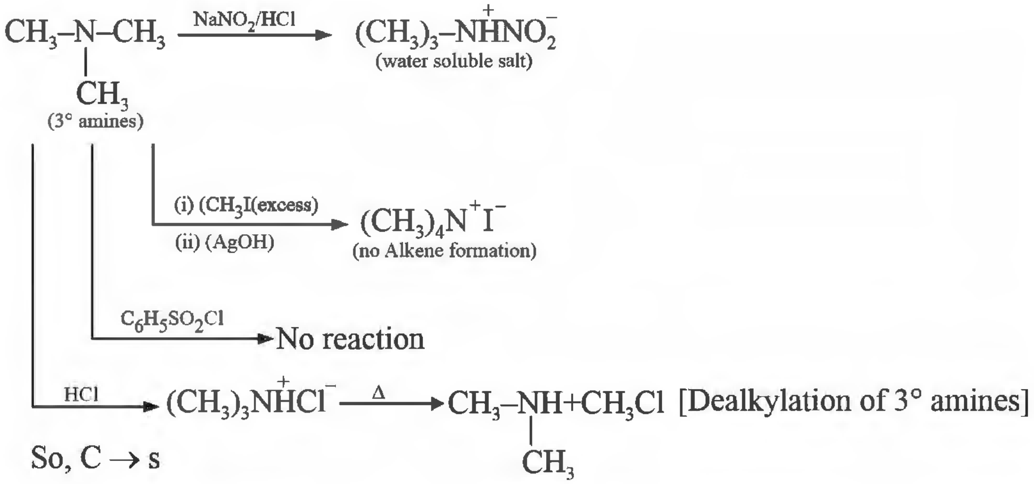
So, A $\rightarrow$ *r*, *t*.

(B)



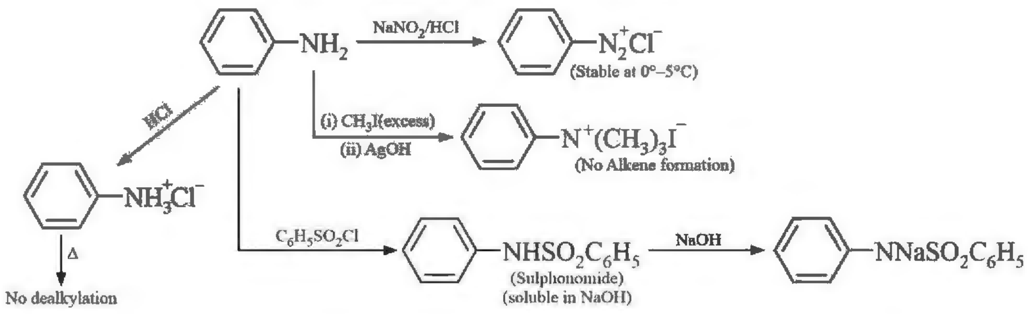
So, B $\rightarrow$ p, r, s

(C)



So, C $\rightarrow$ s

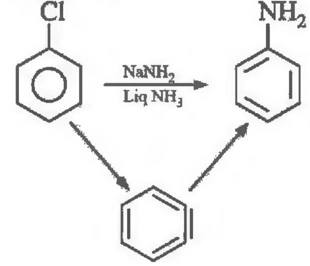
(D)



So, $D \rightarrow q, t$

32.A →s; B →r ; C →q; D →p

(A)



; N Nucleophilic substitution through benzyne intermediate

(B)

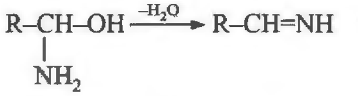
; electrophilic substitution (Nitration reaction)

(C)

$$\begin{tikzcd}
\text{R–CH}_2\text{–NH}_2 \arrow[r] \arrow[d, "\text{NaNO}_2\text{/HCl}"] & \text{R–COOH} \\
\text{R–CH}_2\text{–OH} \arrow[ur, "{[O]}"'] &
\end{tikzcd}$$

; oxidation reaction (addition of oxygen)

(D)

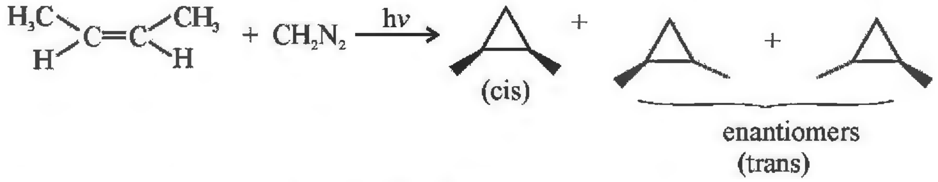


$$\underset{\displaystyle \text{NH}_2}{\text{R–CH–OH}} \xrightarrow{-H_2O} \text{R–CH=NH}$$

; Elimination Dehydration

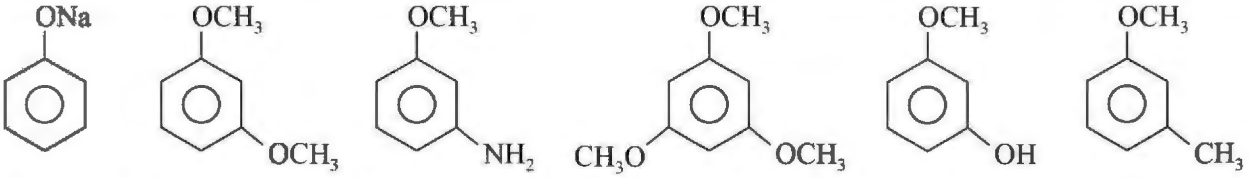
33.(3) It is Hofmann's Bromamide reaction and in this reaction cross over products are not obtained.

34.(3)



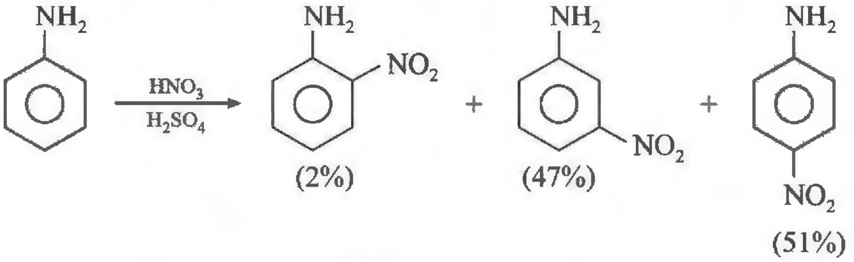
35.(4) $PhNO_2 + 4H^+ + 4e^- \longrightarrow PhNHOH + H_2O$

36.(6)

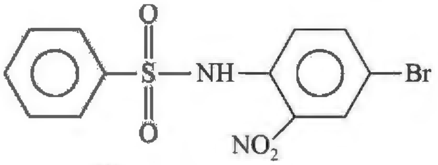


Presence of electron releasing group in anisole will make it more reactive toward coupling reaction with diazonium salt.

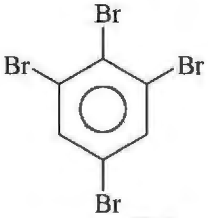
37.(2)



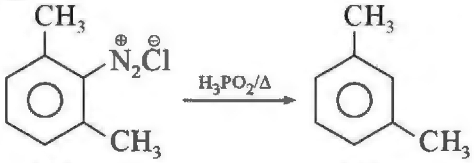
38.(4)



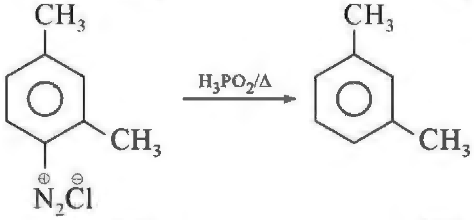
39.(4)



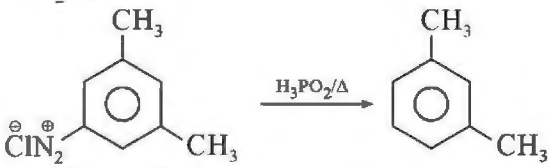
40.(03) (i)



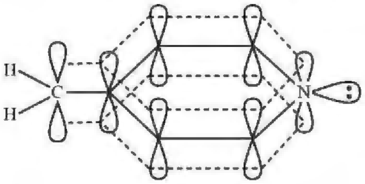
(ii)



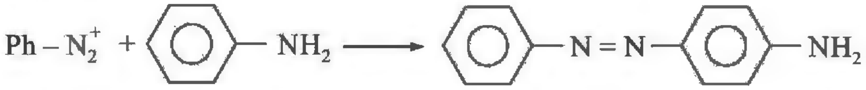
(iii)



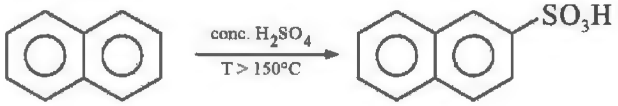
42.(7)



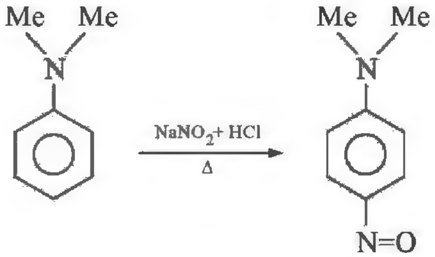
43.(3) (i) Correct



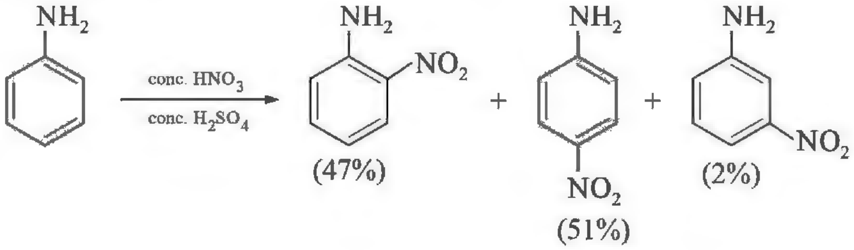
(ii) Incorrect



(iii) Correct



(iv) Incorrect



Surface Chem, Biomolecules, Practical Organic Chem & Polymers

1.(B) Phenols give violet colour with $FeCl_3$ solution while alcohols do not.

2.(B) $RCOOH \longrightarrow RCONH_2 \xrightarrow[H^+]{H_2O} NH_3 + RCOOH$

$n_{NH_3} = 1 = n_{RCONH_2}$

$\therefore$ Mo(amide) $= 59g$

$\therefore$ Mo(acid) $= 59 - 15 + 16 = 60g$ i.e. CH_3COOH

3.(A) $\%C \Rightarrow 38.7 \Rightarrow \dfrac{38.7}{12} = 3.225\,\text{mol}$

$\%H \Rightarrow 16.17 \Rightarrow \dfrac{16.17}{1} = 16.17\,\text{mol}$

$\%N \Rightarrow 45.17 \Rightarrow \dfrac{45.17}{14} = 3.225\,\text{mol}$

Divide by 3.225
$C = 1,\ H = 5,\ N = 1$
so, empirical formula is CNH_5 i.e. CH_3NH_2

4.(D) CAN is a test of –OH group and not –COOH group

5.(D) $C_xH_y + \left(x + \dfrac{y}{4}\right)O_2 \longrightarrow xCO_2 + \dfrac{y}{2}H_2O$

Moles of organic compound $= \dfrac{20}{12x + y}$

$\therefore$ moles of $H_2O = \dfrac{10y}{12x + y} = \dfrac{10}{18} \Rightarrow 18y = 12x + y \quad \therefore \quad 17y = 12x$

$$\% H = \frac{y}{12x + y} \times 100 = \frac{\frac{12x}{7}}{12x\left[1 + \frac{1}{17}\right]} = \frac{1}{18} \times 100 = 5.55\%$$

or Mass of Hydrogen (H_2) in the sample $= \dfrac{10}{18} \times 2\,g$ ($\because$ after combustion all the hydrogen in the hydrocarbon will be present in the water formed) $\Rightarrow$ % of hydrogen $= \dfrac{\frac{10}{18} \times 2}{20} \times 100 = 5.55\%$

6.(C) Mass of sulphur $= \dfrac{0.35}{233.43} \times 32g \Rightarrow$ % sulphur $= \dfrac{\frac{0.35 \times 32}{233.43}}{0.2595} \times 100 = 18.5\%$

7.(D) Mass of nitrogen $= 200 \times 10^{-3} \times 14\,g \Rightarrow$ % of nitrogen $= \dfrac{(200 \times 1) \times 10^{-3} \times 14}{6} \times 100 = 46.67\%$

8.(A) –OH group below the plane of paper at C–1 in Haworth projection

9.(C) Other three have aldehyde linkage.

10.(A) Mutarotation is an equilibrium phenomenon of $\alpha -$ form, open chain & $\beta -$ form

11.(C) Muta rotation result (Learn as a fact)

12.(D) Adding NaCl will not cause any change in the pH of the solution.

13.(D) $[H^+]=\sqrt{Ka_1Ka_2}$ as [(conjugate acid)] = [conjugate base]

14.(A) Silk is a natural product made from the fibres found in the cocoon of the mulberry silk worm. It is actually made up of long strands of protein sericin and fibrosin which are polymers of amino acids.

15.(B) Vulcanised rubber contains linear chains having some branches.

16.(C) $CH_3-CH_2-NH_2$ has only one functional group, have it can't undergo self-polymerisation

17.(B) Polyethyene, PVC and polycryalonitrie (orlon) are addition polymers.

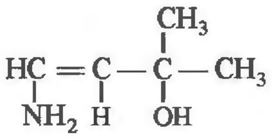
18.(B) Steric crowd makes $NaHSO_3$ addition difficult around carbonyl group.

19.(C) Because C–I of both units are linked through glycoside linkage.

20.(D) $\text{Fructose}\overset{OH^-}{\rightleftharpoons}\text{Mannose}\rightleftharpoons\text{Glu cos e}$ (Fact)

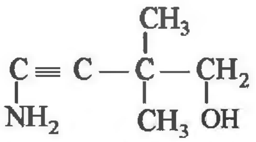
21.(C) Because C–I of both units are linked through Glycosidic linkage.

22.(C)



$HC(NH_2)=CH-C(CH_3)(OH)-CH_3$

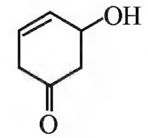
(I)



$C(NH_2)\equiv C-C(CH_3)(CH_3)-CH_2(OH)$

(II)

(I) gives immediately turbidity by lucas reagent and (II) does not give turbidity appreciably.

23.(C) The compound  gives positive test with Na metal, 2, 4-DNP and it gives single product with O_3

24.(B) The compound $C_{30}H_{60}O$ has one degree of unsaturation since it gives negative test with Br_2/H_2O, 2, 4-DNP and Na metal it must be an epoxide.

25.(A) Sodium aluminium silicate (zeolite) acts as an ion exchange medium. Calcium and magnesium cations in hard water are exchanged for the sodium ions of the zeolite.

26.(B) Silver sol is an example of lyophobic colloid.

27.(A) When Freshly precipitated $Fe(OH)_3$ is shaken with little amount of dilute solution of $FeCl_3$ electrolyte, peptization process takes place by converting the $Fe(OH)_3$ precipitate into positively charged colloidal solution of $Fe(OH)_3$.

28.(C) Rubber plating and chrome tanning are based on electrophoresis.

29.(A) Gold number $\propto \frac{1}{\text{protective power}}$

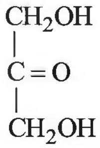
30.(C) Both absorption and viscosity are bulk phenomenon.

31.(D) Colloidal particle range → 1nm to 1000nm.

32.(B) An oligosaccharide is a carbohydrate whose molecules are composed of relatively small number of monosaccharide units (typically 3 to 10).

33.(C) Nucleic acid is deoxyribose.

34.(A) The simplest ketose is dihydroxyacetone or ketotriose which has only 3 carbon atoms and is the only one with no optical actively



$CH_2OH-C(=O)-CH_2OH$

35.(A) The given unsymmetrical molecule has 4 chiral carbon so it has $2^4 = 16$ optical isomers.

36.(A) Ziegler-Natta polymerization is an example of addition polymerization.
37.(D) All three (A, B & C) correctly represents addition polymerization process.

38.(A) pKa_3 value of side chain determines the nature of amino acid.

39.(B) For acidic amino acids $PI = \frac{Pka_1 + Pka_3}{2} = \frac{1.88+3.65}{2} = \frac{5.53}{2} = 2.77$

40.(B) For basic amino acids $PI = \frac{Pka_2 + Pka_3}{2} = \frac{8.95+10.53}{2} = \frac{19.48}{2} = 9.74$

41.(AC) **(A)** $\Delta G = \Delta H - T\Delta S < 0$ as $\Delta S < 0$ SO $\Delta H = -ve$

(B) Micelles formation will take place above T_K and above CMC

(C) Read NCERT

(D) Fe^{3+} ion will have greater flocculability power so smaller flocculating value.

42.(AC) By the condition of the question I & IV both compounds do not give iodoform test and I and II both give similar test.

43.(AB) Methylaniline is the only base in the mixture and benzoic acid is a much stronger acid than phenol.

44.(AC) Physisorption requires low temperature and approx zero activation energy.

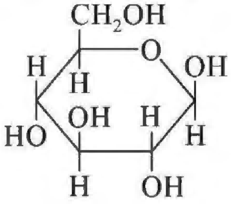
45.(BC) The pressure decreases due to the adsorption of gas molecules on the surface of charcoal.

46.(AB) When positive & negative colloids are added in suitable amounts, mutual coagulation takes place.

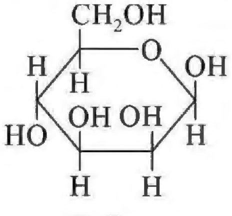
47.(AC) Sulphur and gold sol $\Rightarrow$ multimolecular colloid, egg albumin in water = macromolecule colloid, soap solution associated colloid

48.(AC) Blue color of sky is due to tyndall effect and ultra microscope is also based on the same principle of light scattering.
49.(ACD) The given structure is similar to pyran, so it is said to be in pyranose form. It is a β – anomer since the –OH at anomeric C is facing upwards. It is a D sugar.

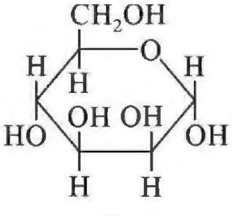
50.(AC) D– Glucose is



So D–Manose is



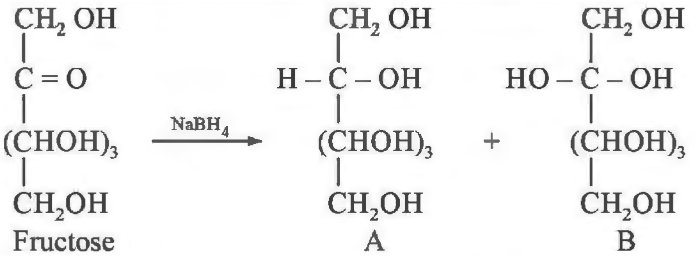
β–form



α–form

51.(BC) Glucose and fructose are reducing sugars since they react with Tollen's Reagent and Fehling solution.
52.(AB) Starch and cellulose are polysaccharides of glucose. Sucrose is a disaccharide composed of glucose and fructose. Lactose is a disaccharide composed of glucose and galactose.
53.(BD) II and III are D sugars since the lowest chiral C has –OH group on the right side on the contrary. I has –OH on the left side and so it is a L-sugar.

54.(ABD)



$$\underset{\text{Fructose}}{\begin{array}{c}CH_2OH\\|\\C=O\\|\\(CHOH)_3\\|\\CH_2OH\end{array}} \xrightarrow{NaBH_4} \underset{A}{\begin{array}{c}CH_2OH\\|\\H-C-OH\\|\\(CHOH)_3\\|\\CH_2OH\end{array}} + \underset{B}{\begin{array}{c}CH_2OH\\|\\HO-C-OH\\|\\(CHOH)_3\\|\\CH_2OH\end{array}}$$

A and B are diastereomers. They are C-2 epimers. They are both optically active hexahydroxy compounds.

55.(ABCD) All the statements are correct.

56.(ABC) Protein, nylon-6, 6 and nylon-6 are polyamide polymers since all of them have amide linkage.

57.(CD) Since here two different substances polymerise, copolymerization is said to have occurred. Also since a water molecule is lost in the process it is condensation polymerisation.

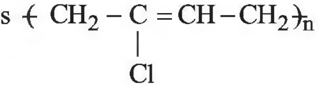
58.(BCD) Starch is a mixture of two different polysaccharides : Amylose (15 – 20%) and Amylopectin (80 – 85%). It involves the $(C_1 - C_4)$ α–glycosidic linkage between two $\alpha - D$ glucose units.

It involves branching by $(C_1 - C_6)$ glycosidic linkage.

59.(CD) $\alpha - D$ glucose undergoes mutarotation when dissolved in water to form $\beta - D$ glucose.

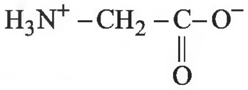
Sucrose is a disaccharide composed of $\alpha - D -$ glucose and $\beta - D -$ fructose.

60.(ACD) Neoprene is



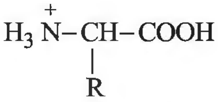
$$-\!\!\!\left(CH_2 - \underset{Cl}{\underset{|}{C}} = CH - CH_2 \right)\!\!\!-_n$$

61.(ABC) At isoelectric point:



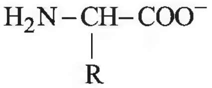
$$H_3N^+ - CH_2 - \underset{O}{\underset{\|}{C}} - O^-$$

In acidic medium :



$$H_3\overset{+}{N} - \underset{R}{\underset{|}{CH}} - COOH$$

In basic medium :



$$H_2N - \underset{R}{\underset{|}{CH}} - COO^-$$

62.(ABCD) Anomers have different stereochemistry at C – 1 (anomeric carbon).

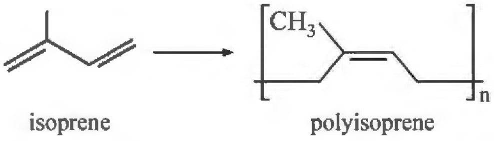
When pure $\alpha - D -$ glucopyranose is dissolved in water mutarotation occurs.

63.(AC)

(A) $nHOOC-(CH_2)_4-COOH + nH_2N-(CH_2)_6-NH_2 \longrightarrow \text{Nylon}-6,6 + H_2O$

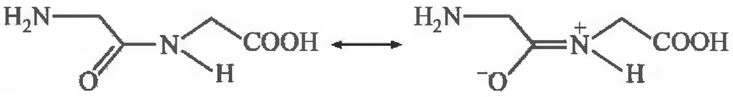
(B) Cellulose triacetate is semi synthetic polymer

(C)



(D) Sucrose is disaccharide

64.(ABCD)



Peptide linkage is an amide linkage capable to form H-bond (hydrophilic in nature) and connects polypeptide chain in protein through H-bond.

65. **[A-r] → [B-s] → [C-p, q] → [D-r]**
Kjeldahl's method and dumas method for nitrogen

Calius method for halogen and sulphur Leibig's method for carbon and hydrogen

66. **[A-p, q, s] → [B-p, q, r] → [C-r] → [D-s]**
CAN Test = for alcohol and phenol
Ester test = for carboxylic acid and alcohols
Oxidation test = for alcohols and aldehydes

Libermann's test = For 2° amines (Nitroso amines) and phenol

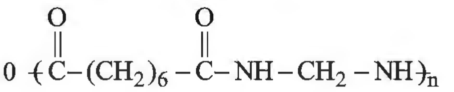
67. **[A-p, r, t] → [B-p, s, t] → [C-p, s, t] → [D-q, r]**

- Reducing sugar ⇒ Where the aromatic carbon has an OH group attached that can reduce other compounds
- Non-reducing sugar ⇒ where the aromatic carbon don't have an OH group attached so they can't reduce other compounds.
- Anomers ⇒ they are diasteroisomers of cyclic forms of sugar or similar molecules differing in configuration at anomeric carbon.
- Epimers ⇒ Two isomers with different configuration of atoms about one or several asymmetric carbon atoms present.
- Mutarotation ⇒ change in optical rotation because of the change in equilibrium between, anomers, when the corresponding stereocentres interconvert.

68. **[A-q, r, s] → [B-r, s] → [C-p, r, s] → [D-p, r, s]**

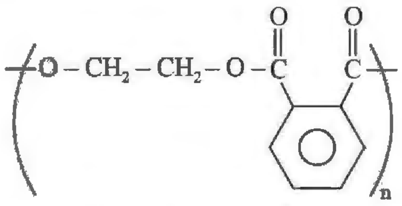
- Acidic amino acids ⇒ Aspartic acid, Glutamic acid
- Basic amino acids ⇒ Serine, Threonine, asparagine, Glutamic acid
- Optically active amino acids ⇒ All except glycine

69. **[A-q, r] → [B-p, r] → [C-s] → [D-r]**

(A) Nylon 6, 10 
$+\!\!\left(\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_6-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-NH\right)_n$

Monomers ⇒ $HOOC-(CH_2)_8-COOH$ and $H_2N-(CH_2)_6-NH_2$

(B) Glyptal ⇒

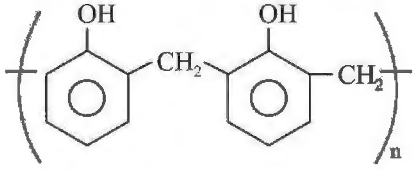


Monomers : Pthalic acid and glycol

(C) Teflon ⇒ $\left(CF_2-CF_2\right)_n$

Monomer ⇒ $CF_2=CF_2$

(D) Bakelite ⇒

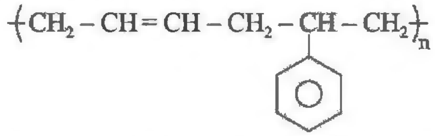


70. **[A-p, r] → [B-p, s] → [C-q, s] → [D-q, s]**

(A) Polythene $\Rightarrow$ $\left(CH_2-CH_2\right)_n$

Monomer $\Rightarrow$ $CH_2=CH_2$

(B) Buna-S-rubber $\Rightarrow$

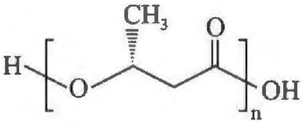


Monomer $\Rightarrow$ $H_2C=CH-C_6H_5$ and $CH_2=CH-CH=CH_2$

(C) Melamine – Formaldehyde resin

Monomer $\Rightarrow$ Melamine and formaldehyde

(D) Poly-hydroxy butyrate-Co-β-Hydroxy valerate



71. **[A-p, s] → [B-r] → [C-q] → [D-p, s]**

(A) $Fe(OH)_3$ $\Rightarrow$ Lyophobic colloid & hence irreversible

(B) Micelles $\Rightarrow$ They are associated colloids

(C) Gelatin $\Rightarrow$ It is a lyophilic colloid

(D) Arsenious sulphide (AS_2S_3) $\Rightarrow$ lyophobic colloid and hence irreversible

72. **[A-s] → [B-r] → [C-q] → [D-p]**

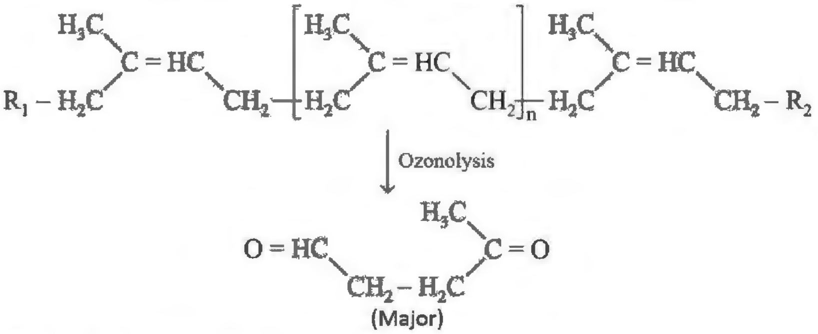
(A) Coagulation $\Rightarrow$ It is done by addition of electrolyte

(B) Dialysis $\Rightarrow$ If is a method of preparation of colloid

(C) Peptization $\Rightarrow$ It is defined as the process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte

(D) Tyndall effect : The scattering of light as the light beam passes through a colloid.

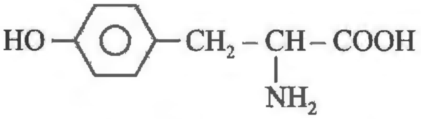
73.(5)



R₁ and R₂ are chain terminating agents.

74.(8) Except (ix) all other observations are correct.

2-amino-3 (p-hydroxy phenyl) propanoic acid is



This is not formed on hydrolysis.

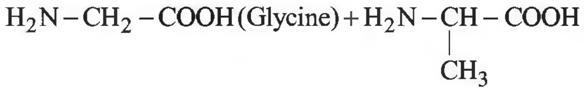
75.(8) Compounds (I), (IV), (V), (VII) and (IX) give positive haloform test. Compound (III), (VII) and (IX) gives positive Lucas reagent test, $x=5$, $y=3$ so, $(5+3)=8$.

76.(6) Na Metal, $HCl + ZnCl_2$, $FeCl_3$, NaOH + Phenolpthalein, dil. $KMnO_4$, Br_2/H_2O gives positive test with ascorbic acid.

77.(5) 1, 2, 3, 6, 8

78.(8)

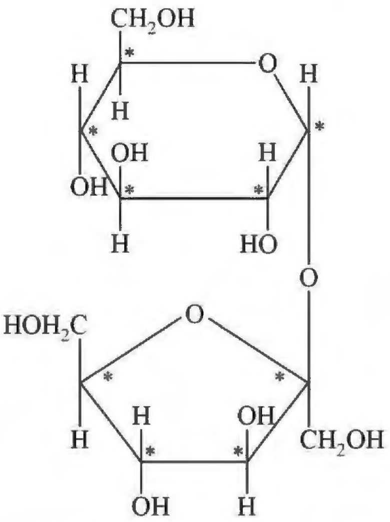
79.(9)



$H_2N-CH_2-COOH\,(\text{Glycine}) + H_2N-\underset{\displaystyle CH_3}{\underset{|}{C}H}-COOH$

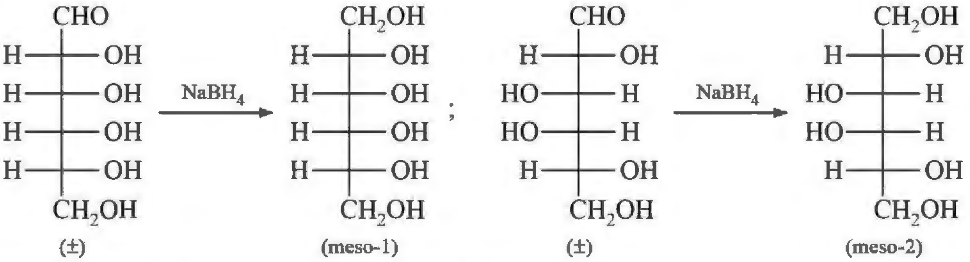
(1) Gly – Gly
(2) Gly – ala(+)
(3) Gly – ala(–)
(4) Ala(+) – Gly
(5) Ala(–) – Gly
(6) Ala(+) – Ala(+)
(7) ala(+) – ala(–)
(8) ala(+) – ala(–)
(9) ala(–) – ala(+)

80.(9)



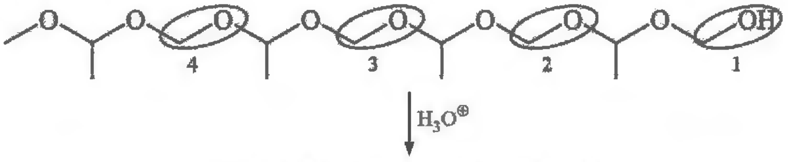
The star sign indicates chiral centre.

81.(4)



So in total 4 stereoisomers are reduced to meso products.

82.(4)



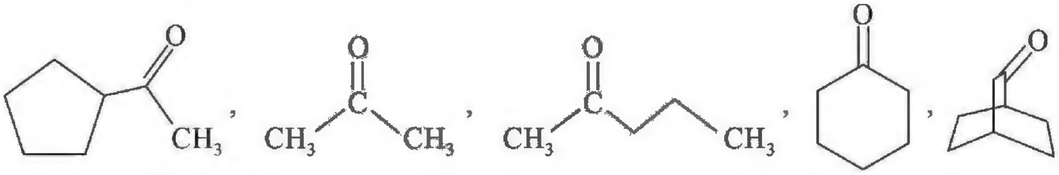
$CH_3-OH + 4CH_3-CH=O + 4HCHO$

83.(4) (A) has no C–OH group, α to the CH = O group. So it forms only phenylhydrazone with 1 mole of $PhNH\,NH_2$.

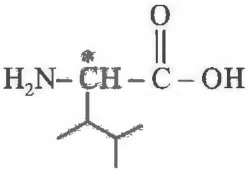
(B) has (C–OH) group α to the CH = O group, so it forms only ozazone by reaction with 3 mole of $PhNH\,NH_2$.

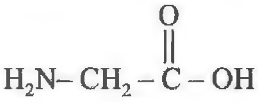
84.(6) Neutral amino acid & acidic amino acid are negatively charged at pH = 7.0
Alanine, Cysteine, Glutamic acid, Glycine, Leucine, Aspartic acid

85.(5) 2, 4-DNP test given by,

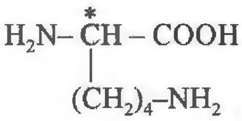


86.(3)

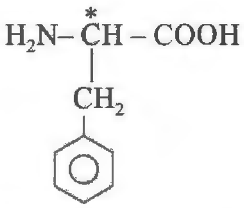




$H_2N-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$



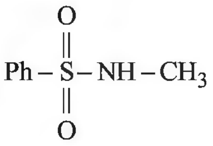
$H_2N-\overset{*}{C}H(-(CH_2)_4-NH_2)-COOH$



$H_2N-\overset{*}{C}H(-CH_2-C_6H_5)-COOH$

87.(1) In case both N and S are present in an organic compound. Blood red color is obtained due to formation of sodium thiocyanate.

(c)



$Ph-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-NH-CH_3$

88.(2.5)

$\frac{x}{m}=k\cdot P^{1/n}$ since $\log k = 0.699$, hence $k = 5$; Hence $k = 5$

Slope $=\frac{1}{n}=\tan 45° = 1$, thus, $\frac{x}{m}=5\times 0.5 = 2.5\,g/g$ adsorbent

Coordination Compounds

1.(B) Both Cr^{2+} and Fe^{2+} contain 4 unpaired electrons in each.

2.(B) According to Effective atomic number rule, EAN of Co is 36. Hence $Co(CO)_4$ attain stability either by reduction or by dimerization.

Effective atomic number of $[Co(CO)_4]^- = 27-(-1)+2\times4=36$

Effective atomic number of $[Co_2(CO)_8] = \dfrac{(27\times2)+(1\times2)+(2\times8)}{2}=36$

3.(A) $\left[Pt(gly)_2\right]^{2+}$ is square planar complex and glycinate is bidentate ligand with different donor atoms

4.(B) (a) $[Cr(EDTA)]^{2-}$

Here Cr is in +2 oxidation state

EAN = 24 – 2 + 12

= 34

(b) $[Co(en)_3]^{2+}$

EAN = 27 – 2 + 12

= 37

(c) $[Fe(C_2O_4)_3]^{3-}$

EAN = 26 – 3 + 12 = 35

(d) $[Ni(CN)_4]^{2-}$

EAN = 28 – 2 + 8 = 34

5.(B) Primary valency is equal to oxidation state while secondary valency is the number of electron pairs accepted.

6.(A) Number of unpaired electrons are based on oxidation state and crystal field theory.

7.(A) Basis on unpaired electron.

8.(A) Based on number of ions produced by ionization.

9.(C) Formula of given complex is $\left[Co(en)_2Cl_2\right]Cl$ which ionizes to give one mole of Cl^- per mole of compound.

10.(A)

Conductance $\propto$ no. of ions

		Molecular formula	No. of ions
A	$PtCl_4.6NH_3$	$[Pt(NH_3)_6]Cl_4$	5
B	$PtCl_4\cdot5NH_3$	$[Pt(NH_3)_5Cl]Cl_3$	4
C	$PtCl_4\cdot4NH_3$	$[Pt(NH_3)_4Cl_2]Cl_2$	3

(A) Has maximum conductance

11.(B) No action of HCl suggests that all NH_3 are present in coordination sphere.

12.(B) $\Delta T_f = iK_fm$; $0.0054 = i\times1.8\times0.001$; $i=3$

13.(D) Statement 1 is incorrect

$[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$ are linkage isomers

Statement 2 is also correct as both compounds give Cl^- in solution.

14.(A) Trans isomer has plane of symmetry.

15.(A) F^- is weak field ligand while NH_3 acts as strong field ligand.

16.(A) Exchange of negatively charged ligand of coordination sphere and anion of ionization sphere produce ionization isomerism.

17.(C) The two forms are $[Cr(NH_3)_4ClBr]Cl$ and $[Cr(NH_3)_4Cl_2]Br$

18.(C) The given square planar complex is $\left[M(NH_3)_2Cl_2\right](CrO_4)$. Further A can react with $Ag_2C_2O_4$, indicates it could be cis form because the two similar monodentate ligands from cis positions can be replaced by one bidentate ligand.

19.(B) For 100% dissociation, Van't Hoff's factor(i) = no. of ions produced (n). Thus ratio is 5/7.

20.(C) $\left[Cu(NH_3)_4\right]^{2+}$ is a square planar complex.

21.(D) I. $[Fe(H_2O)_6]^{3+}$

$Fe^{3+} : 3d^5$

– It is high spin complex

– No. of unpaired $e^- = 5$

II. $[Cr(NH_3)_6]^{3+}$

– $Cr^{3+} : 3d^3$

– No. of unpaired $e^- = 3$

III. $[CoCl_4]^{2-}$

– $Co^{2+} : d^7$ complex

- High spin complex

- No. of unpaired $e^- = 3$

22.(B) $Cl^- = HCl = NaOH$

$nCl^- + nH^+ \rightarrow nHCl$

Thus 1 mol of complex will form n mol of HCl

1 mole of complex = n mol of HCl = n mole of NaOH

Mole of complex $= \dfrac{0.319}{266.5} = 0.0012$; mole of NaOH used $= \dfrac{28.5 \times 0.125}{1000} = 0.0036$

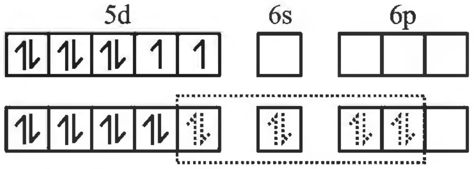
So 0.0012 mole of complex = 0.0036 mole of NaOH = 0.0036 mole of HCl

1 mole of complex $= \dfrac{0.0036}{0.0012} = 3$ mole of HCl $\quad \therefore \; n = 3$ So complex is $[Cr(H_2O)_6]Cl_3$.

23.(B) CFSE depends on the relative magnitude of crystal field splitting, Δ_0 and pairing energy and in turns Δ_0 depends upon the field produced by ligand and charge on the metal ion. The order of increasing crystal field strength is $F^- < H_2O < NH_3 < CN^-$

24.(A) $Pt^{2+}\left([Xe]4f^{14}5d^8\right)$

$\left[PtCl_2(NH_3)(H_2O)\right]$



dsp^2 hybrid orbitals

Four pairs of electrons from four Cl^-

Ma_2bc have cis and trans isomers.

25.(B) Chelate complexes are more stable than non chelate complexes

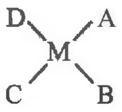
26.(D) $[Cr(H_2O)_6]^{3+}$ has the largest CFSE because of stable configuration

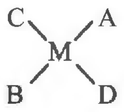
$Cr^{3+} = d^3 = t_{2g}^{\ 3}$

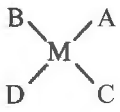
$$CFSE = (-0.4 \times 3)\Delta_0 = -1.2\Delta_0$$

27.(B) IUPAC Name : Potassium trioxalatoaluminate (III)

28.(C) M(ABCD) have 3 geometrical isomers







29.(C)

	No of ions
$[Pt(NH_3)_4]Cl_4$	5
$[Pt(NH_3)_2Cl_4]$	0
$[Pt(NH_3)_5Cl]Cl_3$	4
$[Pt(NH_3)_2Cl_2]Cl_2$	3

30.(C) cis $[Co(NH_3)_2(en)_2]^{3+}$ is Optically Active because of absence of symmetry element.

Trans $[M(AA)_2a_2]$ is optically inactive due to presence of POS while cis$[M(AA)_2a_2]$ is Optically Active due to absence of Symmetry element.

31.(B) $[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$

100 ml 0.1 M

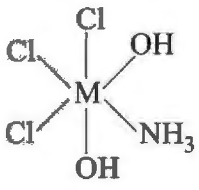
= 10 mmol

– 20 mmol

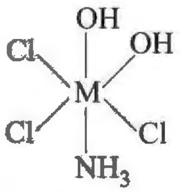
Moles of AgCl obtained = 0.02 mol

32.(A)
- (A) Is correct as Tetrahedral complexes do not show Geometrical Isomerism
- (B) Is incorrect as square planar Complexes show G.I.
- (C) Incorrect . Ma_3b will not shown G.I.
- (D) $[Pt(gly)_2]$ show cis-trans isomerism

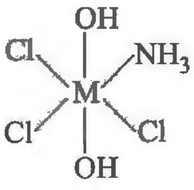
33.(B)



"Fac"



"Mer"



"Mer"

34.(C) 4.91 BM Indicates 4 unpaired e^-.

- Ion could be Fe^{2+}

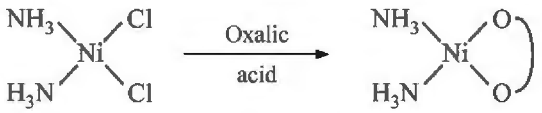
- Fe^{2+} has 4 unpaired electron. ($3d^6$ configuration)

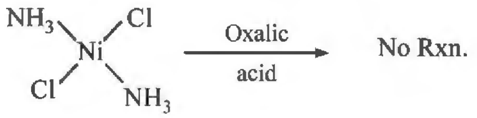
- Fe^{2+} with strong field ligand has 0 unpaired electron

35.(B) $[Ni(NH_3)_4]^{2+} \xrightarrow{HCl} [Ni(NH_3)_2Cl_2]$

exist in 2 forms

Cis and Trans





36.(D) $[Co(NH_3)_5Br]SO_4$ shows Ionisation Isomerism because of presence of ion in co-ordination and Ionisation sphere.

37.(A) Magnitude of Δ_0 directly proportional to principal quantum number of d sub-shell.

38.(C) In octahedral field, ligands pointing towards lobes of $d_{x^2-y^2}$ and d_{z^2} orbitals.

39.(C) $Ti^{3+}_{(aq)}$ coloured because of d-d transition while Ti^{4+} is colourless because of d^0 configuration.

40.(D) $[Ni(PPh_3)_2Br_2]$ is tetrahedral complex

		Hybridisation	
a)	$[Ni(CN)_4]^{2-}$	dsp^2	Square planar
b)	$[Ni(CO)_4]$	sp^3	Tetrahedral
c)	$[NiCl_4]^{2-}$	sp^3	tetrahedral

41.(A) (A) $[RhCl(CO)(pph_3)_2]$

$Rh^+ : 4d^8$

Hybridization : dsp^2 (square planar)

(B) $K_3[Cu(CN)_4] : d^{10} \longrightarrow sp^3$

(C) $k_2[Zn(CN)_4] : d^{10} \longrightarrow sp^3$

(D) $[Ni(CO)_4] : d^{10} \longrightarrow sp^3$

42.(D) $[Pt(gly)_2]$ shows cis-trans isomerism

$[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ shows cis-trans isomerism

43.(D) $[Ni(CO)_4] : 3d^8 4s^2 \xrightarrow{SFL} 3d^{10}$

- It is sp^3 hybridized
- Tetrahedral

(D) is False because Metal-Carbon bond order increases due to synergic Bonding

44.(C)

$Ni(CO_4)$	sp^3	- diamagnetic
$Fe(CO)_5$	dsp^3	- diamagnetic
$V(CO)_6$	d^2sp^3	- Paramagnetic
$Cr(CO)_6$	d^2sp^3	- diamagnetic

45.(D) All statements are correct

Metal carbon bond in metal carbonyls possess double bond character due to synergic bonding. As extent of synergic bonding increases, Metal-carbon bond order increases and C-O bond order decreases.

46.(ABD) EDTA is Polydentate (denticity = 6)

- Flexidentate (it can change its denticity if required)
- Chelating ligand as it form Ring with metal.

- $[Ni(H_2O)_6]^{2+}$ is more stable than $[Co(H_2O)_6]^{2+}$ due to more Z_{eff}.

47.(BCD) - (B) is correct Octahedral complexes of Ma_3b_3 show fac-mer isomer.

- $[Mg(EDTA)]^{2-}$ - contains 5 Rings

EDTA is hexadentate ligand. No. of Rings formed by a ligand = 5
- MABCD Optically Active – Possess 2 stereo isomers

48.(ABD) Square planar complex of Ma_2b_2, octahedral complexes of Ma_4b_2, Ma_3b_3 and $M(AA)_2a_2$ exhibit geometrical isomerism.

49.(ABD) $\left[CoCl_2\left(NH_3\right)_2 en\right]^+$ has 3 geometrical isomers out of which, one is optically active to give d and l forms.

50.(ABC) Absence of unpaired electron.

51.(ABC) To exhibit coordination isomerism, both cation and anions should be complex ions

52.(ABCD) $[Ag(NH_3)_2]^+$ is linear with sp hybridization.

$NiCl_4^{2-}$, VO_4^{3-}, MnO_4^- - tetrahedral geometry

$[Cu(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$ - Square planar

$Fe(CO)_5$ - trigonal bipyramidal

53.(BC) Based on oxidation state and crystal field theory.

54.(ABCD) It is expected that there is charge transfer between Fe and NO.

55.(CD) From Werner's theory the formula of the given complex in $\left[Co\left(NH_3\right)_5 Cl\right]Cl_2$

56.(ABD) (A) $\Delta_0 \propto$ ligand field strength

(B) Ti^{3+} : $3d^1$

$= t_2g^1$

CFSE = $-0.4\Delta_0$

(C) $NiCl_4^{2-}$ is paramagnetic while $Ni(CO)_4$ is diamagnetic

(D) correct

57.(D) (A), (B) and (C) are colourless due to d^0 configuration

58.(ACD) (A) Co^{3+} : $3d^6$

- It form low spin complex with NH_3, CN^- and NO_2^-
- diamagnetic
- d^2sp^3

(B) $[Zn(NH_3)_4]^{2+}$: $3d^{10}$ configuration

- sp^3 hybridized

(C) $[Fe(H_2O)_6]^{3+}$:

- Fe^{+3} : $3d^5$
- Paramagnetic with 5 unpaired electron
- sp^3d^2 hybridized
- $\mu = 5.92$

$[Fe(CN)_6]^{3-}$:

$Fe^{3+} : 3d^5$

-Form low spin complex with CN^-
-No. of unpaired electron = 1
- $\mu = 1.73$

(D) $K_4[MnF_6]$ and $K_3[FeF_6]$ have 5 unpaired electron $\mu = 5.92\,BM$

59.(ABCD) Crystal Field Theory explain Ionic Interactions between metal and ligands.
According to this theory, ligands are point charges and Metal is test charge. CFT considered Only Metal Ion d-orbitals in bonding.

60.(ABCD) Emperical Formula : $[Co(en)_2Cl_2]\,(NO_2)$

- It can show ionization isomerism :

$[Co(en)_2Cl_2]\,NO_2$ and $[Co(en)_2Cl(NO_2]Cl$

- It can show linkage Isomerism due to Presence of NO_2

$[Co(en)_2Cl(NO_2)]$ and $[Co(en)_2Cl(ONO)]$

- it can show Geometrical Isomerism also i.e. Cis and Trans. Cis is Optically Active and trans Isomer is Optically Inactive.

61.(BC) S_1 : Non Correct. Square planar complex are generally Optically inactive due to presence of plane of Symmetry.

S_2 : Correct. Δ_t is less than Δ_o as ligands are not interacting directly with metal.

S_3 : Correct

62.(AB) $\Delta_o \propto$ Zeff of Metal

$\propto$ ligand Field strength

(A) correct as CN^- is stronger ligand than H_2O

(B) correct as Zeff of $Co^{+3} > Co^{+2}$

(C) Not correct as Zeff of Rh > Co

(D) not correct as NH_3 is stronger ligand than H_2O

63.(B) $[Co(gly)_3]$ and Cis $[Co(en)_2Cl_2]$ show optical isomerism because of absence of symmetry element.

64.(BD) (A) Incorrect. $\Delta_0 \propto$ ligand Field strength correct order is:

$[Co(H_2O)\,(NH_3)_5]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$

(B) Correct

(C) Incorrect :According to Irving William Series Order of Stability is:

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

(D) $[Fe(H_2O)_6]^{3+}$:

$Fe^{3+} - 3d^5$

- No. of unpaired electrons = 4

- Magnetic moment $= \sqrt{35}$

$[CoF_6]^{3-}$:

$Co^{3+} - 3d^6$

- No. of unpaired electrons = 4

- Magnetic moment $\sqrt{24}$

$[Cr(CN)_6]^{3-}$:

Cr^{3+} : $3d^3$

- No. of unpaired electrons = 3

- Magnetic moment $= \sqrt{15}$

65.(ABC) (A) $[Ni(pph_3)_2Cl_2]$:

Ni^{2+} : $3d^8$

- tetrahedral and Paramagnetic

(B) $Ni(CO)_4$

Ni : $3d^8 4s^2$

With CO as ligand, it gets converted to $3d^{10}$

Hybridisation sp^3

Tetrahedral and diamagnetic

(C) $[Ni(CN)_4]^{2-}$:

Ni^{2+} : $3d^8$

With CN^- as ligand, it forms low spin complex

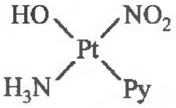
Hybridistation $= dsp^2$

Square planar and diamagnetic

66.(ACD) (A) $[Co(ox)_3]^{3-}$ is diamagnetic

(B) $CoCl_3 \cdot 3NH_3$ exist as $[Co(NH_3)_3Cl_3]$ is non conductor of electricity

(C) Number of Possible GI are 3



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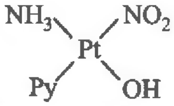

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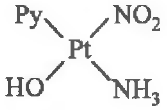


(D) Oxidation state of Iron in Brown Ring Complex is + 1

67.(AD) A and D can show Geometrical Isomerism

68.(BCD) (A) Not correct as Ti^{3+} Complexes are coloured

(B) $[Co(NH_3)_4Br_2]Cl$ can show Ionisation isomerism due to presence of Ions in Co-ordination and Ionisation Sphere. It show Cis-Trans Isomerism

(C) Correct

$[Pd(NO_2)_2(NH_3)_2]$

Pd^{2+} : d^8 low spin complex

: Square planar

69.(ABCD) (A) Shows Cis-trans Isomerism

(B) Shows fac-mer Isomerism

(C) Shows Optical Isomerism

(D) Shows Cis-trans Isomerism

70.(ABC) $[Fe(H_2O)_5NO]^{2+}$

- Here Fe is in +1 Oxidation state

- Number of unpaired e^- =3

- Hybridisation = sp^3d^2

71.(ABCD) (A) In Potassium Ferrocyanide $K_4[Fe(CN)_6]$, Iron is in +2 oxidation state and in potassium Ferricyanide $K_3[Fe(CN)_6]$, Iron is in +3 oxidation state.

(B) by adding aqueous solution of $BaCl_2$, $[Co(NH_3)_5Br]SO_4$ gives white ppt.

(C) Correct

$$AgNO_3 + Cl^- \longrightarrow \underset{\text{white ppt}}{AgCl\downarrow}$$

$$AgNO_3 + Br^- \longrightarrow \underset{\text{Pale yellow ppt}}{AgBr\downarrow}$$

(D) Correct

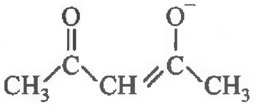
Conductance $\propto$ No. of Ions

72.(ABD) $[Fe(en)_2(H_2O)_2]^{2+} + en \longrightarrow \underset{\text{low spin complex}}{[Fe(en)_3]^{2+}}$

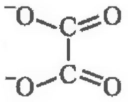
Fe^{2+} : $3d^6$ (diamagnetic)

It will not show Geometrical Isomerism but is Optically Active.

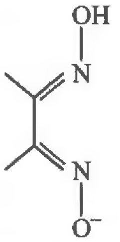
73.(AC) Acetylacetanato :



Oxalato ion : dianion



dimethyl glyoximatio :



74.(AB) Organometallic compounds have metal – carbon linkage. A and B are correct

75.(ABCD) $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ can be distinguished by

(A) $BaCl_2$: $BaCl_2$ gives white ppt with SO_4^{2-} ion but will not give any ppt with Br^-.

(B) $AgNO_3$: $AgNO_3$ gives pale yellow ppt with Br^- ion but will not give any ppt with SO_4^{2-}

(C) It can be distinguished by conductance due to different size

(D) It can be distinguished by dipole moment measurement due to difference in EN

76.(AD) (A) $MnCl_4^{2-}$:

Mn^{2+} : $3d^5$ configuration

: sp^3 hybridized and Paramagnetic

(B) $[Mn(CN)_6]^{2-}$:

Mn^{+4} $(3d^3)$: Octahedral and Paramagnetic

(C) $[Cu(CN)_4]^{3-}$ has Square planar geometry and is diamagnetic due to d^{10} configuration.

77.(ABD) Given Isomers cannot be distinguished by Magnetic moment due to same number of unpaired electrons.

78.(BC) A and D are Optically Inactive due to presence of plane of Symmetry.

79.(C) To exhibit ionization isomerism, complex should have anionic ligand and anion in ionization sphere. Presence of ambidentate ligands produce linkage isomerism.

80.(B) 1) $[Co(NH_3)_4(H_2O)_2]Cl_2$

Co^{2+} :$3d^7$

: Paramagnetic

: exhibit geometrical Isomers i.e. Cis and Trans

2) $[Pt(NH_3)_2Cl_2]$:

Pt^{2+} : $5d^8$

: exhibit geometrical Isomer i.e. Cis and trans

3) $[Co(H_2O)_5Cl)]Cl$:

Co^{2+} : $3d^7$

: Paramagnetic

4) $[Ni(H_2O)_6]Cl_2$:

Ni^{2+} : $3d^8$

: Paramagnetic

1, 3, 4 gives ppt of AgCl by action of $AgNO_3$ due to presence of Cl^- in Ionisation sphere.

1, 3, 4 show conductance due to presence of ions.

81.(D) 1) $[MnCl_6]^{2-}$:

Mn^{4+} : $3d^3$

Hybridisation : sp^3d^2

2) $[Fe(CN)_6]^{3-}$

Fe^{3+} : $3d^5$

: low spin complex

: d^2sp^3

3) $[Co(NH_3)_6]^{3+}$

Co^{3+} : $3d^6$

: low spin complex

4) $[Fe(H_2O)_6]^{2+}$

Fe^{2+} : $3d^6$

: High spin complex

82.(B) 1) PPh_3 – Monodentate

2) en – bidentate, chelating

3) SCN^- – Monodenate, Ambidentate

4) dmg – bidentate, chelating

- All polydentate ligands are chelating ligands

83.(D) 1) $[Fe(H_2O)_5NO]SO_4$ - Brown Ring Complex

Fe^{+1} : $3d^7$

: Octahedral (sp^3d^2)

: 3 unpaired electron

2) $[Mn(CN)_6]^{4-}$

$Mn^{2+} : 3d^5$

: forms low spin complex

: Contains 1 unpaired electron

3) $Fe(CO)_5$

- Trigonal bipyramidal
- dsp^3 hybridized

4) $[Ni(CN)_4]^{2-}$

$Ni^{2+} - 3d^8$

- Diamagnetic
- dsp^2 hybridized

84.(6) The given complex is an octahedral complex of formula $[Ma_2bc_3]$ with b is ambidentate ligand. The possible number of structural and stereo isomers are six.

85.(4) Given complex is $Ma_2b_2(AA)$ which contain three geometrical isomers out of which one is optically active.

86.(5) The formed complex is $Na_3\left[Ag(S_2O_3)_2\right]$

87.(3) While making complex we need to have at least 1 counter ion outside.

88.(2) Product may be fac or mer isomer only

89.(6) EAN = 42 + 2x = 54, so x = 6

90.(9) $[Co(en)_2Cl(NO_2)]Cl$

Isomers of $[Co(en)_2Cl(NO_2)]Cl$

Structural Isomers : $[Co(en)_2Cl(NO_2)]Cl$

$[Co(en)_2Cl(ONO)]Cl$

$[Co(en)_2Cl_2]NO_2$

Each structural Isomer exist in 2 forms Cis and trans. Cis is Optically Active and trans is Inactive. Each structural Isomer show 3 stereoisomers.

Total Isomers = 9

91.(4) Optically Active Compounds exist in *d* and *l* form

	$[Co(NH_3)_4Cl_2]^+$	$\longrightarrow$	Optically Inactive
	$[Co(NH_3)_3Cl_3]$	$\longrightarrow$	Optically Inactive
trans	$[Co(en)_2Cl_2]+$	$\longrightarrow$	Optically Inactive
cis	$[Co(en)_2Cl_2]^+$	$\longrightarrow$	Optically Active
	$[Cr(ox)_3]^{3-}$	$\longrightarrow$	Optically Active
	$[Cr(en)_3]^{3+}$	$\longrightarrow$	Optically Active
	$[Pt(en)_2Cl_2]$	$\longrightarrow$	Cis from is Optically Active

92.(3) Paramagnetic octahedral compound

$K_2[CoF_6]$

$K_3[CoF_6]$

$[Ni(NH_3)_6]SO_4$

Metallurgy

1.(B) Sulphide ores are concentrated by froth floatation method.

2.(C) Basic flux is used to remove acidic impurities. Lime stone produce CaO which is basic.

3.(C) Roasting is done to remove volatile matter as well as to convert ore to metal oxide.

4.(A) Silver in native form or in sulphide form is concentrated by dissolving in NaCN solution in presence of air.

5.(B) High electropositive elements such as alkali metals, alkaline earth metals and Al etc. are extracted by electrolytic reduction.

6.(C) Aluminium cannot be deposited from aqueous solution by passing electric current.

7.(C) Zone refining is a method of purification and it is used to obtain ultrapure metal.

8.(A) In thermite process reaction is started by the use of an ignition mixture containing magnesium and barium peroxide.

9.(B) Leaching is a chemical method of concentration of the ore.

10.(B) In smelting an oxide ore is heated with carbon in which metal oxide is reduced to metal.

11.(C) Roasting process is used to convert sulphide ore to metal oxide.

12.(B) Cupellation is a method of refining and it is used for Ag.

13.(B) Copper pyrite is $CuFeS_2$ and after roasting CuO and FeO are formed. FeO is removed by adding SiO_2 that form slag $FeSiO_3$.

14.(B) $Al_2O_3 \cdot 2H_2O$ is concentrated by chemical method known as leaching, in this method ore is dissolved in suitable solvent.

15.(B) Calamine $(ZnCO_3)$; Siderite $(FeCO_3)$ Argentite (Ag_2S); Cuprite (Cu_2O)

Zinc blende (ZnS); Iron pyrite (FeS_2) Malachite $(CuCO_3 \cdot Cu(OH)_2)$

Azurite $(2CuCO_3 \cdot Cu(OH)_2)$

16.(A) Silver and gold are extracted by cyanide process.

17.(C) Malachite is an ore of copper. It is $CuCO_3 \cdot Cu(OH)_2$.

18.(D) Heating an ore in the absence of air is known as calcination. Roasting is heating of the ore in the presence of air. Smelting is heating in the presence of carbon.

19.(C) A molten mixture of Al_2O_3 and Na_3AlF_6.

20.(D) Most electropositive metals are extracted by electrolytic reduction method.

21.(D) Blister copper contains the impurities of copper oxide which is removed by poling method.

22.(C) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ slope $= -\Delta S^\circ$

23.(B) Pitch blende (U_3O_8) is an ore of uranium.

24.(D) Copper is extracted by self reduction process while silver is extracted by cyanide process.

25.(A) $2CuFeS_2 + 4O_2 \rightarrow Cu_2S + FeO + 3SO_2$

26.(D) $FeO + SiO_2 \rightarrow FeSiO_3$

27.(C) $Cu_2S + O_2 \rightarrow Cu_2O + SO_2$ $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

28.(A) Poling process is a method of refining and it is used to remove Cu_2O from Cu.

29.(A) In electrorefining process impure copper acts as anode while a thin sheet of pure copper is used as cathode.

30.(ABCD) Trona; $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ Malachite; $CuCO_3 \cdot Cu(OH)_2$

Dolomite; $CaCO_3 \cdot MgCO_3$ Siderite; $FeCO_3$

31.(ABC) Sulphide ores are concentrated by froth floatation process except argentite. Argentite is leached by NaCN in presence of air.

32.(AC) Calcination is used to convert hydrated oxide or hydroxide and carbonates into respective oxides.

33.(ABC) Self reduction process is used for less electro positive metals like Cu, Hg and Pb.

34.(ABCD) Copper pyrite; $CuFeS_2$ Carnalite; $KCl \cdot MgCl_2 \cdot 6H_2O$

Dolomite ; $CaCO_3 \cdot MgCO_3$ Cryolite ; Na_3AlF_6

35.(ACD) Roasting is carried out to convert sulphide ore to oxide ore. In this process volatile impurities and organic matters are also removed.

36.(ABC) $MgO + SiO_2 \rightarrow MgSiO_3$

$3MgO + P_2O_5 \rightarrow Mg_3(PO_4)_2$

$MgO + SO_2 \rightarrow MgSO_3$

37.(AB) Sulphide ores are roasted.

38.(AD) The ores which are already in anhydrous oxide form are directly used for reduction i.e. Rutile (TiO_2). Cassiterite (SnO_2).

39.(C) The mineral bauxite is used for extraction of Al.

40.(ABCD) Galena; Froth floatation process

Bauxite; Leaching

Cassiterite; Gravity separation

Magnetite; Electromagnetic separation

41.(BC) Silver and gold are concentrated by leaching process in which ore is dissolved in sodium cyanide solution in the presence of air to form soluble cyano complex.

42.(ABCD) Mond's process; Refining of Nickel

Van Arkel's process; Ultrapure metal

Cyanide process; Extraction of silver

Froth-floatation process; Concentration of sulphide ores.

43.(ABC) $Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$

$4Na_2S + 5O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4NaOH + S$

$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$

44.(ABCD) $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O;$

$U_3O_8 + 3H_2SO_4 + \frac{1}{2}O_2 \rightarrow 3UO_2SO_4 + 3H_2O$

$4Au + 8KCN + O_2 + 2H_2O \rightarrow 2Na[Au(CN)_2] + 4NaOH$

$4Ag + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Ag(CN)_2] + 4NaOH$

45.(ABCD) Lead; self-reduction

Boron; Decomposition of iodide

Nickel; Decomposition of carbonyl complex

Silver; Complex formation and displacement by metal

46.(ABC) $Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO;\ 2BI_3 \xrightarrow{\Delta} 2B + 3I_2;\ TiI_4 \xrightarrow{\Delta} Ti + 2I_2$

47. **[A-r] → [B-p] → [C-s] → [D-q]**

Smelting is a process in which metal oxide is heated with carbon. Self reduction process is used for sulphide ores. Aluminium is extracted from bauxite by electrolytic reduction. In hydrometallurgy ore is concentrated by leaching process and bauxite is concentrated by leaching process. Copper glance (Cu_2S), Silver glance (Ag_2S), Haematite (Fe_2O_3), Bauxite $Al_2O_3 \cdot 2H_2O$

48. **[A-r] → [B-r, s] →[C-p, q] →[D-q]**

Al & Au are purified by electrolysis. The process of extraction of Al is known as Baeyer's process. Self reduction is used for extraction of Pb. Impure metals like Bi, Sn, Pb etc. are purified by liquation method.

49. **[A-r] → [B-s, t] → [C-p] → [D-q]**

Mond's process is used for purification of nickel. Van Arkel method is used for obtaining ultra pure metals. Titanium is purified by Van Arkel method. Distillation is used for those metals which are volatile. Zn, Cd and Hg are purified by distillation method. Cupellation is used to remove impurity of lead in silver.

50. **[A-p] → [B-q] → [Cr] → [D-s]**

Fe and Sn are extracted by carbon reduction method. Cu and Pb are extracted by self reduction method from their sulphide ores. Mg and Al are extracted by electrolytic reduction of their fused salts. Ag and Au are extracted by cyanide process.

51. **[A-p] → [B-q] → [C-r, s] → [D-t]**

Electrolytic reduction is used for extraction of more electropositive metals like Na, Mg and Al. Non metals are extracted by electrolytic oxidation from their salts. Iron is extracted by carbon reduction of its oxide while silver is extracted from its soluble cyano complex by reduction with Zn (chemical reduction). Sulphur is extracted by chemical oxidation method.

$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$$

$$2H_2S + \underset{(air)}{O_2} \rightarrow 2H_2O + 2S \text{ or}$$

$$2Fe_2S_3 + \underset{(air)}{3O_2} \rightarrow 2Fe_2O_3 + 6S$$

52.(6) [Oxygen 46.6%]

53.(6) Copperpyrite $CuFeS_2$; Zinc blende ZnS; Argentite Ag_2S; Cinnabar HgS; Galena PbS; Iron pyrite FeS_2; Haematite Fe_2O_3; Malachite $CuCO_3 \cdot Cu(OH)_2$; Dolomite $MgCO_3 \cdot CaCO_3$

54.(8) Bauxite $Al_2O_3 \cdot 2H_2O$; Magnetite Fe_3O_4; Cuprite Cu_2O; Chromite $FeO \cdot Cr_2O_3$; Cassiterite SnO_2; Cryolite Na_3AlF_6; Haematite Fe_2O_3; Galena PbS; Limestone $CaCO_3$; Rutile TiO_2; Pyrolusite MnO_2

55.(3) Among metals, aluminium is the most abundant.

56.(1) Iron pyrite (FeS_2) is known as fool's gold. Oxidation state of sulphur in FeS_2 is -1.

57.(5) Na, K, Mg, Ca and Al are extracted by electrolysis of their fused salts because their oxides cannot be reduced easily with carbon at moderate temperatures.

58.(4) Cassiterite is SnO_2.

59.(9) All are correctly matched.

60.(9) All the steps are involved in the extraction of iron from magnetite.

61.(4) Siderite : $FeCO_3$

Calamine : $ZnCO_3$

Dolomite : $CaMg(CO_3)_2$

Malachite : $CuCO_3 \cdot Cu(OH)_2$

Hydrogen & s-Block Elements

1.(D) $CO + H_2 + \underset{\text{(steam)}}{H_2O} \xrightarrow{\text{Catalyst}} CO_2 + H_2$

2.(B) $V = N \times 5 \cdot 6$

3.(C) $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

4.(D) H_2SO_4 catalyses disproportionation of H_2O_2.

5.(C)

6.(B) $MgCl_2 \cdot 6H_2O_{(s)} \xrightarrow{\Delta} MgO_{(s)} + 2HCl_{(g)} + 5H_2O_{(g)}$

7.(D) When H_2O_2 acts as oxidizing agent O_2 is not evolved.

8.(C) Critical temperature is temperature above which a gas cannot be liquefied. Water is polar molecule having high value of dipole moment hence its critical temperature is high.

9.(A) Dielectric constant increases with dilution.

10.(A) $BeSO_4$ is soluble in water. $Be(OH)_2$ is soluble in NaOH due to amphoteric nature.

11.(A) $BaSO_4 + Na_2CO_3 \longrightarrow BaCO_3 + Na_2SO_4$.

12.(A) Because of more covalent character.

13.(C) H_2O_2 is unstable and decomposes into water and O_2 upon standing. To prevent decomposition of H_2O_2, phosphoric acid, acetanilide or glycerol are added. These acts as negative catalyst.

14.(A) Maximum covalancy of Be is four and that of Al is six.

15.(C) Alkaline earth metals are extracted by electrolytic reduction of their fused salts.

16.(A) Calgon is hexa sodium metaphosphate $(NaPO_3)_6$. It is formulated as $Na_2[Na_4(PO_3)_6]$. It is used to remove Ca^{2+} ions from hard water.

17.(A) $2H_2SO_4 \xrightarrow{\text{Electrolysis}} \underset{\text{at anode}}{H_2S_2O_8} + \underset{\text{at cathode}}{H_2}$

$$2H_2O + H_2S_2O_8 \xrightarrow[\text{distination}]{\text{vaccum}} 2H_2SO_4 + H_2O_2$$

No peroxide bond in H_2SO_4 but there is one peroxide bond in H_2O_2.

18.(C) H_2O_2 reduces Cl_2 to HCl. Hence pH decreases. $H_2O_2 + Cl_2 \rightarrow 2HCl + O_2$.

19.(D) F_2 is strong oxidizing agent.

$2H_2O + 2F_2 \rightarrow 4HF + O_2$

20.(C) $Cl_2 + \underset{\text{cold}}{2NaOH} \longrightarrow NaCl + NaOCl + H_2O$

$NH_4Cl + NaOH \longrightarrow NH_4OH + NaCl$

$3Cl_2 + \underset{\text{(Hot)}}{6NaOH} \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

21.(D) Alkali metals reacts with H_2O and N_2.

22.(B) $NaH + HOH \rightarrow NaOH + H_2$

23.(D) Ionization energy increases

24.(C) Smaller cation and anion

25.(C) $MgCl_2$ because of smaller size of Mg^{2+} and bigger size Cl^-.

26.(A) Low ionization energy of sodium.

27.(D) Na golden yellow; Ba apple green; Ca brick red; K violet

28.(C) Alum; $K_2SO_4; Al_2(SO_4)_3 \cdot 24H_2O$

29.(A) Microcosmic salt is $Na(NH_4)HPO_4 \cdot 4H_2O$

30.(A) CrO_4^{2-} salts are yellow colour. H_2O_2 oxidizes $Cr(OH)_3$ to CrO_4^{2-}.

31.(B) Alkali and alkaline earth metals are extracted by electrolysis of their fused salt.

32.(D) LiCl is least stable due to more covalent character because of high polarization power of Li^+.

33.(B) Alkali metals are strong reducing agents.

34.(C) $Ca(OH)_2$ can remove temporary hardness and forms $CaCO_3$ on reaction with CO_2.

35.(B) Basic strength of alkaline earth metal oxide increases down the group.

36.(D) $Zn(OH)_2$ is amphoteric

37.(C) K is more active than Mg.

38.(C)

Malachite	$CuCO_3 \cdot Cu(OH)_2$	Cassiterite	SnO_2
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	Gelena	PbS

39.(A) Be is less reactive than Mg.

40.(B) $BeCl_2$ is least ionic because of high polarizing power of beryllium ion.

41.(D) Magnesium forms oxide and nitride.

42.(D) $Ca(H_2PO_4)_2 \cdot 2CaSO_4 \cdot 2H_2O$ is super phosphate of lime.

43.(D) Because of high degree of hydration of alkaline earth metal ion.

44.(D) Alkaline earth metals are obtained by electrolysis of fused halides.

45.(B) It is due to oscillation of mobile valence electrons.

46.(D) Alkali metals are soluble in liquid ammonia $Na + NH_3 \rightarrow Na^+_{(am)} + e^-_{(am)}$.

47.(C) Because of high ionic character.

48.(C) $NaOH + CO \rightarrow HCOONa$

49.(A) NaOH is basic and $NaHCO_3$ is acidic hence cannot exist together.

$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$.

50.(A) $Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2$

51.(B) $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

52.(A) $NaOH + AgNO_3 \longrightarrow NaNO_3 + AgOH$

$2AgOH \xrightarrow{\Delta} Ag_2O + H_2O$

53.(C) Bleaching powder liberates Cl_2.

$CaOCl_2 \rightarrow CaO + Cl_2$

54.(B) $2Na + O_2 \xrightarrow{300°C} Na_2O_2 \xrightarrow{CO_2} Na_2CO_3 + \underset{(Y)}{O_2}$

55.(A) $CaNCN + 3H_2O \longrightarrow CaCO_{3(s)} + 2NH_3$

56.(C) NaOH is hygroscopic absorb moisture and gets diluted.

57.(A) $Li^+_{(aq)}$ is biggest in size due to higher degree of hydration of Li^+.

58.(C) It is based on lattice energy and ionic character.

59.(C) $\underset{(A)}{Na} + H_2O \longrightarrow \underset{(C)}{NaOH} + \underset{(B)}{H_2}$

$\underset{(C)}{NaOH} + \underset{(D)}{Zn} \longrightarrow Na_2ZnO_2 + \underset{(B)}{H_2}$

Sodium imparts golden yellow colour to flame.

60.(D) $NaOH + S \longrightarrow Na_2S_2O_3 + Na_2S + H_2O$

61.(B) $Na_2S_2O_3$ forms complex with $AgBr$ and used for fixing of photographic film.

$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

62.(D) $Na + O_2 \longrightarrow Na_2O_2 \xrightarrow[-H_2O_2]{H_2O} NaOH \xrightarrow{CO_2} Na_2CO_3 \xrightarrow{HCl} \underset{\text{(molten)}}{NaCl} \xrightarrow{\text{Electrolysis}} Na + Cl_2$

$Na + H_2O \longrightarrow NaOH + H_2$

63.(B) $Na_2S_2O_3$ is used as antichlor to remove Cl_2.

$Na_2S_2O_3 + 5Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 10HCl$

64.(D) Carnallite is $KCl \cdot MgCl_2 \cdot 6H_2O$

K imparts violet colouration while Mg do not show flame test.

65.(A) $Mg(HCO_3)_2 \xrightarrow{\text{boiled}} MgO_{(s)} + 2CO_{2(g)} + H_2O$

66.(A) $2NaNO_2 + 2KI + 2H_2SO_4 \longrightarrow Na_2SO_4 + K_2SO_4 + 2NO + I_2 + 2H_2O$

67.(D) Smaller alkali metal ion is bigger hydrated metal ion hence has least ionic conductance.

68.(B) Paramagnetic character decreases with concentration of solution.

69.(D) These solutions are strong reducing, dilute solution is paramagnetic while concentrated solution is diamagnetic.

70.(C) Ammoniated solutions of alkali metals are used for reduction of aromatic compounds.

71.(D) Group I and II.

72.(D) No decomposition would occur because of high thermal stability.

73.(A) Magnesium oxide would be more stable because of comparable size of ions.

74.(D) Because nitrite anion is probably about the same size as the group I cations.

75.(B) $Li - \underset{\cdot\cdot}{\ddot{O}} - Li$

76.(ABD) $PbO_2 + H_2O_2 \longrightarrow Pb(OH)_2 + O_2$ Acidified $KMnO_4 + H_2O_2 \longrightarrow O_2$

$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

77.(ABC) Saline hydride are ionic in nature.

78.(BD) For Na_2SO_4 hydration energy is more than lattice energy while for $BaSO_4$ lattice energy is more than hydration energy.

79.(BD) Ca^{2+} and Mg^{2+} ions are exchanged with Na^+. **80.(ABD)** Mg can also forms complex.

81.(ABD) Mg salt does not show flame test

82.(BCD) NaOH reacts with Cl_2 and because of its hygroscopic nature it can't be used as primary standard in volumetric analysis.

83.(ACD) Li is much harder than the other group 1 metals.

84.(ACD) Magnalium (95% Al + 5% Mg) is used in construction of airships and pistons of motor engines.

85.(ABC) Basic nature is due to anionic hydrolysis. Conductivity of aqueous solution of alkali metals chloride increases down the group due to smaller size of hydrated alkali metal ion.

86.(BCD) $P + H_2O + NaOH \longrightarrow PH_{3(g)} + NaH_2PO_2$

$$Al + NaOH \xrightarrow{\Delta} NaAlO_2 + H_2$$

$$Zn + NaOH \xrightarrow{\Delta} Na_2ZnO_2 + H_2$$

87.(ABCD) Only $LiNO_3$ give NO_2 and O_2. Only Li_2CO_3 decompose to give CO_2 and Li_2O. Only Li form Li_2O. Only lithium reacts with nitrogen.

88.(ACD) $Mg + CO_2 \longrightarrow MgO + CO$

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

$$Mg + B_2O_3 \longrightarrow MgO + 2B$$

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + 5H_2O + 2HCl$$

89.(ABD) Beryllium shows diagonal relationship with Al hence its most of the chemistry resembles with Al. $Be(OH)_2$ is amphoteric.

90.(ABC) The reaction in which H_2O_2 changes to O_2.

91.(ABD) 50% H_2SO_4 on electrolysis liberate H_2 at cathode and $H_2S_2O_8$ at anode.

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

At cathode : $2H^+ + 2e^- \rightarrow H_2$

At anode : $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$

$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$

92.(ABC) Different conformeric structures are possible for H_2O_2, C_2H_6 and N_2H_4 due to free rotation about O–O, C–C and N–N bond.

93.(ABCD) H_2O_2 is non planar molecule having open book like structure.

94.(ABC) O_3 acts as oxidizing agent. It oxidises H_2O_2. $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$

95.(AC) Hardness of water is due to HCO_3^- and SO_4^{2-} salt of calcium and magnesium.

96.(ABC) H_2 can reduce oxides of less active metals.

97.(BC) $CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$ $\quad Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$ $\quad Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

98.(BD) $2Na + 2H_2O \longrightarrow 2NaOH + H_2$ $\quad Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$ $\quad NaNH_2 + H_2O \rightarrow NaOH + NH_3$

$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$ $\quad CaO + H_2O \longrightarrow Ca(OH)_2$

$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

99.(BC) Because of electron deficient nature BeH_2 and $BeCl_2$ exist in polymeric form.

100.(ABCD) Hydrogen is nonmetallic element reacts with nonmetals and acts as reducing agent. Its electronic configuration is $1s^1$

101.(ABCD) Alkali metal forms salt like hydrides.

102.(ABD) Calcium oxide and calcium hydroxide are basic hence soluble in acetic acid while $CaCO_3$ is a salt of weak acid. Calcium oxalate is a salt of stronger acid.

103.(CD) $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

$Al + NaOH \longrightarrow NaAlO_2 + H_2$

H_2 is combustible gas.

$S + NaOH \longrightarrow Na_2S_2O_3 + Na_2S + H_2O$

$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$

104.(BCD) Nitride salt gives NH_3 when come in contact with moisture.

$Mg + N_2 \longrightarrow Mg_3N_2$

$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

105.(BC) Calcium chloride and potassium fluoride are used to increase conductivity and to lower melting point.

106. **[A-r] → [B-p, r, s] → [C-p, q, s] → [D-p, q, s]**

Li, Na and Cs shows flame lest

Li is the strongest reducing agent

$LiNO_3 \longrightarrow Li_2O + NO_2 + O_2$

$NaNO_3 \xrightarrow{\Delta} NaNO_2 + O_2$

$Ca + 2C \xrightarrow{\Delta} CaC_2$

$Ca(NO_3)_2 \xrightarrow{\Delta} CaO + 2NO_2 + O_2$

$Mg(NO_3)_2 \xrightarrow{\Delta} MgO + 2NO_2 + O_2$

107. **[A-p, q, s] → [B-p, s] → [C-p, q, r, s] → [D-p, q, s]**

Alkali metal sulphates are thermally stable. Alkali metals and alkaline earth metals when dissolved in liquid ammonia form blue coloured solution.

108. **[A-q, r] → [B-p, s] → [C-p, q, r] → [D-p, s]**

Sulphur disproportionate in alkali. Na_2S and Na_2SO_3 reduces ferric salts. $2FeCl_3 + Na_2S \longrightarrow 2FeCl_2 + 2NaCl + S$

109. **[A-p, q, r, s] → [B-p] → [C-p, q] → [D-r, s]**

Be^{2+} has very strong tendency to form complex due to small size, Mg^{2+}, Ca^{2+} and Sr^{2+} form complexes with EDTA.

110. **[A-r, s] → [B-r] → [C-q, r] → [D-p, t]**

BeH_2 is polymeric hydride

AsH_3 is covalent hydride

B_2H_6 is Lewis acid and covalent hydride

$LiAlH_4$ is a complex species.

111.(8) Eq. of base = Eq. of acid.

112.(5) Anhydrous halides can often be prepared by the removal of water from hydrated metal chlorides. Simply heating the sample in a dry gas stream is usually not satisfactory for metals with high charge to radius ratio because significant hydrolysis may lead to the oxide or oxohalide.

$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O.$

113.(1) Trona is $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$

114.(2) KO_2, K_2MnO_4 are paramagnetic.

115.(4) $Na_2O_2, NaOCl, CaOCl_2, KO_2,$ are used as bleaching agent.

116.(9) Caustic potash; KOH Glaubers salt; $Na_2SO_4 \cdot 10H_2O$
Alum; $K_2SO_4; Al_2(SO_4)_3 \cdot 24H_2O$ Microcosmic salt; $Na(NH_4)HPO_4 \cdot 4H_2O$
Hypo; $Na_2S_2O_3 \cdot 5H_2O$ Rock salt; $NaCl$
Washing soda; $Na_2CO_3 \cdot 10H_2O$ Epsom salt; $MgSO_4 \cdot 7H_2O$
Carnallite; $KCl \cdot MgCl_2 \cdot 6H_2O$ Lime stone; $CaCO_3$
All the compounds of Na,K and Ca shows flame test.

117.(6) $2LiNO_3 \xrightarrow{\Delta} Li_2O + \frac{1}{2}O_2 + 2NO_2$ (acidic) $NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$

$Mg(NO_3)_2 \xrightarrow{\Delta} MgO + \frac{1}{2}O_2 + 2NO_2$ (acidic) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ (acidic)

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$ (acidic) $MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + 5H_2O + 2HCl$ (acidic)

$Na_2CO_3 \xrightarrow{\Delta}$ No effect $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$ (acidic)

118.(6) $Na_2CO_3 + 2SO_2 \xrightarrow{H_2O} \underset{(A)}{2NaHSO_3} + CO_2$ $NaHSO_3 + Na_2CO_3 \longrightarrow \underset{(B)}{2Na_2SO_3} + H_2O + CO_2$

$Na_2SO_3 + S \xrightarrow{\Delta} \underset{(C)}{Na_2S_2O_3}$ $Na_2S_2O_3 + Cl_2 + 2H_2O \longrightarrow \underset{(D)}{2NaHSO_4} + 2HCl$

119.(6) All compounds containing Ca imparts brick red colouration to the flame. Except carnallite, alum, and rock salt all other are calcium containing compounds.

120.(5) Dolomite; $CaCO_3 \cdot MgCO_3$ Carnallite; $KCl \cdot MgCl_2 \cdot 6H_2O$
Alum; $K_2SO_4; Al_2(SO_4)_3 \cdot 24H_2O$ Microcosmic salt; $Na(NH_4)HPO_4 \cdot 4H_2O$
Bleaching powder; $CaOCl_2$ Gypsum; $CaSO_4 \cdot 2H_2O$

121.(5) $\underset{(X)}{CaCO_3} \xrightarrow{\Delta} \underset{(A)}{CaO} + \underset{(B)}{CO_2}$

$\underset{(Y)}{CaC_2} \xrightarrow{H_2O} \underset{(D)}{C_2H_2(g)} + \underset{(C)}{Ca(OH)_2(aq)}$

Oxidation state of C in $CO_2 = +4$

C in $C_2H_2 = -1$

Difference in oxidation state = 5

122.(0) $KO_2, RbO_2, CsO_2;\ x = 3$
Mg, Be ; $y = 2$
Li, Na, K, Rb, Cs ; $y = 5$ $x + y - u = 0$

p-Block Elements - I

1.(C) $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl(g)$

2.(D) Anhydrous $AlCl_3$ is covalent in nature and exist as dimer (Al_2Cl_6) to complete octet.

3.(B) Due to presence of polar B—N bonds in borazole.

4.(A) Octet of Al in $AlCl_3$ is complete due to dimeric structure.

5.(C) Non-metal hydroxides are acidic while metal hydroxides are basic or amphoteric.

6.(B) Diborane is a dimer of BH_3 having 3c-2e bonds, as well as 2c-2e bonds. There are two bridged bonds and four terminal bonds.

7.(C) Due to dimeric structure having bridged 3c-2e bonds, B is sp^3 hybridized.

8.(D) In graphite every carbon atom has one delocalizable electron.

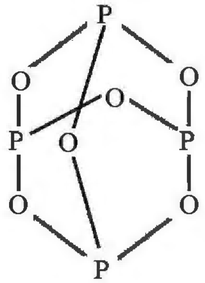
9.(A) CO is every strong ligand and can form complexes with transition metal ions.

10.(B) The ability of a substance to assume two or more crystalline structures is called polymorphism

11.(D) **(A)** H_3PO_4 (orthophosphoric acid) **(B)** H_3PO_2 (hypophosphorous acid)

(C) HPO_3 (metaphosphoric acid) **(D)** $H_4P_2O_7$ (pyrophosphoric acid)

12.(C)



13.(C) $2HNO_3 \longrightarrow 2NO_2 + H_2O + \frac{1}{2}O_2$

14.(C) Non-metal oxides are acidic while metal oxides are basic. Heavier members are metallic in nature.

15.(C) Due to larger size of central atom.

16.(A) Due to more difference in electronegativity of N and H.

17.(D) Both N_2O and CO_2 have 22 electrons and are linear in shape.

18.(B) NH_3 shows H-bonding therefore has high boiling point. PH_3 has lowest boiling point because of small size and lower molecular mass.

19.(C) Because of more difference in electronegativity of N and F.

20.(A) Compound in higher oxidation state are less ionic due to more polarization of anion by cation.

21.(C) $N_2O + Cu \longrightarrow CuO + N_2$

22.(A) Strongly electro positive metals evolve H_2 on reaction with dil HNO_3.

23.(A) The biological reduction of nitrogen to ammonia and further conversion to NO_3^- is carried out by bacteria.

24.(A) Species having more electronegative central atom is strongly oxidizing agent.

25.(A) Producer gas : $(CO + N_2)$ water gas : $(CO + H_2)$

26.(D) $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

27.(A) $PH_4I + NaOH \longrightarrow PH_3 + NaI + H_2O$

28.(D) It has cross linked sheet structure hence less strain in the rings

29.(C) $2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

30.(B) $Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

$B_2O_3 + CuSO_4 \xrightarrow{\Delta} Cu(BO_2)_2 + SO_3 \uparrow$

31.(B) Ultrapure form is obtained by zone refining and vapour phase refining.

32.(C) It is disproportionation reaction in which oxidation state of phosphorous changes from zero to –3 and +1.

33.(B) $\underset{\text{Triphosphate}}{(Na_3PO_4)_3} + 2H_2O \longrightarrow Na_5P_3O_{10} + 4NaOH$; $3NaH_2PO_4 \xrightarrow{\Delta} \underset{\text{Sodium cyclicmetaphosphate}}{Na_3P_3O_9} + 3H_2O$

34.(A) Hypo phosphorus is monobasic oxoacid of phosphorus having two P—H bonds.

35.(B) $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$

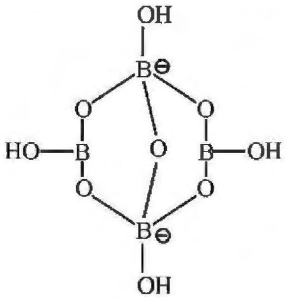
36.(C) $Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$; Al is more electropositive than Fe and this reaction is highly exothermic.

37.(A) Anion in Egyptian blue is $Si_4O_{10}^{4-}$ i.e. $Si_{2n}O_{5n}^{2n-}$ hence it is a sheet silicate.

38.(D) $6Na(NH_4)HPO_4.4H_2O \xrightarrow{\Delta} Na_2[Na_4(PO_3)_6] + 6NH_3 + 30H_2O$

39.(C) Hydride of elements of group 13 are electron deficient. $H_3N.BH_3$ is 1 : 1 complex of NH_3 and BH_3.

40.(D) It is complex anion of Borax $Na_2[B_4O_5(OH)_4].8H_2O$.



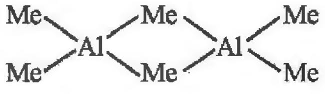
41.(A) $(CH_3)_2SiCl_2$ form $(CH_3)_2Si(OH)_2$ and it on polymerization gives linear chain silicones. CH_3SiCl_3 on hydrolysis gives $CH_3Si(OH)_3$ which on polymerization forms cross linked silicones.

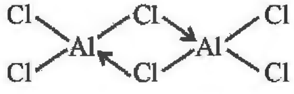
42.(D) BF_3 is planar because its dipole moment is zero.

43.(A) Borazole or Borazine is inorganic benzene and its structure resembles with benzene.

44.(C) In B_2H_6 only four nonbridging H atoms can be substituted.

45.(B) Al_2Me_6 because of $3c-2e^-$ bond



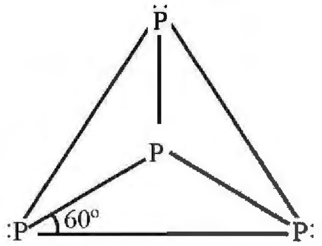


46.(C) Boric acid form complex with cis-diol for complete ionization.

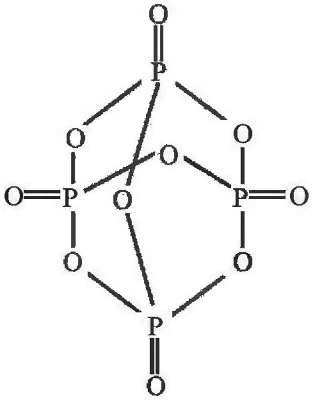
47.(C) White phosphorus is tetratomic reactive form due to strain in the rings.

48.(D) $H_2P_2O_7$ is non reducing due to absence of P—H or P—P bonds

49.(B)



50.(D)



51.(B) $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4 \cdot 12MoO_{3(s)} + 21NH_4NO_3 + 12H_2O$

Or

$(NH_4)_3[P(MoO_{10})]_4$

52.(C) Fe^{2+} and S^{2-} both will get oxidized.

53.(C) Concentrated nitric acid is a strong oxidizing agent and attacks most metals except noble metals such as gold and platinum. It also oxidizes non-metals and their compounds.

54.(A) Fe, Cr and Al becomes passive in conc. nitric acid because of the formation of a passive film of oxide on the surface.

55.(C) Because of more solubility of nitrate salts.

56.(C) NH_3 is sp^3 hybridized and better σ donor because of small size of nitrogen and more directional nature of hybrid orbital.

57.(B) $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (Disproportionation)

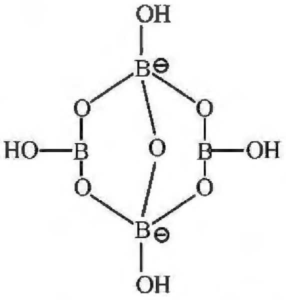
58.(B) Bond angle in NH_3 is 107° due to presence of lone pair electron.

59.(A) On increasing pressure equilibrium shift towards higher density solid.

60.(D) Layers can slide over each other due to weak Van der Waal's forces.

61.(A) $\Delta_r H = \Delta_{comb} H_{graphite} - \Delta_{comb} H_{diamond} = [-393.3 - (-395.3)] = 2$

62.(D)



2 triangular units, 2 tetrahedral units, four –OH units.

63.(B) One oxygen atom is shared, $(HO)_2B—O—B(OH)_2$.

64.(A) In chain silicates two oxygen atoms of every SiO_4^{4-} unit are shared with neighbouring units. Hence formula is $(SiO_3^{2-})_n$.

65.(B) $I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

66.(C) Carbon suboxide is C_3O_2 and its structural formula is $:\ddot{O}=C=C=C=\ddot{O}:$ **67.(B)** Cyclic anhydride is formed.

68.(ABCD) Due to partial double bond character C—C bond order is higher in graphite.

69.(BCD) Hydrated aluminium chloride do not form anhydrous $AlCl_3$ on heating.

$$2AlCl_3.6H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$

70.(ABD) SO_3 is soluble in water hence can't be collected over water.

71.(BCD) Hydrides of group 15th elements are poisonous and poisonous nature increases down the group, stability of Hydrides and basic strength decreases down the group.

72.(ABCD) Trona is $Na_2CO_3.NaHCO_3.2H_2O$ or $Na_3(CO_3)(HCO_3).2H_2O$

Borax is $Na_2B_4O_7.10H_2O$ or $Na_2[B_4O_5(OH)_4].8H_2O$

Grahm's salt is sodium hexametaphosphate $(NaPO_3)_6$ or $Na_2[Na_4(PO_3)_6]$

Alum is $K_2SO_4.Al_2(SO_4)_3.24H_2O$ or $[K(H_2O)_6]_2SO_4.[Al(H_2O)_6]_2(SO_4)_3$

73.(C) Mixture of conc. HNO_3 and conc. H_2SO_4 is called as nitrating mixture and HNO_3 acts as base (Bronsted base) in its reaction with H_2SO_4.

$$HONO_2 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$

74.(ABC)

$$NO_2^+BF_4^- + 3H_2O \longrightarrow 2H_3O^+ + NO_3^- + BF_4^-$$

$$NO_2^+NO_3^- + 3H_2O \longrightarrow 2H_3O^+ + 2NO_3^-$$

$$NO_2^+ClO_4^- + 3H_2O \longrightarrow 2H_3O^+ + NO_3^- + ClO_4^-$$

$$NH_4^+NO_3^- + H_2O \longrightarrow \text{No reaction}$$

75.(ABCD) All are nitrating agents and are used for nitration of aromatic compounds.

$$NO_2BF_4 \longrightarrow NO_2^+ + BF_4^-$$

$$NO_2ClO_4 \longrightarrow NO_2^+ + ClO_4^-$$

$$N_2O_5 \longrightarrow NO_2^+ + NO_3^-$$

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$

76.(B) NO is colourless, gaseous, paramagnetic oxide

$$\underset{(A)}{NO_{(g)}} + O_{2(g)} \longrightarrow NO_{2(g)} \xrightarrow[-120°C]{} \underset{(B)}{N_2O_{4(s)}}$$

77.(B) Nitric oxide combine very rapidly with ozone

$$NO(g) + O_{3(g)} \longrightarrow NO_2(g) + O_2(g)$$

78.(B)

$$\underset{\substack{\text{Colourless}\\ \text{diamagnetic}}}{N_2O_{4(s)}} \xrightarrow{F_2} 2NO_2F(g) \xrightarrow{BF_{3(g)}} NO_2^+BF_4^-{}_{(s)} \xrightarrow{3H_2O} 2H_3O^+ + NO_3^- + BF_4^-$$

79.(ABC) H–bond is formed with more electronegative atoms F, O and N.

80.(C) N_3H is acidic in nature, $H—N=\overset{+}{N}=\overset{-}{N}$

81.(ABCD) Compounds having —OH group and/or double bonded oxygen can reacts with PCl_5.

$$PCl_5 + CH_3COOH \longrightarrow CH_3COCl + POCl_3 + HCl$$

$$2PCl_5 + H_2SO_4 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$

$PCl_5 + SO_2 \longrightarrow SOCl_2 + POCl_3$

82.(BCD) Except orthosilicate all other silicates have one or more number of oxygen atoms of SiO_4^{4-} unit shared with neighbouring units.

83.(ABCD) N_2O is a good supporter of combustion as it provide more oxygen. N_2O and CO_2 are isoelectronic as well as isostructural.

$2N_2O \xrightarrow{\Delta} 2N_2 + O_2$ (support combustion).

84.(ABCD) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$\underset{\text{(dil.)}}{4Zn + 10HNO_3} \longrightarrow N_2O + 4Zn(NO_3)_2 + 5H_2O$

$NH_2OH + NaNO_2 + HCl \longrightarrow N_2O + NaCl + 2H_2O$

$2NO + SO_2 + H_2O \longrightarrow N_2O + H_2SO_4$

85.(ACD) According to molecular orbital theory **86.(ABCD)** White tin changes to grey tin at lower temperature

87.(ABD) Ammonium salt having oxidizing anion will not release NH_3 on heating.

88.(ABCD) All carbon atoms in graphite are sp^2 hybridized and in diamond all carbon atoms are sp^3 hybridized.

89. **[A-r] → [B-s] → [C-p, q] → [D-p]**

O_2 is absorbed by alkaline pyrogallol

NH_3 is absorbed by both water and H_2SO_4

CO is absorbed by ammonical Cu_2Cl_2 solutions.

90. **[A-q] → [B-r] → [C-s] → [D-p]**

$Mg + \underset{\text{very dil.}}{2HNO_3} \rightarrow Mg(NO_3)_2 + H_2$

$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2$

$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$

91. **[A-p, s, t] → [B-p, s] → [C-q, r] → [D-r, s, t]**

Hypophosphoric acid $(H_4P_2O_6)$ (Tetrabasic and reducing)

Pyrophoshoric acid $(H_4P_2O_7)$ (Tetrabasic)

Boric acid H_3BO_3 (Lewis acid)

Hypophorus acid (H_3PO_2) (Monobasic and reducing)

In all oxoacids of phosphorus, P is sp^3 accept meta phosphoric acid.

92. **[A-p, q] → [B-q, t] → [C-p, r, s] → [D-q, t]**

Non metal oxides are mostly acidic except (CO, NO and N_2O, these are neutral). Odd electron species are coloured and paramagnetic.

93. **[A-p, s, t] → [B-p, t] → [C-q, r, s] → [D-q, r]**

Borax and alum swells up on heating. Ammonium salt and aluminium salt reacts with NaOH.

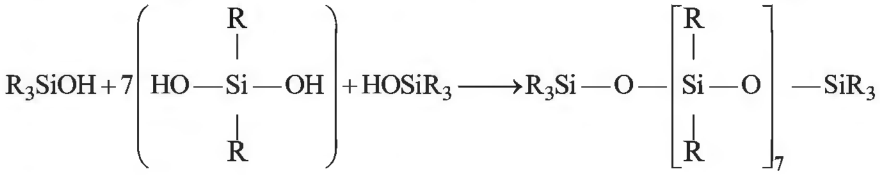
94. **[A-p] → [B-q, r] → [C-q, r] → [D-r, s]**

Non metal hydroxide are acidic while metal hydroxide are generally basic and some are amphoteric.

95. **[A-p, r] → [B-p, q, s] → [C-p, q, t] → [D-p, q, t]**
In all silicates co-ordination number of Si is four. Except ortho silicate in all other silicates one or more number of oxygen atoms are shared. Pyro silicate (one), single chain silicate and rings silicate two oxygen atoms are shared.

96. **[A-p, q, r] → [B-p, q, r] → [C-p, q, r] → [D-s, t]**
O_3, HNO_3 & H_2O_2 are oxidizing agent while H_3PO_3 acts as reducing agent.

97.(7)



$$R_3SiOH + 7\left(HO-\underset{R}{\overset{R}{Si}}-OH\right) + HOSiR_3 \longrightarrow R_3Si-O-\left[\underset{R}{\overset{R}{Si}}-O\right]_7-SiR_3$$

98.(6) $CaMg_3O(Si_4O_{11}) \longrightarrow CaO + 3Mg^{2+} + Si_4O_{11}^{6-}$

99.(5) Bigger size Lewis base are used for symmetrical cleavage of B_2H_6. $(C_2H_5)_3N$, $(CH_3)_3N$, $(C_2H_5)_2NH$, $(i\text{-}Pr)_3N$, quinuclidine

100.(3) It is cyclic silicate in which two oxygen atoms of every SiO_4^{4-} units are shared hence its empirical formula is SiO_3^{2-}.

101.(5) Salt having non-oxidizing anion on heating evolve NH_3. NO_3^-, NO_2^-, $Cr_2O_7^{2-}$ and ClO_4^- are oxidizing anions.

102.(2) B—H—B bond is 3c-2e bond hence it is formed by sharing of two electrons.

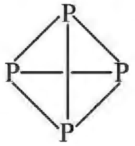
103.(1) In graphide one mobile or delocalizable electron is present on each carbon atom.

104.(2) Both phosphorus are sp^3 hybridized, hence there are two $d\pi - p\pi$ bonds because of two P = O bonds.

105.(1) Both Fe and NO have +1 oxidation state in brown ring complex.

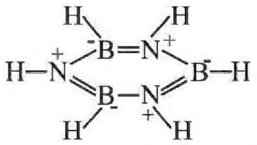
106.(6) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$

107.(6)

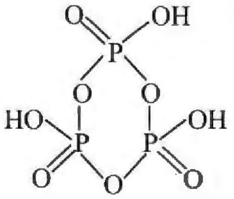


108.(1) $MeSiCl_3$ is used for synthesis of cross linked polymer.

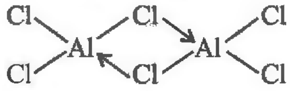
109.(3)



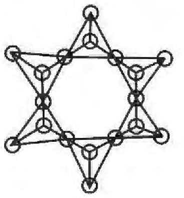
110.(3) $(HPO_3)_3 \cdot$ (Trimer)



111.(4)



112.(2) It is a cyclic silicate hence two oxygen atoms of every unit are shared.



113.(1) Hydrazoic acid is acidic nitrogen hydride, N_3H.

114.(1) $NO_2^+ BF_4^- + 3H_2O \rightarrow 2H_3O^+ + NO_3^- + BF_4^-$

Mole of H_3O^+ = mol of OH^-

$$0.01 \times 2 = x \times \frac{20}{1000}$$

$$x = 1$$

115.(4) Silica is a network silicate in which every silicon atom is bonded with four oxygen atoms.

p-Block Elements - II

1.(A) Hypochlorous acid is oxoacid and its anhydride is Cl_2O.

2.(C) $COCl_2$ is phosgene and it does not contain metallic ion.

3.(A) H_2O because of H-bonding.

4.(A) HI is strongest reducing agent because I^- can be easily oxidized.

5.(C) Electron gain enthalpy decreases.

6.(D) Oxoacids having lower oxidation state of halogen are stronger oxidizing agent.

7.(C) Chlorate salts decomposes on heating, $4AgClO_3 + 3Cl_2 \longrightarrow 6ClO_2 + 4AgCl$

8.(B) HCl is most volatile due to weakest inter molecular attractive forces. While HF is least volatile because of H-bonding.

9.(C) F do not show positive oxidation state.

10.(B) Cl_2 is greenish yellow gas and $KClO_3$ is used in safety matches.

11.(C) $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

12.(C) I—I bond is the weakest bond.

13.(A) Salt of weakest acid. Acidic strength of HClO is minimum amongst oxoacid of chlorine.

14.(A) Acidic strength of non-metal oxide increases with increase in oxidation state.

15.(D) Because of Hydrogen bond between F^- and $H—F$ hence mixture contains $K^+HF_2^-$.

16.(C) Xe form compounds with fluorine and oxygen and heavier noble gases can be easily liquefied.

17.(D) Ar is the most abundant rare gas in atmosphere and Radon is obtained as a decay product of radium. ${}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$

Helium is most abundant in universe.

18.(B) XeF_4 is square planar and sp^3d^2 hybridized.

19.(C) Ar is most abundant in the atmosphere while He is most abundant in universe.

20.(A) $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$; $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

21.(A) $KClO_{3(s)} \xrightarrow{\Delta} KClO_{4(s)} + KCl_{(s)}$; $KClO_{4(s)} \longrightarrow KCl_{(s)} + 2O_2(g)$

22.(A) Mercury loses its meniscus when come in contact with Hg.

23.(B) $2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI$; $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

24.(D) More reactive halogen can displace less reactive halogen from their salts.

25.(B) $Cl_2 + H_2O \longrightarrow HOCl + HCl$

26.(C) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

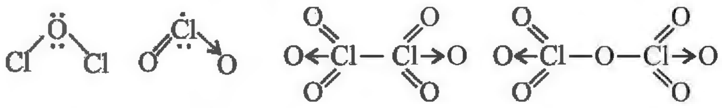
27.(B) Total electron pairs around central atom are 5 hence its structure is trigonal bipyramidal.

28.(A) Br_2 vapours will get dissolved in carbon tetrachloride and carbon disulphide while animal charcoal will adsorb Br_2 vapours.

29.(D) $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$;

$Br_2 + SO_2 + H_2O \longrightarrow 2HBr + SO_3$

30.(C) $H_2S_2O_7(S-O-S\text{bond})$; $H_2S_2O_8(S-O-O-S\text{bond})$; $H_2S_2O_6(S-S\text{bond})$; $H_2S_2O_3(S=S\text{bond})$

31.(B) 

32.(D) These are polar covalent compounds like ICl, ClF_3 etc.

33.(C) $H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$ (peroxomonosulphuric acid)

34.(D) Lone pair of electrons and the least electronegative Cl atom are in equatorial plane at 120° with more electronegative F atoms in axial position.

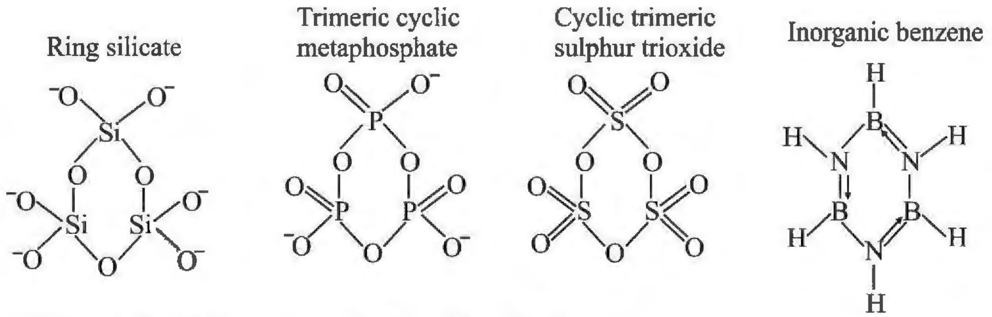
35.(D) Oxygen cannot form more than three bonds.

36.(D) HSO_3^- and $S_2O_7^{2-}$ are formed in one of the step of reaction and then reused hence these are intermediates.

37.(C) Molar mass of H_2O is lower than that of N_2 and O_2.

38.(D) Sulphur is used for vulcanization of rubber.

39.(B) Selenium is a poor conductor of electricity, but is a good photoconductor.

40.(A) 

Ring silicate

Trimeric cyclic metaphosphate

Cyclic trimeric sulphur trioxide

Inorganic benzene

41.(D) $4XeO_3 + 6Ba(OH)_3 \rightarrow 3Ba_2XeO_6 + Xe + 6H_2O$

42.(D) $XeF_6 + BF_3 \rightarrow XeF_5^+BF_4^-$ (Flouride ion donor)

$NaF + XeF_6 \rightarrow NaXeF_7^-$ (Flouride ion acceptor)

43.(C) It is thermally unstable and decomposes to produce Xe and O_2.

44.(A) In $XeOF_4$ there are total 6 electron pairs around central atom.

45.(B) $2H_2SO_4 + Cu \rightarrow CuSO_4 + SO_2 + H_2O$

46.(B) HNO_3 vapours condense below 100°C to form liquid HNO_3.

47.(D) Sulphur and sulphur containing compound on combustion from SO_2.

48.(C) Because formation of SO_3 is reversible reaction and by remaining SO_3 shift equilibrium toward forward direction.

49.(B) Mole of water $= \dfrac{\text{mass of solution} \times \text{\% of water}}{18} = \dfrac{1.84 \times 1 \times 2}{18 \times 100}$

50.(A) Argon is chemically inert hence it is used to create inert atmosphere.

51.(C) XeO_3 is pyramidal because of one lone pair and three bond pairs.

52.(C) XeF_4 and XeF_6 can acts as oxidizing as well as reducing due to intermediate oxidation state.

53.(B) N_2O is used as propellant for whipped cream.

54.(A) $NH_4NO_{3(s)} \xrightarrow{250^\circ} \underset{(B)}{N_2O_{(g)}} + 2H_2O$ $\quad 3NO_2 + H_2O \rightarrow 2HNO_3 + \underset{(E)}{NO}$

$CaCO_{3(s)} \xrightarrow{\Delta} \underset{(A)}{CO_{2(g)}} + CaO_{(s)}$ $\quad NO + NO_2 + 2NaOH \rightarrow \underset{(F)}{2NaNO_2} + H_2O$

$S_{8(s)} + 4O_{2(g)} \xrightarrow{\Delta} \underset{(D)}{8SO_{2(g)}}$ $\quad NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + \underset{(G)}{HNO_2}$

$\underset{(E)}{2NO_{(g)}} + O_{2(g)} \longrightarrow \underset{(C)}{2NO_{2(g)}}$ $\quad 3HNO_2 \rightarrow HNO_3 + H_2O + \underset{(E)}{2NO}$

55.(C) $NO_{(g)} + NO_{2(g)} \xrightarrow{-30^\circ C} \underset{\text{Blue}}{N_2O_{3(l)}}$

56.(B) $2NaClO_3 \rightarrow 2NaCl + 3O_2$ $\quad w_{NaClO_3} = \frac{2}{3} \times \frac{60}{24} \times 106.5 = 177.5g$

57.(A) Volume of oxygen produced is equal to area under the curve.

58.(B) $BaO_2 + 2HClO \longrightarrow BaCl_2 + \frac{1}{2}O_2 + H_2O$

59.(A) SO_2 can decolourises characteristic colouration of these solution while CO_2 can't decolourise.

60.(B) Bleaching action of SO_2 is due to its reducing nature. It reduces colouring matter and reduced colouring matter will restore its colour by oxidation from air.

61.(D) $Na_2SO_3 + S \longrightarrow Na_2S_2O_3$

62.(C) A = F; B = I; $BA_3 = IF_3$; $KHA_y = KHF_2$; $H_xA = HF$; $H_xB = HI$

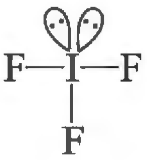
$2NaF + H_2SO_4 \rightarrow Na_2SO_4 + 2HF$

$2NaI + 2H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + I_2 + 2H_2O$

63.(C) F_2 do not disproportionate in water or alkali.

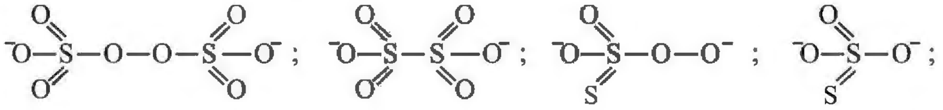
$F_2 + H_2O \rightarrow 2HF + O_2$

64.(C)



65.(AB) P_4O_{10} on complete hydrolysis gives H_3PO_4.

66.(B)



67.(ABC) Gallium have very low melting point (303K) it exist in liquid form at or near normal room temperature. Bromine and mercury are two well-known liquid substances.

68.(ABCD) Species having unpaired electrons are paramagnetic.
O_2^-, O_2 and S_2 are paramagnetic on the basis of molecular orbital theory. In ClO_2 there is unpaired electron in chlorine atom.

69.(BD) Inter halogen compounds are all covalent molecules and are diamagnetic in nature. Their physical properties are intermediate between those of constituents halogens except that their m.p. and BP are little higher than excepted. In general, inter halogen compounds are more reactive than halogens except fluorine.

70.(ABC) Comproportionation is reverse of disproportionation

71.(ABCD) Deacon's process:- $4HCl + O_2 \xrightarrow[723K]{CuCl_2} 2Cl_2 + 2H_2O$: it is also prepared by electrolysis of chloride salt solutions.

72.(ABCD) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$; $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$Cl_2 + Na_2S_2O_3 + 2H_2O \longrightarrow 2NaHSO_4 + 2HCl$

73.(ABCD)

Element	**Allotropic forms**
Carbon	Diamond, Graphite, Fullerene
Phosphorous	White phosphorous, Red phosphorous and black phosphorous
Sulphur	Monoclinic, Rhombic
Tin	White tin, Grey tin

74.(ABC) Iodine is a molecular solid rest all are covalent solids.

75.(AB) Sulphur and Iodine are molecular solids

76.(ABCD) $FeCl_3.6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 6SO_2 + 12HCl$

$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$

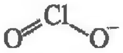
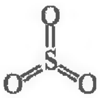
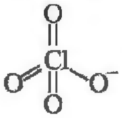
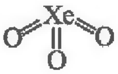
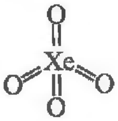
$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

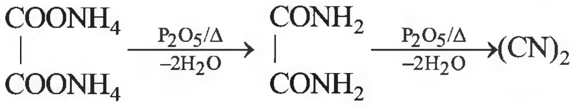
77.(BC) C_2 is diamagnetic while B_2 and S_2 are paramagnetic forms according to molecular orbital theory.

78.(D) White tin is stable at room temperature but at low temperature (<13.2°C) it transforms into grey tin on prolonged exposure at temperature well below this. Other allotropic transformations are possible at higher temperature.

79.(ABCD)

Molecular species	**No. of π - bond**	
B_2	1	{According to MO Theory}
C_2	2	{According to MO Theory}
$:\dot{N} = \ddot{O}:$ 	1	
$:\bar{C} \equiv \overset{+}{O}:$ 	2	
  	3	
	4	

80.(ABC) $CuSO_4 + 2KCN \longrightarrow K_2SO_4 + Cu(CN)_2$, $2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$



$$\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} \xrightarrow[-2H_2O]{P_2O_5/\Delta} \begin{matrix} CONH_2 \\ | \\ CONH_2 \end{matrix} \xrightarrow[-2H_2O]{P_2O_5/\Delta} (CN)_2$$

$Tl(CN)_3 \xrightarrow{\Delta} TlCN + (CN)_2$

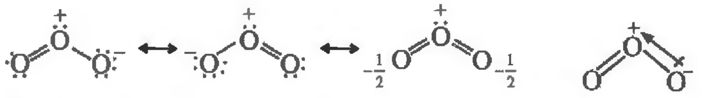
$HCOONH_4 \xrightarrow[-2H_2O]{P_2O_5/\Delta} HCN$

81.(ABCD) O_2, NO, NO_2, and S_2 all are paramagnetic while O_3, N_2O_3, N_2O_4, and S_8 all are diamagnetic.

82.(D) $OSCl_2$ reacts vigorously with water and is particularly valuable for drying or dehydrating readily hydrolysable inorganic halides. $MX_n \cdot mH_2O + mOSCl_2 \longrightarrow MX_n + mSO_2 + 2mHCl$.

With conc.H_2SO_4 sulphates and with P_4O_{10} phosphate and with CaO hydroxides may be precipitated.

83.(ABCD)

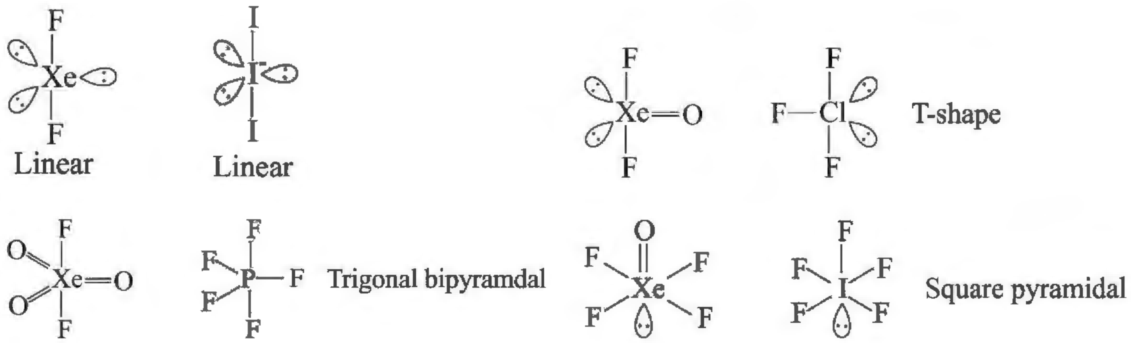


O_2 is paramagnetic while O_3 is diamagnetic. O_3 has nonzero dipole moment due to angular shape and presence of polar ends.

84.(ABCD)

85.(ABCD) All the substance in their elemental forms have standard free energy of formation equal is zero.

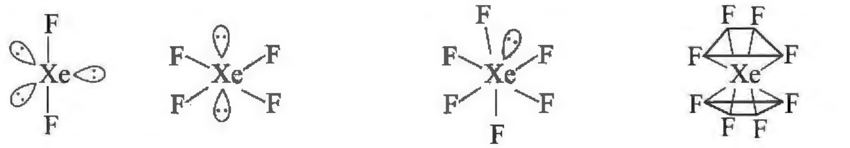
86.(ABCD)



87.(ABCD) All are correctly matched refer NCERT text book.

88.(BC) Reactions mentioned in options (A) and (D) are non redox reactions. Any reaction in which a substance is present in its elemental form is a redox reaction and Xenon fluorides are strong oxidizing agents.

89.(ABCD)



(Linear) (Square planar) (Distorted octahedral) Square antiprism

XeF_8^{2-} is square antiprism, this shape does not provide a site for the lone pair on Xe.

90.(ABD) $\underset{\text{(Reducing)}}{XeF_4} + O_2F_2 \rightarrow XeF_6 + O_2$

$\underset{\text{(Oxidising and fluorinating)}}{XeF_4} + 4NO_2 \rightarrow Xe + 4NO_2F$

$\underset{\text{(Oxidising agent)}}{XeF_4} + 2H_2 \rightarrow Xe + 2H_2F_2$

91.(B) Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. Reaction of fluorine with water and H_2O_2 gives O_2.

92.(ABCD) All these compounds are endothermic and their decomposition is favourable.

$$2O_{3(g)} \longrightarrow 3O_{2(g)}; \Delta_r H < 0; \Delta_r S > 0$$

$$\left.\begin{array}{l} 2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_2(g)\ ;\ \Delta_r H < 0;\ \Delta_r S > 0 \\ 2XeO_{3(s)} \longrightarrow Xe(g) + 3O_2(g)\ ;\ \Delta_r H < 0;\ \Delta_r S > 0 \\ O_2F_2(g) \longrightarrow O_2(g) + F_2(g) \end{array}\right\}$$

93.(ABC) Compounds of Xe with O_2 and F_2 are not formed by direct combination at 298K. Phosphorus readily burns in air to give P_4O_{10}. N_2 also do not reacts with O_2 at 298 K.

94.(C) Xenon oxides are endothermic $(\Delta_f G^\circ > 0)$ and cannot be prepared by direct interaction of the elements. The oxides are prepared by the hydrolysis of xenon fluorides.

95.(ABCD) HF cannot form three dimensional array of H–bonds as in water and so has less b.p. than water but it has stronger hydrogen bonds than water hence it is more viscous than water. It is stronger acid than water.

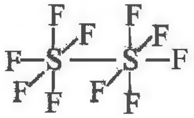
96.(ABCD) OF_2 is not an oxide it is a fluride.

97.(ABC) I^- can be oxidized by oxygen in acidic medium just the reverse of the reaction observed with fluorine.

98.(ABCD) All are common bleaching substances used for different bleaching purpose. ClO_2 is used as a bleaching agent for paper pulp and textsles and in water treatment.

99.(ABCD) Chlorine oxides are highly reactive oxidizing agents and tend to explode.

100.(ABCD) All are correct facts refer NCERT text book.

101.(ABCD)  sp^3d

102. **[A-q] → [B-p] → [C-s] → [D-r]**

Order of bond energy HF > HCl > HBr > HI

Order of b.p. $\underset{\text{(H-bond)}}{H_2O} > H_2O > H_2Te > H_2Se > H_2S$

Order of stability of monochloride. TlCl > InCl > GaCl [inert pair effect]

SiO_2 is a high m.p. network solid while CO_2 is a gas.

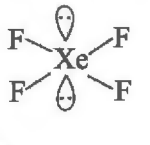
103. **[A-p] → [B-r] → [C-p] → [D-q]**

Maximum bond dissociation enthalpy is for Cl_2 not for F_2 because of lone pair repulsions. Solubility of F_2 is maximum due to its small size and ability to form hydrogen bond. Br_2 is a liquid and maximum inter molecular distance is in F_2 because of small Vander Waal's radii.

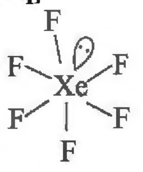
104. **[A-p] → [B-s] → [C-q] → [D-r]**

Potash solution absorb all acidic gases and Cl_2. Oxygen is absorb by alkaline pyrogallol solution. $FeSO_4$ solution absorb nitric oxide (NO). Carbon monoxide is absorb by ammonical cuprous chloride solution.

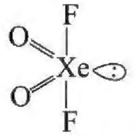
105. **[A-s] → [B-r] → [C-p] → [D-q]**



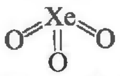
(Square planar)



(Distorted octahedral)



Trigonal bipyramdal



Pyramidal

106. **[A-p, q, s] → [B-q, r, t] → [C-q, r] → [D-p]**

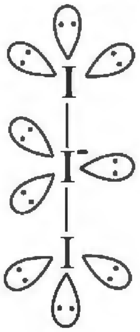
All halogens are coloured substances. Although electron gain enthalpy of fluorine is less negative as compared to chlorine. Fluorine is a stronger oxidizing agent than chlorine to

(1) Low enthalpy of dissociation of F – F bond and

(2) High hydration enthalpy of F^-. Fluorine shows only –1 and 0 oxidation states.

107.(3) F(–1), Na(+1), Mg(+2)

108.(9) There are total 9 lone pairs as shown in figure.



109.(2) Acidified $KMnO_4$ is an oxidizing agent and CO_3^{2-} and SO_4^{2-} cannot be oxidized.

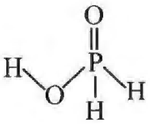
110.(4) $H_4P_2O_7$ is formed when H_3PO_4 is heated at 250–260°C. This acid contains 4–OH groups thus it can form four series of salts.

111.(2) No. of *l*p = 16, No. of S–S bonds = 8, ratio $= \frac{16}{8} = 2$

112.(5) CN^-, SCN^-, OCN^-, CNO^-, NNN^- are pseudo halides.

113.(3) H_3BO_3, H_3PO_2, HPO_3.

114.(2)



115.(8)

$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$, $SiCl_4 + 4H_2O \rightarrow H_4SiO_4 + 4HCl$

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$, $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$, $SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$

$SCl_4 + 2H_2O \rightarrow SO_2 + 4HCl$, $ICl_3 + 2H_2O \rightarrow HIO_3 + 3HCl$

116.(3) $N_2O_3+H_2O\rightarrow 2HNO_2$, $\mathbf{2NO_2+H_2O\rightarrow HNO_2+HNO_3}$

$P_4O_6+6H_2O\rightarrow 4H_3PO_3$, $\mathbf{P_4O_8+6H_2O\rightarrow 2H_3PO_3+2H_3PO_4}$

$P_4O_{10}+6H_2O\rightarrow 4H_3PO_4$, $\mathbf{Cl_2O_6+H_2O\rightarrow HClO_3+HClO_4}$

$Cl_2O_7+H_2O\rightarrow 2HClO_4$, $SO_3+H_2O\rightarrow H_2SO_4$,

$I_2O_5+H_2O\rightarrow 2HIO_3$, $N_2O_5+H_2O\rightarrow 2HNO_3$

117.(9) $2HgO\xrightarrow{\Delta}2Hg+O_2$ $NaNO_3\xrightarrow{\Delta}NaNO_2+\frac{1}{2}O_2$

$2Pb_3O_4\xrightarrow{\Delta}6PbO+O_2$ $2LiNO_3\xrightarrow{\Delta}Li_2O+2NO_2+\frac{1}{2}O_2$

$2Ag_2O\xrightarrow{\Delta}4Ag+O_2$ $2KClO_3\xrightarrow{\Delta}2KCl+3O_2$

$Ag_2CO_3\xrightarrow{\Delta}2Ag+CO_2+\frac{1}{2}O_2$ $Mg(NO_3)_2\xrightarrow{\Delta}MgO+2NO_2+\frac{1}{2}O_2$

$AgNO_3\xrightarrow{\Delta}Ag+NO_2+\frac{1}{2}O_2$

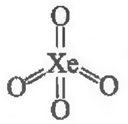
118.(7) As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character. The acidic oxides are $SO_2, Cl_2O_7, CO_2, N_2O_5, Mn_2O_7, CrO_3$ and V_2O_5.

119.(3) CO, NO and N_2O are neutral oxides.

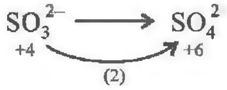
120.(9) $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Xe}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$

121.(5) The synthetic conditions indicate that formation of the higher halides is favoured by a higher proportion of fluorine and higher total pressure. $\underset{1:5}{Xe+F_2}\xrightarrow[873K,7bar]{}XeF_{4(s)}$

122.(4) In XeO_4 central atom is sp^3 hybridized hence all π bonds are $d\pi-p\pi$ bonds.



123.(2) $SO_3^{2-}\xrightarrow{dil\,HCl}\underset{Gas'A'}{SO_2}\xrightarrow[(Orange)]{K_2Cr_2O_7,H^+}H_2SO_4+\underset{(green)}{Cr^{+3}}$



d-Block Elements

1.(B) Cu can displace Ag from $AgNO_3$

2.(A) There is dynamic equilibrium between CrO_4^{2-} and $Cr_2O_7^{2}$ at pH = 4.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

3.(B) There is no unpaired electron in Mn but there is charge transfer from O to Mn.

4.(A) Transition elements are more metallic than representative elements because of availability of vacant d orbitals for bonding.

5.(A) $KMnO_4$ is purple coloured solution and during reaction there is decolourization of purple colouration.

6.(A) The most common oxidation state of lanthanides is +3 involving loss of electrons from 5d and 6s orbitals.

7.(B) Blue colouration is due to formation of aqua complex and CuI_2 is unstable and decompose to give Cu_2I_2 and I_2.

8.(B) Electronic configuration of Zn is [Ar] $3d^{10}4s^2$. Hence because of completion of (n – 1)d orbitals.

9.(D) $CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4;\ 2Cu(CN)_2 \rightarrow 2CuCN + (CN)_2;\ CuCN + 3KCN \rightarrow K_3[Cu(CN)_4]$

10.(A) F and O stabilize the higher oxidation states because of their strong oxidizing nature.

11.(B) Au and Ag are extracted by cyanide process.

12.(A) $CuSO_4 \cdot 5H_2O$ has only are unpaired electron.

13.(D) It is an aqua complex, $[Cu(H_2O)_4]SO_4 \cdot H_2O$ having co-ordination number equal to four.

14.(B) $HgCl_2 + Na_2CO_3 \rightarrow HgO + 2NaCl + CO_2$

15.(D) $[Cu(H_2O)_4]^{2+}$ is blue coloured and $Cr_2O_{7(aq)}^{2-}$ is orange coloured.

16.(A) Manganese steel is used for making Railways because of its hardness.

17.(A) Measurement of magnetic moment in solid state can be used to determine oxidation state by knowing number of unpaired electrons.

18.(A) Due to the presence of vacant orbitals.

19.(B) Due to the presence of lone pair electron on Sn.

20.(D) $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

21.(A) $\underset{\text{Red hot}}{Cu} + H_2O \rightarrow CuO + H_2$

22.(B) $2CuCl_2 + SO_2 + 2H_2O \rightarrow Cu_2Cl_2 + 2HCl + H_2SO_4$

23.(B) $AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + \frac{1}{2}O_2$

24.(D) $Hg_2Cl_2 + 2NH_4OH \rightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black}} + NH_4Cl + 2H_2O$

25.(B) $HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

26.(C) Zinc is a non – transition element. It has low enthalpy of atomization and is a volatile metal. It is not brittle.

27.(C) Mercury form amalgam with metals except Fe and Pt hence can be transported in containers made up of iron.

28.(D) On heating molten mass of silver absorbs oxygen which is released on cooling?

29.(D) Because of covalent nature $CuCl_2$ and $CuBr_2$ exist in polymeric form.

30.(C) Fe^{2+} of Mohr's salt can be oxidized.

31.(A) Noble metals are not attacked by acid and alkalies. $AuCl_3$ is used in tonning of photographic film.

32.(A) $\underset{\text{Amphoteric}}{ZnO} + \underset{\text{Basic}}{BaO} \rightarrow BaZnO_2$

33.(A) $HgCl_2$ is corrosive in nature and sublimes on heating and therefore, known as corrosive sublimate.

34.(D) $Zn(OH)_2$ is soluble in excess of NaOH.

35.(C) $2CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2 + K_2SO_4$

36.(D) Aqua regia releases nascent Cl.

37.(C) $2FeCl_3 + 3Na_2S_2O_3 \rightarrow \underset{\text{(violet colour)}}{Fe_2(S_2O_3)_3} + 6NaCl$

38.(A) Some of the visible spectrum is being removed from white light as it passes through the sample of coloured substance, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over. If orange-red light is absorbed by the complex, it appears blue.

39.(A) $Fe + 2HCl \longrightarrow FeCl_2 + H_2$. Liberation of H_2 prevents the formation of $FeCl_3$.

40.(B) $\underset{\text{(A)Green}}{FeSO_4 \cdot 7H_2O} \xrightarrow[-7H_2O]{300°C} \underset{\text{White(B)}}{2FeSO_4} \xrightarrow{\Delta} \underset{\text{(C)}}{Fe_2O_3} + \underset{\text{(E)}}{SO_2} + \underset{\text{(D)}}{SO_3}$

41.(C) $6FeSO_4 + 6HgCl_2 \longrightarrow \underset{\text{White}}{3Hg_2Cl_2} + 2Fe_2(SO_4)_3 + 2FeCl_3$

42.(D) $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_2 + 3H_2O$

43.(B) C is Fe_2O_3

$Fe_2O_3 + HCl \longrightarrow \underset{\text{Yellow}}{FeCl_3}$

$FeCl_3 + H_2S \longrightarrow \underset{\text{Green}}{FeCl_2} + \underset{\text{Turbidity}}{S}$

44.(C) Catalyst provide an alternate reaction mechanism that has lower activation energy.

45.(D) Overall there is no change in chemical composition of catalyst and it increases rate of reaction due to decrease in activation energy.

46.(A)

47.(B) Due to presence of unpaired electron.

48.(D) $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$

49.(B) $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{green}}{2K_2MnO_4} + 2H_2O$

50.(B) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

51.(D) In $KMnO_4$ there is no unpaired electron hence its purple colouration is due to charge transfer.

52.(B) $2Fe + 3Cl_2 \xrightarrow{\Delta} 2FeCl_3$

$Fe + 2HCl_{(g)} \xrightarrow{\Delta} 2FeCl_2 + H_2$ (H_2 prevent formation of $FeCl_3$)

53.(D) $K_3[Fe(CN)_6] + Fe^{2+} \longrightarrow Fe_3[Fe(CN)_6]_2$ (Turn bull's blue)

54.(A) Brown coloured ring is due to $[Fe(H_2O)_5(NO)]SO_4$. On heating complex decomposes to release NO.

55.(D) Aqueous solution of CO_2 is acidic and in acidic solution Na_2CrO_4 changes to $Na_2Cr_2O_7$.

$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ (pH = 4)

56.(B) Zn is a strong reducing agent.

57.(D) Generally, the higher the oxidation state of the metal, the greater is the crystal field splitting.

58.(D) $Na_2CrO_4 + Ba^{2+} \longrightarrow \underset{\text{Yellow PPt}}{BaCrO_4}$

Barium salts give green colour to flame.

59.(A) Nitrate and bromide salt on heating evolve brown gas NO_2 and Br_2 respectively. Ammonical silver nitrate solution oxidises glucose.

60.(B) $\underset{\text{(A)}}{AgNO_3} \rightarrow \underset{\text{(C)}}{Ag} + \underset{\text{(B)}}{NO_2} + \frac{1}{2}O_2$

61.(C)

62.(D) $\underset{(A)}{AgNO_3} + 2NH_3 \rightarrow \underset{(D)}{[Ag(NH_3)_2]NO_3}$

63.(D) $2AgNO_3 + K_2CrO_4 \rightarrow \underset{\substack{\text{Brick red} \\ (E)}}{Ag_2CrO_4} + 2KNO_3$

64.(B) **65.(B)** **66.(C)** **67.(B)**

68.(A) $\underset{(A)}{MnO_2} + 2HCl \xrightarrow{\Delta} \underset{(B)}{MnCl_2} + \underset{(C)}{Cl_2}$

$\underset{(C)}{Cl_2} + KI \longrightarrow 2KCl + \underset{(D)}{I_2}$

$\underset{(D)}{I_2} + KI \longrightarrow \underset{(\text{yellow solution})}{KI_3}$

$\underset{(A)}{MnO_2} + 2KOH + \frac{1}{2}O_2 \longrightarrow \underset{(\text{green mass})}{K_2MnO_4} + H_2O$

$2\underset{(E)}{K_2MnO_4 + O_3} + H_2O \longrightarrow \underset{(\text{purple})}{2KMnO_4} + 2KOH + O_2$

$\underset{\text{dry}}{2KOH} + 2O_3 \longrightarrow 2KO_3 + H_2O + \frac{1}{2}O_2$

69.(ABC) Amalgam is an alloy of metal with mercury **70.(AB)** **71.(AB)** **72.(BC)** **73.(ABC)**

74.(ABC) Acidified $KMnO_4$ can oxidise SO_2, H_2O_2 and $FeSO_4$. **75.(AB)**

76.(ABCD) Due to completely filled orbitals. Uub is 112th element and it belong to 4th series of d-block elements.

77.(ABC) Due to partially filled orbitals in the atom or in their ions

78.(CD) Sc and Zn do not show variable oxidation states (Sc^{3+} and Zn^{2+}) while Cu and Fe shows variable oxidation state. (Cu^{+}, Cu^{2+}, Fe^{2+} and Fe^{3+})

79.(ABCD) All are correct facts. **80.(BCD)**

81.(BCD) Beyond Mn no metal has a trihalide except FeX_3 and CoF_3 in first series of d-block elements.

82.(ABCD) All are mixed oxides because oxidation state of metal is fractional which represent average of different oxidation state.

83.(AC) Fluorides are unstable in the lower oxidation state while iodies are unstable in higher oxidation states.

84.(ABC) $E^{\circ}_{Cu^{2+}/Cu}$ is 0.34V and $Cu^{2+}_{(aq)}$ is more stable than $Cu^{+}_{(aq)}$ because of the much more negative $\Delta_{hyd}H^{\circ}$ of $Cu^{2+}_{(aq)}$ than $Cu^{+}_{(aq)}$.

85.(BCD) MnF_7 is not known because of steric hindrance. VCl_5 undergo hydrolysis to give oxochloride.

86.(ABD)

Brass;	Cu and Zn
Bronze;	Cu and Sn
Zinc-amalgam;	Zn and Hg
German silver;	Cu, Zn and Ni

87.(ABD) F^- is weak field ligand. $[Fe(CNS)_6]^{3-}$ shows linkage isomerism while FeF_6^{3-} do not show isomerism.

88.(AB) Due to absence of unpaired electron.

89.(ABC) Li and Mg, Be and Al shows diagonal relationships hence shows similar chemical properties. While Hf and Zr possess similar atomic size because of lanthanide contraction hence shows similar chemical properties.

90.(AC) Steam when passed over hot metals like Zn, Fe, Ni, Mn, Co, Cr and Sn is decomposed to liberate hydrogen.

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$ $\quad 3Fe + \underset{\text{steam}}{4H_2O} \rightarrow 4H_{2(g)} + Fe_3O_4$

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ $\quad Zn + \underset{\text{steam}}{H_2O} \rightarrow ZnO + H_2$

91.(ABCD) $CuSO_{4(aq)} + 2PH_{3(g)} \longrightarrow Cu_3P_{2(s)} + 3H_2SO_{4(aq)}$

$CuSO_{4(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]SO_4$

$4CuSO_{4(aq)} + 4KI_{(aq)} \longrightarrow Cu_2I_2 + I_2 + K_2SO_4$

$2CuSO_{4(aq)} + 10KCN_{(aq)} \longrightarrow 2K_3[Cu(CN)_4] + (CN)_2 + 2K_2SO_4$

92.(ABCD)

93.(AC) Ce^{4+} is a strong oxidizing agent because Ce^{3+} is its common oxidation state, La^{3+}, Ce^{4+} and Yb^{2+} are diamagnetic due to absence of unpaired electrons.

94. **[A-r] → [B-p, q, r, s] → [C-p, r] → [D-q]**
Kipp's apparatus is used for preparation of H_2S in the laboratory. It contains FeS and H_2SO_4.

$$FeSO_4 \rightarrow \underset{(Brown)}{Fe_2O_3} + SO_2 + SO_3; \quad (NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O \longrightarrow \underset{(Brown)}{Fe_2O_3} + SO_2 + 2SO_3 + 2NH_3 + 7H_2O$$

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

$Cu(OH)_2 \cdot CuCO_3$ is malachite and it is green coloured.

$$Cu(OH)_2 \cdot CuCO_3 \rightarrow \underset{Black}{CuO} + H_2O + CO_2$$

95. **[A-p, q, r, s, t] → [B-p, q, r] → [C-r] → [D-p, q, s]**
Transition metals shows variable oxidation state. Zn shows only one oxidation state +2. Fe becomes passive due to deposition of protective film of oxide on the surface. Aqua complexes of ions of Fe, Cu and Mn are coloured due to presence of unpaired electrons. Fe and Mn are mainly extracted from oxide ores while Zn and Cu are extracted from sulphide ores.

96. **[A-p, r, s] → [B-q, r, s, t] → [C-q, r, s] → [D-q]**
Hydrated ferric chloride can't be converted to anhydrous form just by heating due to hydrolysis.

$$FeSO_4 \xrightarrow{\Delta} \underset{(Brown)}{Fe_2O_3} + SO_2 + SO_3; \quad CuSO_4 \cdot 5H_2O \xrightarrow{\Delta} CuSO_4 + 5H_2O; \quad ZnSO_4 \cdot 7H_2O \xrightarrow{\Delta} ZnSO_4 + 7H_2O$$

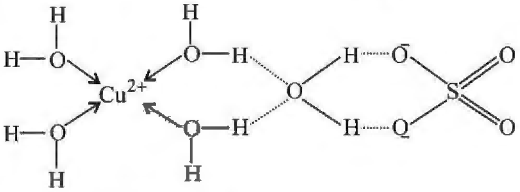
Except $ZnSO_4 \cdot 7H_2O$ all others are paramagnetic.

97. **[A-p, s] → [B-q] → [C-q, r, s] → [D-q, t]**

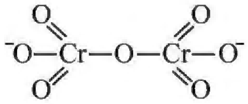
Fe and Pt do not form amalgam. Pd absorb large amount of H_2 due to formation of interstitial hydrides.

98. **[A-p, q, r, s] → [B-p, q, r, s] → [C-p, q, r, s] → [D-r, s]**
Acidified $KMnO_4$, Acidic $K_2Cr_2O_7, FeCl_3$ are oxidizing agent. $CuSO_4$ can oxidize iodide to I_2.

99.(1)



100.(6)

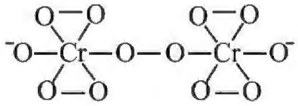


101.(5) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightarrow Fe^{2+} + 2NH_4^{+} + 2SO_4^{2-}$

102.(1) $BaCl_2 \cdot 6H_2O$, other undergoes hydrolysis to form oxide or oxohalide.

103.(4) Iron is 4th most abundant element in the earth's crust.

104.(5)



105.(5) $2CuSO_4 + 10NaCN \rightarrow 2Na_3[Cu(CN)_4] + (CN)_2 + 2Na_2SO_4$

106.(7) $7Cu + 20HNO_3 \rightarrow 7Cu(NO_3)_2 + 4NO + 2NO_2 + 10H_2O$

107.(9) $[Xe]4f^{14}5d^{9}6s^{1}$ **108.(0)** $[Kr]4d^{10}$ **109.(7)** $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$

110.(6) Ion having unpaired electrons and these are $Ti^{3+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}$.

111.(3) 59, 95, 102 are the atomic numbers of the inner transition elements, because last electron enters in f-orbital.

112.(2) Sc and Zn do not exhibit variable oxidation states. Sc(+3) and Zn(+2).

113.(5) Lanthanoid metal ($\sim 95\%$) and iron ($\sim 5\%$).

114.(1) $Cu^{+2} + \text{ethylene diamine} \longrightarrow \text{Bis(ethylenediamine)copper(II)}$

Qualitative Analysis

1.(A) III group (Iron group) requires low concentration of hydroxide ion as precipitating reagent hence NH_4Cl is added to decrease concentration of OH^- ions.

2.(B) Violet vapours are due to I_2.

3.(B) Acidic solution of nitrite salt on reaction with iodide produce I_2 that forms blue colouration with starch.

4.(B) Orange red vapours are due to chromyl chloride (CrO_2Cl_2).

5.(D) Alkali metal ions and ammonium ion can't be precipitated.

6.(C) Due to hydrolysis of bismuth chloride, $BiCl_3 + H_2O \rightarrow BiOCl_{(s)} + 2HCl$

7.(A) Bromide salt on heating with conc. H_2SO_4 and MnO_2 produce brown vapours of Br_2.

8.(B) Nitrate releases NO that is absorbed by $FeSO_4$ to form brown coloured nitrosoferrous sulphate.

9.(C) $Al(OH)_3$ is soluble in NaOH solution.

10.(B) $Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_{2(s)} \xrightarrow[\text{Excess}]{\text{NaOH}} Na_2ZnO_2$

11.(C) Due to oxidation of H_2S. $H_2S \rightarrow S_{(s)} + 2H^+ + 2e^-$

12.(D) Fourth group radicals can't be precipitated by H_2S and HCl. Ag^+ can be precipitate as Ag_2S.

13.(D) Na_2CO_3 produce high concentration of CO_3^{2-} that may precipitate Mg^{2+} as $MgCO_3$.

14.(B) Alkali metals and alkaline earth metals except Be and Mg can be detected by the flame test.

15.(A) Second group radicals can't be separated by H_2S in dilute HCl.

16.(C) AgI is insoluble in ammonium hydroxide. Silver phosphate is soluble in dil HNO_3 and NH_4OH. Silver chromate is red coloured.

17.(C)

18.(B) AgCl is soluble in NH_4OH due to formation of $[Ag(NH_3)_2]Cl$

19.(B) Ferric salt forms Prussian blue with $K_4[Fe(CN)_6]$

20.(B) Insoluble chloride salts do not give positive chromyl chloride test?

21.(C) PbS is black while CdS is yellow. Sulphides of barium and strontium are soluble.

22.(D) $SnCl_2 + HgCl_2 \rightarrow SnCl_4 + \underset{\text{White}}{Hg_2Cl_2}$

$SnCl_2 + Hg_2Cl_2 \rightarrow SnCl_4 + \underset{\text{(Grey)}}{2Hg}$

23.(D) Sulphides of basic radicals of II B are soluble in alkali.

24.(A) Violet colour is due to solution of I_2 in chloroform.

25.(D) White precipitate is due to ZnS. Sulphides of barium, calcium and alumminium are soluble.

26.(C) SO_2 produces turbidity with baryta water and also turns acidified dichromate solution to green.

27.(D) Sulphide, sulphite and thiosulphate salts decomposes on reaction with H_2SO_4.

28.(C) $BaCrO_4$ starts precipitating first.

29.(B) CuS, CdS and $Fe(OH)_3$ will be precipitated.

30.(D) Hg_2Cl_2 forms black precipitate with NH_4OH due to formation of Hg and $Hg(NH_2)Cl$.

31.(B) Green flame indicate presence of barium.

32.(A) HgS is insoluble in HNO_3. It is soluble in aqua regia.

33.(A) Chromium (III) salt on reaction with NaOH and Na_2O_2 form yellow coloured solution due to formation of CrO_4^{2-}.

34.(D) $PbCl_2$ is soluble in hot water.

35.(A) $PbCl_2$ is insoluble while $BaCl_2$ is soluble.

36.(C) Sulphides of II B radicals are soluble in yellow ammonium sulphide.

37.(B) Ferric salt gives blood red colour with KCNS.

38.(C) Hydroxides of Al, Cr and Zn are amphoteric hence soluble in NaOH.

39.(B) Barium chromate is insoluble in acetic acid while calcium chromate is soluble in acetic acid.

40.(A) $MgSO_4 + NH_4OH + Na_2HPO_4 \rightarrow Mg(NH_4)PO_{4(s)} + H_2O + Na_2SO_4$

41-43. **41.(C)** **42.(B)** **43.(D)**

$$\underset{(A)}{Al_2S_3} \xrightarrow{\text{dil } H_2SO_4} \underset{(B)}{H_2S} + \underset{(C)}{Al_2(SO_4)_3}$$

$$H_2S \xrightarrow[K_2Cr_2O_7]{\text{acidified}} \underset{\substack{\text{green}\\ \text{solution}}}{Cr^{3+}_{(aq)}} + \underset{(D)}{S}$$

$$S + \underset{(air)}{O_2} \longrightarrow \underset{(E)}{SO_2} \xrightarrow{H_2S} \underset{(D)}{S} + \underset{\substack{\text{Colourless}\\ \text{liquid}}}{H_2O} \xrightarrow[CuSO_4]{\text{anhydrous}} \text{Blue colour}$$

$$Al_2(SO_4)_3 \xrightarrow{NaOH} Al(OH)_{3(s)} \xrightarrow{\text{Excess}} NaAlO_{2(aq)}.$$

44-47. **44.(D)** **45.(A)** **46.(D)** **47.(B)**

Bottle 4 - copper II sulphate.

Bottle 3 - sodium carbonate
Bottle 2 - Hydrochloric acid
Bottle 1 - lead nitrate

48.(D) Mixture is NaOH + $ZnSO_4$.

49.(C) $NaOH + ZnSO_4 \longrightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + Na_2SO_4 + 2H_2O$

50.(C) $Na_2ZnO_2 + 2HCl \longrightarrow 2NaCl + Zn(OH)_2 \downarrow$

$Zn(OH)_2 + 2HCl \longrightarrow \underset{\text{Soluble}}{ZnCl_2} + 2H_2O$

51.(B) A should contain Cl^- ion since it gives a white precipitate with $AgNO_3$, soluble in NH_3.

52.(B)

53.(A) 'A' gives black precipitate insoluble in NaOH with HCl and H_2S.

Hence, cation may be $Hg^{2+}, Pb^{2+}, Bi^{3+}$

'A' gives yellow precipitate with K_2CrO_4, it confirms Pb^{2+} ion.

Thus, 'A' is $PbCl_2$. $PbCl_2 + 2NaOH \longrightarrow \underset{\text{White}}{Pb(OH)_2} \downarrow + 2NaCl$

$$Pb(OH)_2 \xrightarrow{NaOH} \underset{(B)}{Na_2[Pb(OH)_4]}$$

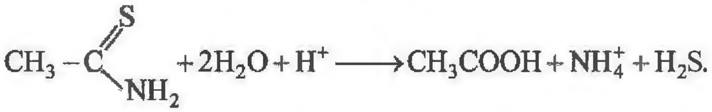
'A' on treatment with KI produces PbI_2, yellow in colour.

54.(ABC) $SO_3^{2-} + H_2SO_4 \longrightarrow SO_4^{2-} + H_2O + SO_2$, $2Cl^- + H_2SO_4 \longrightarrow SO_4^{2-} + 2HCl$

$S^{2-} + H_2SO_4 \longrightarrow SO_4^{2-} + H_2S$

SO_2, H_2S and HCl all turns acidified $K_2Cr_2O_7$ solution to green.

55.(ABC) Sulphides can reduce acidified $FeCl_3$ solution to $FeCl_2$



$$CH_3-C(=S)NH_2 + 2H_2O + H^+ \longrightarrow CH_3COOH + NH_4^+ + H_2S.$$

56.(BC) Microcosmic salt $(Na(NH_4)HPO_4 \cdot 4H_2O)$ and borax $(Na_2B_4O_7 \cdot 10H_2O)$ are used for bead test.

57.(ABD) $Cl^- + H_2SO_4 + K_2Cr_2O_7 \rightarrow KHSO_4 + \underset{\text{red vapours}}{CrO_2Cl_2}$

$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{yellow}}{Na_2CrO_{4(aq)}} + 2NaCl + 2H_2O$

$Na_2CrO_{4(aq)} + Pb(CH_3COO)_{2(aq)} \longrightarrow \underset{\text{yellow}}{PbCrO_{4(s)}} + 2CH_3COONa$

58.(ABCD) $K_4[Fe(CN)_6] + Fe^{3+} \longrightarrow Fe_4Fe(CN)_6]_3$ (blue precipitate.)

$K_4[Fe(CN)_6] + Cu^{2+} \longrightarrow Cu_2[Fe(CN)_6]$ (chocolate brown)

$K_4[Fe(CN)_6] + Zn^{2+} \longrightarrow Zn_2[Fe(CN)_6]$ Bluish white.

$K_4[Fe(CN)_6] + H_2O_2 \longrightarrow K_3[Fe(CN)_6]$.

59.(ABCD) PbS, CuS, HgS and NiS all are black coloured precipitate, and Fe^{3+} ion

60.(ABCD) $Fe^{3+} + NH_4SCN \longrightarrow \underset{\text{Blood red}}{Fe(SCN)_3} + NH_4^+$ $Fe^{3+} + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Blue ppt.}}{Fe_4[Fe(CN)_6]_3}$

$Fe^{3+} + 3CH_3COONa \longrightarrow \underset{\text{Blood red}}{Fe(CH_3COO)_3} + 3Na^+$ $Fe^{3+} + K_3[Fe(CN)_6] \longrightarrow \underset{\text{Brown}}{Fe[Fe(CN)_6]} + 3K^+$

$3Fe^{2+} + 2K_3[Fe(CN)_6] \longrightarrow \underset{\text{Blue}}{Fe_3[Fe(CN)_6]_2} + 6K^+$

61.(ABCD) Cations of coloured salt can be identified by borax bead test.

62.(ABCD) Alkali metal and alkaline earth metal salts imparts characteristic colouration to the flame.

63.(ABCD) $2CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{Smell of vinegar}}{2CH_3COOH}$

$NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + HNO_2$

$HNO_2 \longrightarrow \underset{\text{Brown colour}}{NO_2}$

$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{Smell of rotten egg}}{H_2S}$

$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + \underset{\text{pungent smell}}{SO_2}$

64.(ABCD)

Group No.	Group Reagent	Precipitate as
I	Dil.HCl	Chlorides
III	NH_4Cl/NH_4OH	Hydroxides
IV	$NH_4Cl/NH_4OH + H_2S$	Sulphides
V	$H_4Cl/NH_4OH + (NH_4)_2CO_3$	Carbonates

65. **[A-s] → [B-p, q, r, s] → [C-p, s] → [D-p]**

S^{2-}, NO_2^- and SO_3^{2-} decolourizes acidified $KMnO_4$ solution. NO_2^- evolve NH_3 on reaction with Al and NaOH.

66. **[A-p, q, r] → [B-r, s] → [C-r, s] → [D-r]**

Pb^{2+} can be precipitated by dil HCl as well as by H_2S.

67. **[A-p, q, s] → [B-p, r] → [C-r, s] → [D-q]**

SO_3^{2-} and S^{2-} can decolourize acidified $K_2Cr_2O_7$ solution.

68. **[A-q, s] → [B-p, q] → [C-r] → [D-s]**

$Pb^{2+}$and Ag^+ are precipitate as chlorides.

Cr^{3+} is precipitate as hydroxide while Ni^{2+} is precipitate as sulphide.

69. **[A-p] → [B-p, q, s] → [C-p, r] → [D-r, s]**

⇒ $Pb^{2+} \xrightarrow{HCl} PbCl_2$ (Soluble in hot water)

$Ag^+ \xrightarrow{HCl} AgCl$ (Insoluble in hot water)

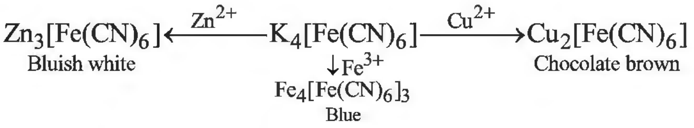
⇒ $Pb^{2+} \xrightarrow{HCl} \underset{\text{White}}{PbCl_2}$

$Cu^{2+} \xrightarrow{HCl} \underset{\text{Bluish green}}{CuCl_2}$

⇒ $Pb^{2+} \xrightarrow{KI} \underset{\text{yellow}}{PbI_2}$

$Cu^{2+} \xrightarrow{KI} \underset{\text{White}}{Cu_2I_2} + I_2$

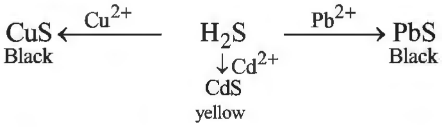
⇒



$$\underset{\text{Bluish white}}{Zn_3[Fe(CN)_6]} \xleftarrow{Zn^{2+}} K_4[Fe(CN)_6] \xrightarrow{Cu^{2+}} \underset{\text{Chocolate brown}}{Cu_2[Fe(CN)_6]}$$

$$K_4[Fe(CN)_6] \xrightarrow{Fe^{3+}} \underset{\text{Blue}}{Fe_4[Fe(CN)_6]_3}$$

⇒



$$\underset{\text{Black}}{CuS} \xleftarrow{Cu^{2+}} H_2S \xrightarrow{Pb^{2+}} \underset{\text{Black}}{PbS}$$

$$H_2S \xrightarrow{Cd^{2+}} \underset{\text{yellow}}{CdS}$$

70. **[A-s] → [B-p] → [C-p] → [D-q]**

$Fe(OH)_3$ redish brown

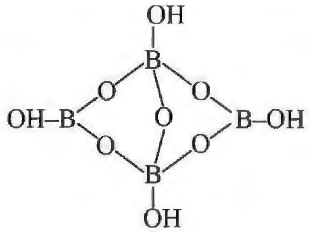
PbS and Bi_2S_3 Black

$PbCl_2$ and $AgCl$ white

71.(6) $BCl_3 + 2LiAlH_4 \longrightarrow \underset{(X)}{B_2H_6}$

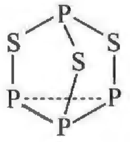
Compound (X) is B_2H_6. Maximum number of atoms of B_2H_6 that lie in same plane are 6.

72.(2) In Borax, 2 Borons are sp^2 hybridised and 2 are sp^3 hybridised.



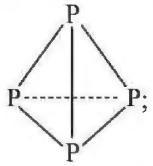
73.(3) Red phosphorous, P_4S_3, P_4

P_4S_3:

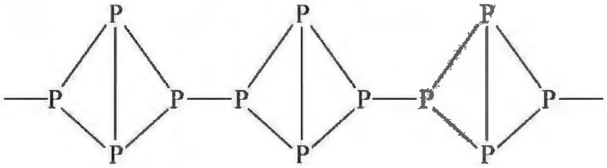


;

Phosphorus (P_4) :



Red Phosphorus :



74.(5) i, iii, vii, viii, ix

$Ag + \text{Conc. } HNO_3 \longrightarrow Ag + NO_2 + O_2$

$Sn + \text{Cold dil } HNO_3 \longrightarrow Sn(NO_3)_2 + NH_4NO_3$

$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2$

$Mg + \text{dil } HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$

$Mn + \underset{(2\%)}{\text{dil } HNO_3} \longrightarrow Mn(NO_3)_2 + H_2$

$P_4 + \text{Conc. } HNO_3 \longrightarrow H_3PO_4 + NO_2$

$S + \text{Conc. } HNO_3 \longrightarrow H_2SO_4 + NO_2$

$Cu + \text{dil } HNO_3 \longrightarrow Cu(NO_3)_2 + NO$

Cr is passive towards conc. HNO_3

75.(2) Al, B_2H_6

(1) $Al + HCl \longrightarrow AlCl_3 + H_2$

$Al + NaOH \longrightarrow NaAlO_2 + H_2$

(2) $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$

$B_2H_6 + NaOH \longrightarrow NaBO_2 + H_2$

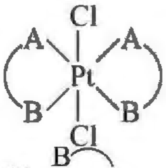
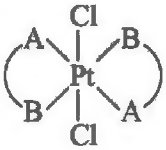
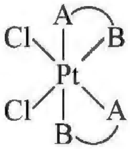
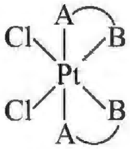
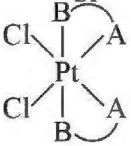
76.(3) $Al_2O_3 \longrightarrow Al$

$Ag_2S \longrightarrow Ag$

Au

77.(3) $BeCl_2, MgCl_2, Mg(OH)_2$

78.(5)

79.(2) C, CO

80.(6) $H_2C_2O_4$, Fe, Cu, Ag, S_8, $Na_2S_2O_3$

$H_2C_2O_4 + \text{Conc. } HNO_3 \longrightarrow CO_2 + NO_2$

$Fe + \text{Conc. } HNO_3 \longrightarrow Fe(NO_3)_2 + NO_2$

$Cu + \text{Conc. } HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2$

$Ag + \text{Conc. } HNO_3 \longrightarrow Ag + NO_2 + O_2$

$S + \text{Conc. } HNO_3 \longrightarrow H_2SO_4 + NO_2$

$Na_2S_2O_3 + \text{Conc. } HNO_3 \longrightarrow Na_2SO_4 + S + NO_2 + H_2O$

81.(5) $SO_3, Cl_2O_7, N_2O_5, Cr_2O_3, GeO_2$

SO_3, Cl_2O_7, N_2O_5 being acidic reacts with NaOH. Cr_2O_3 and GeO_2 are amphoteric oxides and thus soluble in NaOH.

82.(3) Hg, Cu, Pb

Sulphide ores are extracted by Self Reduction method.

83.(6) $PH_5, Pbl_4, NCl_5, OF_4, HFO_4, Fel_3$

84.(4) a, c, e, f

85.(6) $Be_3Al_2Si_6O_{18}$ is example of cyclic silicate

86.(7) $SF_4, XeO_3F_2, XeO_2F_2, Fe(CO)_5, POCl_3$, $[Ni(PPh_3)_2Cl_2]$

⇒ $SF_4, XeO_3F_2, XeO_2F_2, Fe(CO)_5$ are sp^3d hybridized. Here dz^2 is used in hybridization.

⇒ $POCl_3$ and $[Ni(pph_3)_2Cl_2]$ are sp^3 hybridized.

87.(3) SO_2, CO_2, SeO_2

SO_2 is anhydride of H_2SO_3

CO_2 is anhydride of H_2CO_3

SeO_2 is anhydride of H_2SeO_3

88.(4) i, iii, iv, vi

Transition metal lons are coloured because of d-d transition. d^0 and d^{10} species are colourless

89.(3) Al^{3+} and Hg^{2+}

Cd^{2+} and Zn^{2+}

Fe^{3+} and Cu^{2+}

90.(1) $Cu: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

3s orbital has 2 radial nodes

91.(4) $NaCl, MgCl_2, Al_2O_3, CaCl_2$

92.(7) $NO_2, CO_2, P_4O_6, CrO_3, Mn_2O_7, I_2O_5, OsO_4$

93.(6) $Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4 \downarrow$ (yellow ppt)

$Cd^{2+} + Na_2S \longrightarrow CdS \downarrow$

$Ag^+ + Br^- \longrightarrow AgBr \downarrow$ (Pale yellow)

$Na_3PO_4 + (NH_4)_2MoO_4 \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3$ (yellow)

$NH_4^+\ (aq) + [PtCl_6]^{2-}(aq) \longrightarrow (NH_4)_2[PtCl_6]$

94.(5) P_4, Al, Be, Fe, Zn

95.(3) NO_3^-, IF_7, SO_4^{2-}

96.(6) $[Mn(CN)_6]^{4-}, [Ni(CN)_4]^{2-}, [PdCl_4]^{2-}, [Pd(CN)_4]^{2-}, [Co(SCN)_4]^{2-}, [AgF_4]^-$

	Hybridisation
$[Mn(CN)_6]^{4-}$	d^2sp^3
$[Ni(NH_3)_6]^{2+}$	sp^3d^2
$[Co(NO_2)_6]^{4-}$	sp^3d^2
AgF_4^-	dsp^2
$[Ni(CN)_4]^{2-}$	dsp^2
$[PdCl_4]^{2-}$	dsp^2
$[Pd(CN)_4]^{2-}$	dsp^2
$[Co(SCN)_4]^{2-}$	dsp^2

97.(5) Here Fe is in +3 and +2 oxidation state. Total sum = 5

98.(0) $Mn^{2+} + S_2O_8^{2-} \longrightarrow \underset{(X)}{MnO_4^-} + SO_4^{2-} + H^+$

Number of unpaired electrons = 0
Magnetic moment = 0

99.(4) i, ii, iii, v

100.(3) V_2O_5, Cr_2O_3, ZnO

101.(6) $FeCl_3 \cdot 6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 6SO_2 + 12HCl$

102. **(a)** $0.02355\ \text{L HCl} \times \dfrac{0.195\ \text{mol}}{\text{L}} = 0.00459\ \text{mol } H^+ = 0.00459\ \text{mol } Cl^-$

(b) $0.00459\ \text{mol } Cl^- \times \dfrac{35.5\,\text{g}}{\text{mol}} = 0.163\ \text{g } Cl^-$

$$0.396 \text{ g MCl} - 0.163 \text{ g Cl}^- = 0.233 \text{ g} \times \frac{1}{0.00459 \text{ mol}} = \frac{50.8 \text{ g}}{\text{mol}}$$

$$0.396 \text{ g MCl} - 0.163 \text{ g Cl}^- = 0.233 \text{ g} \times \frac{1}{0.00230 \text{ mol}} = \frac{101.3 \text{ g}}{\text{mol}}$$

$$0.396 \text{ g MCl} - 0.163 \text{ g Cl}^- = 0.233 \text{ g} \times \frac{1}{0.00153 \text{ mol}} = \frac{152.3.3 \text{ g}}{\text{mol}}$$

(c)

50.8 g mol^{-1}	most likely V	VCl unlikely to be stable
101.3 g mol^{-1}	most likely Ru	$RuCl_2$ stable
152.3 g mol^{-1}	most likely Eu	$EuCl_3$ stable

103. **(a)** The element above element 114 is lead, Pb ; above element 116 is polonium, Po; above element 118 is radon, Rn

(b) The ionization energy is expected to increase from element 114 to 116 to 118. This due to increasing nuclear charge density thus resulting in greater attraction for outer electrons. The ionization energy of elements 114, 116 and 118 are expected to be lower than those of the elements directly above them due to the presence of electrons in higher energy levels, those with higher value of n

(c) The oxidation states for element 114 are predicted to be +2 (loss of electrons in p orbitals) and +4 (loss of electrons in both s and p orbitals). The oxidation state +2 is likely more stable ; lower oxidation states are usually more stable

(d) Even values of Z are usually more stable due to pairing of protons. Odd values of Z are less stable

104. **(a)** $n = PV/RT = (700.0 \text{ mm Hg}/760 \text{ mm Hg/atm})\ (0.1575 \text{ L})/[(0.0821 \text{ L atm mol}^{-1} \text{K}^{-1})(298 \text{K})]$

$$= 0.00593 \text{ mol } CO_2$$

Alternate approach $0.6500 \text{g} - 0.3891 \text{ g} = 0.2609 \text{g}\, CO_2$

$$0.2609 \text{ g } CO_2 / 44.0 \text{g}/\text{mole} = 0.00593 \text{ mole } CO_2$$

(b) (0.500 mol/L) (0.03860 L) – 0.01930 mol HCl
(0.01930 mol HCl) (1 mol MO/2 mol HCl) = 0.00965 mol MO

(c) (0.3891 g MO)/0.00965 mol MO = 40.32 g/mol MO
(40.32 g/mol MO – 16.0 g/mol O = 24.32 g/mol M $M = Mg^{2+}$

(d) Parts a-c give three constraints on the number of moles of MgO and $MgCO_3$ present.
From a, the total mass of the sample was 0.6500 g, so

$$(10.32 \text{ g}/\text{mol}) \times (n[MgO)] + (84.32 \text{ g}/\text{mol}) \times (n[MgCO_3]) - 0.6500 \text{g}.$$

From b, the total number of moles of magnesium = 0.00965 mol n(MgO) + n($MgCO_3$).
From c, 0.00593 mol CO_2 implies n($MgCO_3$) = 0.005928 mol.
Thus n(MgO) = 0.00965 mol – 0.005928 mol = 0.00372 mol. Since one has three linear equations in two unknowns, one may use any two of the constraints to solve :

n(MgO) = 0.00372 mol, n($MgCO_3$) = 0.00593 mol

Mol % MgO = 0.00372 mol MgO / 0.00965 moles total = $0.385 \times 100\% = 38.5$ mol% MgO

Mol % $MgCO_3$ = 0.00593 mol $MgCO_3$ / 0.00965 moles total = $0.615 \times 100\% = 61.5$ mol% $MgCO_3$

105. **(a)** **(i)** When you descend families on the periodic table, the ionization of the electron occurs from higher n values that are (usually) further from the nucleus.

(ii) The 3d subshell fills just before Ga. There is no 2d subshell to fill prior to Al. The 10 added protons are not completely screened by the 10d electrons, resulting in a higher effective nuclear charge and smaller radius than expected for Ga, hence a higher IE than expected. For Tl, the newly added subshell is the 4f suhshell, and a similar effect is observed. [Relativistic effects also contribute to the higher IE of Tl]

(b) **(i)** The +1 ion corresponds to the loss of the np^1 electrons, while +3 corresponds to the loss of the ns^2 and np^1 electrons. If 2 electrons were lost, a partially filled subshell would be present, which would interfere with bonding and would thus not be energetically favorable.

(ii) As one descends a column, she s electrons are more penetrating, held more tightly, and the therefore more difficult to lose. This is often called the "inert pair effect".

(c) **(i)** In a Lewis acid-base reaction, the Lewis base donates a pair of electrons to the Lewis acid, forming a new bond. Example (many others possible) : $BCl_3 + NH_3 \longrightarrow BCl_3 - NH_3$

(ii) The effectiveness of orbital overlap decreases down the family, so the bond between Lewis acid and Lewis base would weaken as the central atoms of the acid gets larger.

106. **(a)** In water, both HCl and HBr are equally strong, because both are 100% ionized. Water is a "good enough" base to pull the hydrogen ion from those two molecules to about 100% efficiency (this is called "leveling"). In 100% (glacial) acetic acid the acetic acid is a much weaker base than water. HCl only partially protonates acetic acid, while HBr more fully protonates it.

(b) $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$ (fuming sulfuric acid)

$H_2S_2O_7$ is a stronger acid than H_2SO_4 because there are more oxygens around the S holding the $-OH$ bonds so the effective polarity of the $-OH$ bond increases, making the molecule a stronger acid.

(c) In H_2SO_3, the two hydrogens to be ionized are initially bonded to different atoms. Thus the negative charge left behind when the first H^+ is lost is (on average) farther away from the second H^+ and attracts it more weakly. In H_2S, both hydrogens to be lost are bonded to the same atoms.

107. **(a)** (1310 s) (1.24 A)/(96485 C/mol) = 0.0168 mol electrons

0.292 g Cr/52.00 g/mol) = 5.62×10^{-3} mol Cr

0.0168 mol electrons /(5.62×10^{-3} mol Cr) = 2.99 mol electrons/mol Cr

Thus Cr must be in the +3 oxidation state, n = 3.

(b) $3.000\,g - 1.783\,g = 1.217\,g\ H_2O/(18.02\ g/mol) = 0.06754\ mol\ H_2O$

$1.783\ g\ CrCl_3/(158.35\ g/mol) = 0.01126\ mol\ CrCl_3$

m = 0.06754 mol H_2O/0.01126 mol $CrCl_3$ = 6

(c) (i) During the titration, $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

At the endpoint, $2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$

(ii) Mol Cr salt = 0.3000 g/(266.47 g mol) = 1.126×10^{-3} mol

Mol Ag^+ added = mol Cl^- present = (0.400 mol/L) × (2.81×10^{-3} L) = 1.12×10^{-3} mol

There is thus 1.00 mol Cl^- titrated per mol Cr.

(d) Presumably two of the chlorides are bonded directly to the Cr(III) ion and therefore do not react rapidly with Ag^+ (aq); the salt is likely best formulated $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$

108. **(a)** $1s^2 2s^2 2p^6 3s^2 3p^5$ or $[Ne]\ 3s^2 3p^5$

(b) $:\overset{..}{\underset{..}{Cl}} - \overset{..}{\underset{..}{Cl}}:$

(c) Cl has a higher ionization energy than Cl_2. The highest-lying electrons in Cl_2 are π^*, so they are higher in energy, and hence require less energy to ionize, than the 3p electrons in atomic chlorine. (The experimental values are 13.0 eV for Cl, 11.5 eV for Cl_2

(d) Cl^- would have a larger radius, since it has an additional electron.

(e) Cl has 7 valence electrons. An oxoanion with the formula ClO_5^- would require an oxidation state of +9 for Cl, which would require removing core electrons. This is not energetically feasible.

109.(a) $0.5637g\ CO_2 \times (12.01\ g C/44.01\ g\ CO_2) = 0.1538 g C,\ 15.38\%\ C$

$0.6924\ g H_2O \times (2.016 g H/18.016\ g H_2O) = 0.07748 g H,\ 7.75\% H$

(b) $\%O = 100\% - (15.38\% + 7.75\% + 35.89\%) = 40.98\%\ O$

So in 100 g fertilizer there would be :

$15.38 g\ C/(12.01\ g mol^{-1}) = 1.28\ mol\ C$

$7.748 g\ C/(1.008\ g mol^{-1}) = 7.69\ mol\ H$

$35.89 g\ N/(14.01\ g mol^{-1}) = 2.56\ mol\ N$

$40.98 g\ O/(16.00\ g mol^{-1}) = 2.56\ mol\ O$

Dividing by 1.28 mol gives an empirical formula $CH_6N_2O_2$.

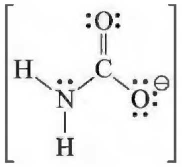
(c) $2.38°C/(1.86°C/m) = 1.28 m$ solution

$(1.28\ mol/1000\ g\ H_2O)$. $(20\ g\ H_2O) = 0.0256$ mol solute

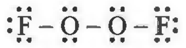
1.000 g solute/0.0256 mol solute = 39.1 g mol^{-1}.

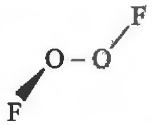
From the empirical formula, the formula mass is $78.1\ g mol^{-1}$! This says that the molar mass appears to be half the formula mass ; the only way this is possible is if each mol of fertilizer gives rise to two moles of particles. Thus, the fertilizer is likely an ionic compound.

(d) The most likely cation given the formula is ammonium ion, which leaves an ion with the formula CH_2NO_2. Several chemically plausible structure can be written, but the only one where the anion is not so basic that it would deprotonate the ammonium ion is carbamate, $NH_2CO_2^-$. (The only other chemical reasonable alternative is hydrazinium formate, $(NH_2NH_3^+)(HCOO^-)$). Ammonium carbamate is a common fertilizer.

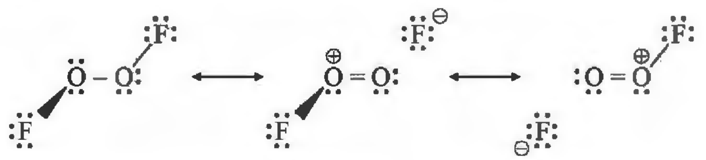
Fertilizer = NH_4^+ 

110.(a) In FOOF, each oxygen is bent, and the two FOO planes are roughly perpendicular to one another :

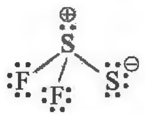




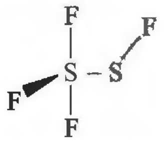
(b) Electron donation from the oxygen lone pairs in FOOF into the $O-F\ \sigma^*$ orbitals ("negative hyperconjugation") lengthens the $O-F$ bond (and shortens the $O-O$ bond, which at 121.7 pm is much shorter than the $O-O$ single bond in H_2O_2, 147.4 pm, and is almost the same length as the double bond in O_2, 121 pm)!



(c) The stable isomer of S_2F_2 is pyramidal :



(d) The four-coordinated sulphur has a "sea-saw" geometry, with the equatorial fluorine distinct from the two axial fluorines. (Obviously the fluorine on the divalent sulfur is distinct from the other three as well)! The two axial fluorines are not equivalent because the $S-F$ bond on the divalent sulfur is pointed towards one of them and away from the other one :



(e) SF_4, because of its sea-saw geometry, has a dipole moment, while SF_6, which is octahedral, does not. The favourable dipole-dipole interactions increase the boiling point of SF_4 compared to SF_6. (The greater number of electrons in SF_6 would be expected to give it greater London dispersion forces compared to SF_4, but the lower polarisability due to the higher oxidation state in SF_6 may make this effect smaller than one would expect).

111.(a) At $25°C$, some liquid water is present, so the pressure of water is equal to the vapor pressure, 23.80 mm Hg. Thus the partial pressure of O_2 is 48.65 mm Hg – 23.80 mm Hg = 24.85 mm Hg. From the ideal gas law,

$$n = PV/RT$$

$$n = (24.85 \text{ mm Hg})\ (1.000 \text{ L})/(62.36 \text{ L [mm Hg] } \text{mol}^{-1}\,\text{K}^{-1})\ (298.15 \text{ K})$$

$$n = 1.337 \times 10^{-3} \text{ mol}$$

(b) At $200°C$, the total moles of gas are given by

$$n = (355.0 \text{ mm Hg})\ (1.000 \text{ L})/(62.36 \text{ L [mm Hg] } \text{mol}^{-1}\,\text{K}^{-1})\ (473.15 \text{ K})$$

$$n = 0.01203 \text{ mol}$$

The number of moles of water vapor – $(0.01203 \text{ mol total gases})\ (1.337 \times 10^{-3} \text{ mol } O_2)$

(c) The total mass of gaseous products

$$= (18.032 \text{ g mol}^{-1})\ (0.01069 \text{ mol } H_2O) + (32.00 \text{ g mol}^{-1})\ (1.337 \times 10^{-3} \text{ mol } O_2) = 0.2355 \text{ g}.$$

Thus 0.7645 g MO_3 remains.

(d) The balanced equation for this reaction is :

$$MO_x(H_2O)_y \rightarrow y H_2O + (x-3)/2 O_2 + MO_3$$

Since x is an integer, the smallest amount of O_2 that can be produced per mol MO_3 is 0.5, of any integer multiple of this could be produced.

If x = 4, then $2(1.337 \times 10^{-3} \text{ mol})$ mol MO_3 is present, and the molar mass of MO_3 is

$(0.7645 \text{ g})/(2.674 \times 10^{-3} \text{ mol } MO_3) = 285.9 \text{ g mol}^{-1}$.

This would imply that the atomic mass of M is $285.9 - 3(16.00) = 237.9 \text{ g mol}^{-1}$.

This is the atomic mass of U.

If x = 5, then only 1.337×10^{-3} mol of MO_3 would be present, and the molar mass of MO_3 would be twice as high, and the atomic mass of M would be over twice that of uranium. This is impossible. (Higher values of x would give even higher values of the atomic mass of M). Therefore M = U. Since x = 4, the 8 : 1 mol ratio of H_2O to O_2 produced implies that y = 4 as well.

(e) Naively, one would expected that $UO_4(H_2O)_4$ would have U(VIII). But this is impossible : since U has only 6 valence electrons, it cannot possibly have an oxidation state greater than +6!. The only reasonable formulation is that some of the oxygens in studtite are in the form of peroxide, O_2^{2-}, with an oxidation state of -1 for oxygen (not the -2 of oxide). Since it is unlikely that a strongly oxidizing species such as peroxide would coexist with a reduced oxidation state of uranium, uranium must be in its highest oxidation state, +6. Studtite should then be formulated as $UO_2(O_2)(H_2O)_4$. This mineral and its partially dehydrated form metastudtite, $UO_2(O_2)(H_2O)_2$, are the only known peroxide-containing minerals.

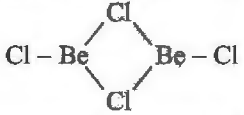
112.(a) **(i)** The electron ionized in Be is a 2s electron, while Ba loses a 6s electron. The higher value of n corresponds to a higher energy, requiring less energy to remove.

(ii) Since both Be and Ba have an ns^2 configuration, an added electron must enter a new subshell, which is higher in energy. The 2p subshell that would be occupied for Be is much higher in energy, but the next available orbital for Ba is a 5d orbital, which is closer in energy to the 6s orbital.

(iii) Ba is more electropositive than Be, so it costs much less energy to remove its valence electrons to form the +2 ion. This difference outweighs the somewhat higher lattice energy of $BeCl_2$ than $BaCl_2$.

(iv) Be can only form 4 bonds, so it can only adopt the left structure. The larger Ba^{2+} ion can easily achieve the coordination number of 8 required by the right-hand structure.

(b) $Cl-Be-Cl$



(c) Let P_M = partial pressure of monomeric $BeCl_2(g)$

P_D = partial pressure of dimeric $Be_2Cl_4(g)$

$$P_D / P_{M^2} = 2.9$$

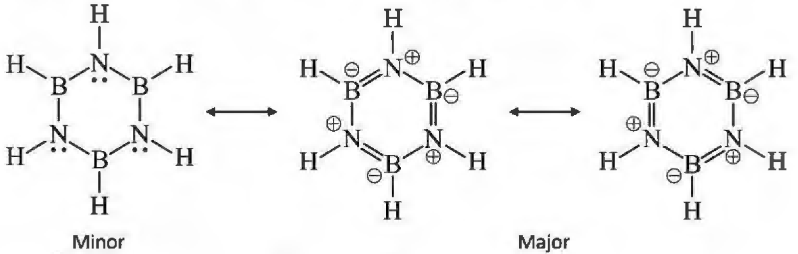
$$0.100 - P_M = 2.9\,P_{M^2}$$

$$2.9\,P_{M^2} + P_M - 0.100 = 0$$

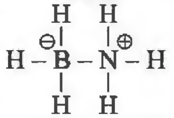
Solving gives $P_M = 0.081$ bar, and therefore $P_D = 0.100 - 0.081$ bar $= 0.019$ bar

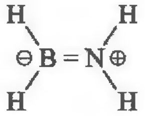
The mole fraction of the dimer is $P_D / 0.100\,\text{bar} = 0.19$

113.(a)



(b)





(c) BH_3NH_3, 156.4 pm

$B_3N_3H_6$, 142.9 pm

BH_2NH_2, 139.1 pm

From the Lewis structures, the bond order increases (from 1 to 1.5 to 2) in the order listed, with the bond lengths decreasing accordingly.

(d) In piperazine, the $N-H$ hydrogen can act as a hydrogen bond donor to another nitrogen lone pair. Changing the H to CH_3 thus decreases the amount of hydrogen bonding and weakens the intermolecular forces. This effect outweighs the increase in London dispersion forces in the $-CH_3$ derivative.

(e) Borazine has no hydrogen bond acceptors! There are not really any lone pairs on nitrogen since they are involved in π donation to the boron atoms. So the $N-H$ hydrogens do not participate in hydrogen bonding, and converting them to CH_3 groups leads only to an increase in London dispersion forces and a corresponding increase in boiling point.

Environmental Chemistry

1.(C) SO_2 is not a component of photochemical smog. It is reducing smog.

2.(A) Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and SO_2.

3.(A) Clean water have BOD value less than 5.

4.(A) Ozone is greenhouse gas and is responsible for greenhouse effect.

5.(B) Photochemical smog has high concentration of oxidising agent and known as oxidising smog.

6.(C) Peroxyacetyl nitrate belongs to secondary air pollutant.

7.(D) SO_2 in low concentration cause respiratory disease.

SO_2 causes irritation to the eyes, resulting in tears and redness. High concentration of SO_2 leads to stiffness of flower buds.

8.(A) Uncatalysed oxidation of SO_2 is very slow.

9.(C) $N_2 + O_2 \xrightarrow{1483\,K} 2NO$ (P)

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

$NO + O_3 \rightarrow NO_2 + O_2$

10.(D) All statements are correct.

11.(D) **12.(C)** **13.(D)** All statements are true.

14.(D) Classical smog is reducing smog and photochemical smog is oxidising smog.

15.(D) Formaldehyde, Acrolein and PAN are components of photochemical smog.

16.(C) X is ozone. **17.(C)** Both statements are correct.

18.(B) pH of acid rain is less than 5.6 due to presence of H^+ ions formed by the reaction of rainwater with carbon dioxide present in atmosphere.

19.(A) Photochemical smog has high concentration of oxidising agent and is therefore oxidising smog.

20.(D) Ozone is formed by UV radiations in upper atmosphere.

21.(A) Chlorine containing insecticide and pesticides are non-biodegradable and pollute soil and H_2O.

22.(C) If BOD level of water is less than 5 it is clean water. High BOD means large activity of Bacteria in water.

23.(CD) Polluted water have BOD more than 5.

24.(AB) Global warming increases the average temperature of earth and cause glacier and ice caps to melt.

25.(ACD)

Troposphere extends upto 10 km from sea level.

26.(ABC)

Oxides of sulphur and nitrogen are gaseous air pollutant.

27.(ABCD)

All statements are correct.

28.(ABCD)

All statements are correct.

29.(ABD)

Municipal and industrial discharge pipes are point source of pollution.

30.(AC) Clean water have BOD value less than 5 ppm whereas highly polluted water have a BOD value of 17 ppm or more.

31.(BCD)

About 75% of the solar energy reaching the earth is absorbed by the earth's surface.

32. **(A)-(r), (s); (B)-(s), (t); (C)-(q); (D)-(p)**

(A) Acid rain is caused due to oxides of carbon, sulphur and nitrogen.

(B) Photochemical smog is formed by unburnt fuel (unsaturated hydrocarbons).

(C) Carbon monoxide with haemoglobin is poisonous

(D) Chlorofluorocarbons $(\mathrm{CHC_{12}-CHF_2})$ cause ozone depletion

33. **(A)-(s); (B)-(t); (C)-(p); (D)-(r); (E)-(q)**

(A) Low concentration of sulphur dioxide causes respiratory disease, e.g., asthma, bronchitis etc

(B) The irritant red haze in traffic and congested places is due to oxides of nitrogen

(C) The increased amount of CO_2 in air is mainly responsible for global warming

(D) Excess nitrate in drinking water cause methemoglobinemia (blue baby syndrome)

(E) Lead can damage kidney, liver, reproductive system etc

34. **(A)-(t); (B)-(s); (C)-(p); (D)-(q); (E)-(r)**

35. **(A)-(p), (s); (B)-(r); (C)-(p); (D)-(q)**

Phosphate fertiliser cause Water pollution and enhance growth of algae

Methane is Greenhouse Gas

Nitrogen Oxides in air cause acid Rain

Chemistry in Everyday Life

1.(A) Aspirin is an example of non-narcotics drug.
2.(A) Penicillin G is a narrow spectrum antibiotic.
3.(B) Equanil is an example of tranquilliser. It is used in controlling depression and hypertension.
4.(C) Shaving soap contain glycerol to prevent rapid drying.
5.(B)
6.(C) Polyethylene glycol is used in preparation of non-ionic detergents.
7.(C) Vitamin is not a target molecule for drug function in body.
8.(D) 2-acetoxy benzoic acid is Aspirin. It is used as antipyretic.
9.(C) Paracetamol is both antipyretic and analgesic.
10.(A) Bithional is an example of disinfectant.
11.(D) Novalgin is a common analgesic and antipyretic.
12.(D) This is informative question.
13.(A) Salol is used as intestinal antiseptic.
14.(B) It is fact.
15.(B) Novalgin is an analgesic it is a fact.
16.(C) Aspartame is stable at cold conditions but unstable at cooking temperature.
17.(C) Adrenaline hormone is produced by adrenal glands after receiving a massage from the brain that a stressfull situation has presented itself. It is commonly known as **fight or flight** hormone.
18.(C) Tranquilizer is used to reduce anxiety and bring calmeness.
19.(C) Gammexane is insecticide.
20.(C) Competitive inhibitors are the drugs which compete with the natural substrate for their attachment on active sites of enzymes.
21.(C) Receptors are proteins that are crucial to body's communication process. They are embedded in the cell membrane but a small part possessing active site projects out of the surface of membrane.
22.(D) There are large number of different receptors in the body. These receptors show selectivity for one chemical messenger over the other.
23.(C)
24.(C) Noradrenaline is one of the neurotransmitters that plays a role in mood change.
25.(B) Non-narcotic analgesics are non-addictive. Barbiturates are hypnotic, sleep producing agents.
26.(B) Aspirin has anti blood clotting property, and is used in prevention of heart attack.
27.(C) In the body, prontosil is converted to a compound sulphanilamide, which is real active compound.
28.(D)
29.(C) Saccharin is 550 times as sweet as cane sugar.

30.(D) **31.(C)** **32.(C)** **33.(C)**
34.(C) Penicillin (G) is not a broad-spectrum antibiotic so it is not effective against some gram positive and gram negative bacteria.
35.(D) Salvarsan is an antibacterial drug containing arsenic and it does not contain sulphonamide group.
36.(D) Drugs compete with natural substrate by attaching by weak bonds such as ionic bonding. H-bonding, van der Waals interaction, etc., the active site of the enzyme.
37.(A) Hydrolysis of esters of long chain fatty acids by alkali gives soap a colloid. The process is called saponification. Sodium chloride is added to precipitate soap which is in colloidal form.
38.(D) In competitive inhibition, inhibitor binds to the active site of the enzyme.
39.(D) Chemical messenger binds the receptor site and gives the message to the cell without entering the cell.
40.(B) Preservatives are added to the food items because they inhibit the growth of microorganisms.
41.(B) Artificial sweeteners do not provide any calories because they are inert and do not metabolise in the body.
42.(C)
43.(BD) Receptor proteins are embedded in the cell membrane and their active sites project outside region of the cell membrane. Shape of the receptor changes during the attachment of messenger.

44.(BD) Table salt and cane sugar are used, as food preservatives while sodium hydrogen carbonate and benzoic acid are not used as food preservatives.

45.(AB) Barbiturates are tranquilizers which are used as hypnotics or sleep-inducing agents.

46.(AB) Sulphapyridine is a sulphonamide antibacterial drug.Prontosil is also called sulphamidochrysoidine. Salvarsan is arsenic based antibacterial drug. Nardil is an antidepressant drug.

47.(CD) Penicillin destroys bacteria by destroying the cell wall of the microorganism or kill the bacteria so, it has bactericidal effect. Penicillin has a narrow or limited spectrum.

48.(AD) Tranquilizers are neurologically active drugs. Veronal and luminal are derivatives of barbituric acid used as tranquilizers.

49.(AD) Sodium salts of sulphonated long chain alcohol and sodium salts of sulphonated long chain hydrocarbons are anionic detergents e.g., Sodium lauryl sulphate $CH_3(CH_2)_{10}CH_2OSO_3^- Na^+$ and sodium dodecylbenzene sulphonate.

50.(ACD)

(A) Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. These detergents have germicidal properties.

(B) Bacteria cannot degrade the detergents containing highly branched chains, therefore, in most of the detergents used these days, the branching is kept to a minimum so that the detergents become easily biodegradable.

(C) Some synthetic detergents can give foam even in ice cold water.

(D) Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap.

51.(ABC)

52.(CD) Antibiotics in low concentration inhibits the growth of microorganisms. Some purely synthetic compounds can have antibacterial activity.

53.(ACD)

Ofloxacin is Bactericidal antibiotic

54.(AD) Chloramphenicol is broad spectrum antibiotic and has bacteria static effects.

55.(ABD)

Vancomycin, Ofloxacin and Chloramphenicol is broad spectrum antibiotics.

56.(ACD)

Chloramphenicol is broad spectrum antibiotic. It is rapidly absorbed from the Gastrointestinal tract and hence can be given orally.

57.(ABCD)

All are antiseptics.

58.(BC) Fact

59.(BCD)

Sucralose is artificial sweetener.

60.(BC) 0.3 ppm aqueous solution of chlorine acts as disinfectant.

61.(AB) Barbiturates are hypnotic and used as tranquilizers.

62.(AD) Brompheniramine and Terfenadine acts as antihistamines.

63. **(A)-(r); (B)-(s); (C)-(p); (D)-(q)**

(A) Ranitidine - It prevents the interaction of histamine with the receptors present in the stomach wall. Thus, it controls the secretion of HCl and pepsin in stomach.

(B) Furacine - Furacine is an antiseptic. It can be applied to the living tissues to kill or to prevent the growth of microorganisms.

(C) Phenelzine - It is also known as Nardil. It is used to treat depression.

(D) Chloramphenicol - It is a broad-spectrum antibiotic. It can be given orally in case of typhoid, acute fever, dysentery, certain urinary infections, meningitis and pneumonia.

64. **(A)-(r); (B)-(s); (C)-(q); (D)-(p)**

65. **(A)-(r); (B)-(s); (C)-(q); (D)-(p)**

(A) Hair shampoos/conditioners are made up of cationic detergents. These are quaternary ammonium salts of amines with chlorides, bromides or acetates, e.g., cetyltrimethylammonium bromide.

(B) Anionic detergents are used in toothpaste e.g., sodium dodecyl benzene sulphonate.

(C) Laundry soaps contain fillers like sodium rosinate. Sodium silicate, borax and sodium carbonate. Sodium rosinate makes the soap to lather well.

(D) Dishwashing powder are non-ionic detergents.

66. **(A)-(q); (B)-(s); (C)-(p); (D)-(t); (E)-(r)**

(A) Antagonist drugs are used when blocking of message is required. For example, dopamine antagonist is a drug which blocks the dopamine receptors by receptor antagonism.

(B) Agonist drugs are useful when there is lack of chemical messenger, e.g., heroin.

(C) These chemical messengers are received at the binding sites of receptor. These communicate message between two neurons and that between neurons to muscles.

(D) Inhibitors block the binding site of the enzyme and prevent the binding of the substrate, or inhibit the catalytic activity of the enzyme.

(E) Receptors are proteins that are crucial to body's communication. They are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

67. **(A)-(t); (B)-(u); (C)-(s); (D)-(v); (E)-(q); (F)-(p); (G)-(r)**

(A) Analgesics reduce or abolish pain without causing impairment of consciousness, mental confusion, in coordination or paralysis or some other disturbances of nervous system, e.g., aspirin.

(B) Antiseptics are the chemicals which either kill or prevent the growth of microorganisms. They are applied to living tissues such as wounds, cuts etc. e.g., tincture of iodine.

(C) Antihistamines are anti-allergic drugs. These drugs interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect, e.g., seldane.

(D) Antacids are used to neutralize excess of acid released in stomach e.g., mixture of $Mg(OFI)_2$ and $Al(OH)_3$.

(E) Tranquilizers are used for the treatment of stress, and mid or even severe mental diseases e.g., equanil.

(F) Antibiotics are antimicrobial drugs. Antibiotics are used as drugs to treat infections because of their low toxicity for humans and animals e.g., chloramphenicol.

(G) Disinfectants are the chemicals which either kill or prevent the growth of microorganisms but they can be applied on non-living objects e.g., 1 per cent solution of phenol.

68.(4) (i), (ii), (iii), (iv)

69.(4) (ii), (iii), (viii), (ix)

70.(7) (i), (ii), (iii), (iv), (v), (vi), (vii)