Solutions to Final Step-A | Chemistry

Stoichiometry - 1 & Redox Reactions

1.(D) As H_2O_2 is loosing $e^{\ominus}$s

2.(D) $\overset{+1}{H}\overset{}{ClO} \longrightarrow \overset{-1}{H}Cl + \overset{+5}{H}ClO_3$

3.(A) $\overset{+6}{H_2S}O_4 \longrightarrow \overset{+4}{S}O_2$ ⤒ $2e^-$ gain

4.(D) $[Cr\,(NH_3)_4Cl_2]^+ : Cr = +3$

5.(C) $\overset{+7}{Mn}O_4^- \xrightarrow{5e^-} Mn^{2+}$; $\overset{+7}{Mn}O_4^- \xrightarrow{1e^-} \overset{+6}{Mn}O_4^{2-}$; $\overset{+7}{Mn}O_4^- \xrightarrow{3e^-} \overset{+4}{Mn}O_2$; $\overset{+7}{Mn}O_4^- \xrightarrow{4e^-} \overset{+3}{Mn_2}O_3$

6.(C) Anode - where oxidation takes place

7.(C) $T(^{\circ}F) = 32 + \dfrac{9}{5}T(^{\circ}C)$

8.(D) $He \longrightarrow 1\,mole$; $Na \longrightarrow 2\,moles$; $Ca \longrightarrow 10^{-2}\,moles$; $He \longrightarrow 3\,moles$

9.(A) $(H_2SO_4)\,moles = 0.1 \times 0.02 = 2 \times 10^{-3} \Rightarrow 2 \times 10^{-3}\,(H_2SO_4) \equiv 2 \times 10^{-3} \times N_A$ molecules

Moles of $= 12.044 \times 10^{20}$ molecules

10.(A) $(3.12 \times 1.5)_g$ to be one decimal as minimum significant figure has one digit after decimal.

11.(C) Example: $H_{2(g)} + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$

12.(B) Typical case of Law of multiple proportions.

13.(AD) $O_2 \longrightarrow 32g$ For 1 mol there are N_A molecules

14.(AB) $[NaOH] \longrightarrow M = \dfrac{20}{40} \times \dfrac{1000}{200} = \dfrac{5}{2}M$; $[KOH] \longrightarrow M = 0.5 \times \dfrac{1000}{200} = \dfrac{5}{2}M$

15.(CD) Refer formula

16.(BD) Refer theory

17.(A) As bromine case more change in oxidation state

18.(A) $NaH \longrightarrow$ Oxidation State $\to (-1)$ as compared to iodine

19.(B) $\left(NH_4^+\right)\left(NO_3^-\right)$
$\quad\quad\downarrow\quad\quad\downarrow$
$\quad\quad -3\quad\quad +5$

20.(D) $Mn \longrightarrow 3d^5 4s^2\ (+7)$

21.(D) $\overset{+4}{N}O_2 \longrightarrow \overset{+3}{N}O_2^-$ reduction $\quad$ $\overset{+4}{N}O_2 \longrightarrow \overset{+5}{N}O_3^-$ oxidation

22.(ABC) oxidation ⤒ $2K\overset{+1}{C}\overset{+5}{l}\overset{-2}{O_3} \longrightarrow 2K\overset{+1}{C}\overset{-1}{l} + 3\overset{0}{O_2}$ reduction ⤒

23.(CD) $\overset{0}{Zn} + 2\overset{+1}{H}Cl \longrightarrow \overset{+2}{Zn}Cl_2 + \overset{0}{H_2}$
Oxidant
reductant

24.(CD) C : Vanadium, D : Phosphorous

25.(B) As oxidizing nature depends on electron gain enthalpy and hydration energy.

26.(C) Mn acts as oxidizing agent and oxidation state changes from +7 to +2.
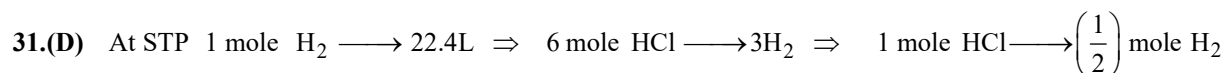
27.(D) $\underset{V}{CxHy} + \left(x + \dfrac{y}{4}\right)O_2 \longrightarrow \underset{(Vx)}{\times CO_2} + \underset{\left(V_{y/2}\right)}{\dfrac{y}{2}H_2O}$
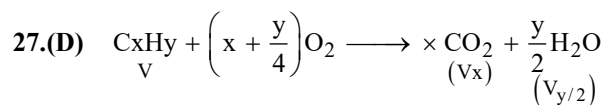
$n_{H_2O} = \left(\dfrac{0.72}{18}\right) n_{CO_2} = \left(\dfrac{3.08}{44}\right) \Rightarrow \dfrac{n_{CO_2}}{n_{H_2O}} = \dfrac{3.08}{44} \times \dfrac{18}{0.72} \Rightarrow \dfrac{x}{y/2} = \dfrac{7}{4} \Rightarrow \dfrac{x}{y} = \dfrac{7}{8}$

28.(D) $\text{Volume} = \left(\dfrac{\overset{\text{Total Mass}}{\uparrow}}{\dfrac{1120}{1.15}}\right) \longrightarrow \text{ml M} = \dfrac{120}{60} \times \left(\dfrac{1000 \times 1.15}{1120}\right) = 2.05M$

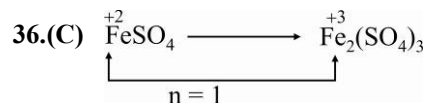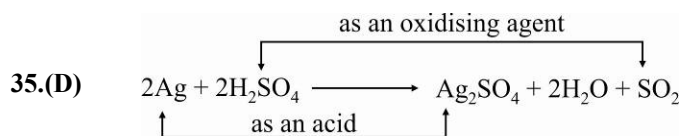**29.(C)** $\dfrac{g}{(294/6)} = 0.75 \times 0.6 \times 1 \quad \Rightarrow \quad g = 22.05g$ **30.(C)** As $Cl^{\ominus}$ reduces Mn to Mn^{2+}

31.(D) At STP 1 mole $H_2 \longrightarrow 22.4L \Rightarrow 6$ mole $HCl \longrightarrow 3H_2 \Rightarrow 1$ mole $HCl \longrightarrow \left(\dfrac{1}{2}\right)$ mole H_2

32.(B) Mass will remain constant

33.(B) $BCl_3 + \dfrac{3}{2}H_2 \longrightarrow B + 3HCl$ (2 moles of $B \equiv 3$ moles of H_2)

34.(A) Mole ratio : $\dfrac{9}{12} : \dfrac{1}{1} : \dfrac{3.5}{14} \Rightarrow 3:4:1$.   **35.(D)**

$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$ (with "as an oxidising agent" and "as an acid" annotations)

36.(C) $\overset{+2}{Fe}SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3$; $n = 1$ **37.(C)** Refer structure from module

38.(B) $\overset{-3}{N}H_4 \overset{+3}{N}O_2 \longrightarrow \overset{0}{N_2} + 2H_2O$
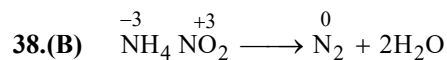
39.(C) meq FeC_2O_4 = meq $K_2C_2O_7$

$3 \times 1 = 6 \times$ mmoles of $K_2Cr_2O_7$

$FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$ (with $1e^-$ and $2e^-$ annotations)
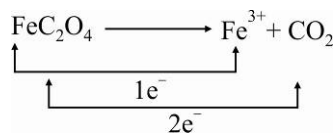
40.(ABC) $(0.1)NaHC_2O_4 \longrightarrow 0.1$ moles of H^+

geq of $C_2O_4^{2-} = 2 \times 0.1 = 0.2$

41.(B) 16.9% solution of $AgNO_3$ means 16.9 g of $AgNO_3$ in 100 mL of solution.

16.9% of $AgNO_3$ in 100 mL solution $\equiv 8.45\,g$ of $AgNO_3$ in $50\,mL \equiv 0.049\,mol$

Similarly, 5.8% of $NaCl \equiv 2.9$ g of NaCl in 50 mL solution $\equiv 0.05$ mol.

The reaction can be represented as :

	$AgNO_3$	+	NaCl	$\rightarrow$	AgCl	+	$NaNO_3$
Initially	0.049		0.05		0		0
Finally	0		0		0.049 mol		0.049 mol

$\therefore$ Mass of AgCl precipitated $= 0.049 \times 143.3 \approx 7.0g$
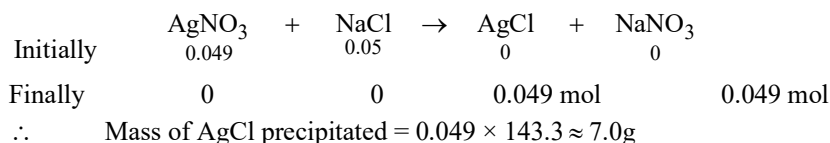
42.(A) Mass of 1 mol (6.022×10^{23} atoms) of carbon = 12 g.

If Avogadro number is changed to 6.022×10^{20} atoms then mass of 1 mol of carbon

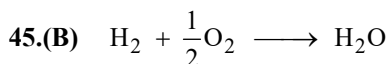$= \dfrac{12 \times 6.022 \times 10^{20}}{6.022 \times 10^{23}} = 12 \times 10^{-3}\,g$

43.(C) According to Avogadro's hypothesis, ratio of the volumes of gases will be equal to the ratio of their moles.

$$n_{H_2} = \frac{g}{2} : n_{O_2} = \frac{g}{32}; \ n_{CH_4} = \frac{g}{16}$$

So, the ratio is $\frac{g}{2} : \frac{g}{32} : \frac{g}{16}$ or $16 : 1 : 2$.

44.(D) Moles of urea $= \dfrac{6.02 \times 10^{20}}{6.02 \times 10^{23}} = 0.001$

Concentration of solution $= \dfrac{0.001}{100} \times 1000 = 0.01\,M$

45.(B) $H_2 + \dfrac{1}{2}O_2 \longrightarrow H_2O$

1 mol   0.5 mol   1 mol
10 g of H_2 = 5 mol and 64 g of O_2 = 2 mol

∴   In this reaction, oxygen is the limiting reagent hence amount of H_2O produced depends on that of O_2.
Since 0.5 mol of O_2 gives 1 mol H_2O

∴   2 mol of O_2 will give 4 mol H_2O

46.(D) Average isotopic mass of X $= \dfrac{200 \times 90 + 199 \times 8 + 202 \times 2}{90 + 8 + 2} = \dfrac{18000 + 1592 + 404}{100} = 199.96\ \text{amu} \sim 200\ \text{amu}$

47.(A) At STP: 22.4 L H_2 = 6.023×10^{23} molecules

$15\,L\ H_2 = \dfrac{6.023 \times 10^{23} \times 15}{22.4} = 4.033 \times 10^{23}$

$5\,L\ N_2 = \dfrac{6.023 \times 10^{23} \times 5}{22.4} = 1.344 \times 10^{23}$

$0.5\,g\ H_2 = \dfrac{6.023 \times 10^{23} \times 0.5}{2} = 1.505 \times 10^{23}$

$10\,g\ of\ O_2 = \dfrac{6.023 \times 10^{23} \times 10}{32} = 1.882 \times 10^{23}$

48.(D) Zeros placed left to the number are never significant, therefore the number of significant figures for the numbers. 161 cm, 0.161 and 0.0161 are same, i.e. 3.

49.(A) Amount of iron in one molecule (in gms) $= \dfrac{67200}{100} \times 0.334 = 224.45\ \text{amu}$

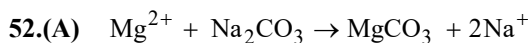Number of iron atoms in one molecule of hemoglobin $= \dfrac{224.45}{56} = 4$.

50.(A) $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(l)}$
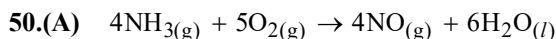
4 mol $NH_{3(g)}$ ≡ 5 moles $O_{2(g)}$ ≡ 4 moles $NO_{(g)}$ ≡ 6 moles $H_2O_{(l)}$

Observe that O_2 is limiting reagent, so it will be consumed totally leaving behind NH_3.

51.(A) 1 mol CCl_4 vapour = $12 + 4 \times 35.5 = 154$ gm

At S.T.P.: Density of CCl_4 vapour $= \dfrac{154}{22.4}\ \text{g L}^{-1} = 6.875\ \text{g L}^{-1}$.

52.(A) $Mg^{2+} + Na_2CO_3 \rightarrow MgCO_3 + 2Na^+$

1 gmeq of Mg^{2+} requires 1 gmeq of soda.

$12.00\,mg \equiv 12.00 \times 10^{-3}\,g \equiv \dfrac{12.00 \times 10^{-3}}{24/2} \times 1000 = 1\ meq\ of\ Mg^{2+}$
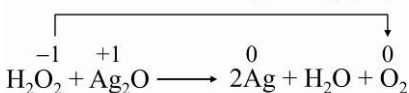
$\Rightarrow$ 1 meq of soda is required.

53.(C) Both $FeCl_2$ and $SnCl_2$ are reducing agents with lower oxidation numbers.
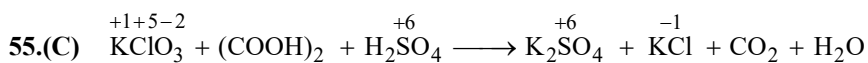
54.(C)

H_2O_2 acts as reducing agent in all those reactions in which O_2 is evolved..

55.(C) $\overset{+1+5-2}{KClO_3} + (COOH)_2 + H_2SO_4 \longrightarrow K_2\overset{+6}{SO_4} + \overset{+6}{K}\overset{-1}{Cl} + CO_2 + H_2O$

Maximum change in oxidation number of chlorine, i.e., from $+5$ to -1.

56.(C) $5e + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$;

$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$ [Both Fe^{2+} ion and $C_2O_4^{2-}$ ions will be oxidized]
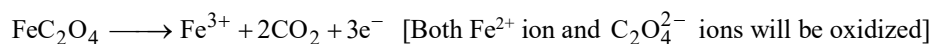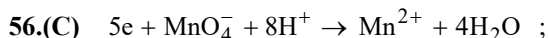
gmeq of $MnO_4^- =$ gmeq of FeC_2O_4 $\Rightarrow$ $5n = 3 \times 1$ $\Rightarrow$ $n = \dfrac{3}{5} = 0.6$

57.(B) $H_2O + \overset{0}{Br_2} \rightarrow H\overset{+1}{O}Br + H\overset{-1}{Br}$
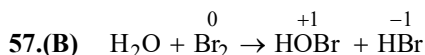
In the above reaction the oxidation number of Br_2 increases from zero (in Br_2) to $+1$ (in $HOBr$) and decreases from zero (in Br_2) to -1 (in HBr). Thus Br_2 is oxidised as well as reduced and hence it is a disproportionation redox reaction.

58.(B) meq of $NaOCl =$ meq of $NaCrO_2$.

$\left[OCl^- + H_2 + 2e \longrightarrow Cl^- + 2OH^- \right]; \left[CrO_2^- + 4OH^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^- \right]$
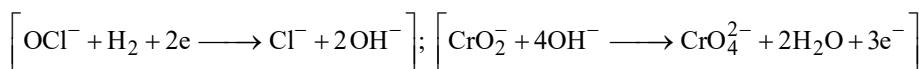
n-factor of $NaOCl = 2$ n-factor of $NaCrO_2 = 3$

$\Rightarrow$ $2 \times 0.15 \times V = 3 \times 0.2 \times 20$ $\Rightarrow$ $V = 40\,mL$

59.(D) meq of $H_2O_2 =$ meq of MnO_4^- / H^+

$\Rightarrow$ $N \times 10 = \dfrac{1}{0.56} \times 10$ $\Rightarrow$ $N(H_2O_2) = \dfrac{1}{0.56}$

Volume strength of H_2O_2 ; $1\ N\ H_2O_2 \equiv 5.6 \times \dfrac{1}{0.56} = 10\,vol$

60.(C) Find oxidation state of each element.

(A) $VO_4^{3-} [V = +5]$ (B) $Mn_2O_3 [Mn = +3]$

(C) $S_4O_6^{2-} [S = +2.5]$ (D) $Cl_2O_7 [Cl = +7]$

61. (820) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$

90 m mole   500 mmole   0

0   500–180   90

                = 320 mmoles

320 mmoles of NaOH and 90 mmoles of Na_2CO_3 will need 410 mmole of HCl. Since HCl is 0.5 M

$\Rightarrow$ Volume required is 820 ml

62. (4)   Mol of $O_2 = \dfrac{44.8}{22.4} = 2.0$ Mol of $CH_3OH = \dfrac{64}{32} = 2.0$

$\because$ 2 mol CH_3OH require 3 mol O_2, hence O_2 is a limiting reagent.

Moles of CO_2 formed $= \dfrac{2}{3} \times 2 = 1.33$

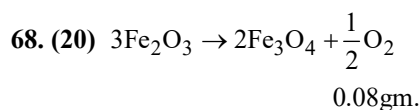**63.(2)**   The balanced chemical reaction equation is $Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

Now, mol of HCl produced $= 0.08 \times 3$

$\Rightarrow$ mol. of $Al(OH)_3$ needed $= 0.08 \Rightarrow$ mass of $Al(OH)_3$ needed $= 0.08 \times 78 = 6.24$

64. (3)   Balancing the chemical reactions $2MnO_4^- + 3C_2O_4^{2-} + 4H_2O \rightarrow 2MnO_2 + 8\,OH^- + 6CO_2$

Since,

$\Rightarrow$ $(2 + 6) - (2 + 3)$

$\Rightarrow$ 3

65. (20) $BaCl_2.2H_2O \xrightarrow{CrO_4^{2-}} BaCrO_4$

$BaCrO_4 \xrightarrow{H^+} Cr_2O_7^{2-}$

$Cr_2O_7^{2-} + 6I^- \xrightarrow{H^+} 3I_2 + Cr^{3+}$

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

$\therefore$ milli moles of $I_2 = \dfrac{90 \times 0.2}{2} = 9$

milli moles of $Cr_2O_7^{2-} = 3$

milli moles of $BaCl_2.2H_2O = 6$

Amount of $BaCl_2.2H_2O = 6 \times 10^{-3} \times 244 = 1.464$

% purity $= \dfrac{1.464}{7.32} \times 100$

$= 20\%$

66. (5) $Al(MnO_4)_3 + FeC_2O_4 \rightarrow Al^{3+} + Mn^{2+} + Fe^{2+} + CO_2$

        n=15   n=3

67. (2)   Normality of acid $= \dfrac{39}{82/n \times 1}$

Normality of NaOH $= \dfrac{40}{40} \times \dfrac{1000}{1000} = 1$

Now, meq. of acid = meq. of NaOH $\Rightarrow \dfrac{39n}{82} \times 100 = 1 \times 95$

n = 2

68. (20) $3Fe_2O_3 \rightarrow 2Fe_3O_4 + \dfrac{1}{2}O_2$

$\qquad\qquad\qquad$ 0.08gm.

$w = \dfrac{0.08}{32} \times 2 \times 3 \times 160$

$= 2.4gm$

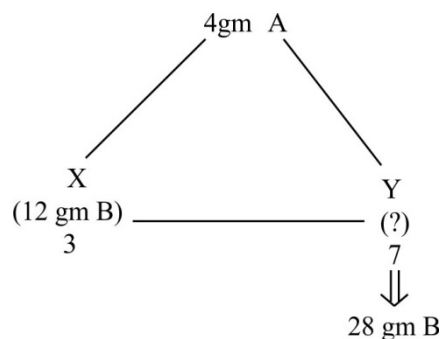$\therefore \quad \% \ SiO_2 = \dfrac{0.6}{3} \times 100$

$= 20\%$

69. (24) $\dfrac{a \times 16 + b \times 28}{a + b} = 20$

$\Rightarrow \qquad a = ab$

$\dfrac{b \times 16 + a \times 28}{a + b} = ?$
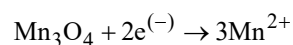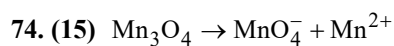
$\Rightarrow \qquad M = 24$

70. (56) 56 gm

$\therefore \ 8 \ gm \ A \rightarrow 56 \ gm \ B$

71. (10) $\dfrac{a}{72} \times 1 + \dfrac{b}{160} \times 2 = \dfrac{7}{56}$ $\qquad\qquad$ …(1)

$\dfrac{a}{72} \times 1 + \dfrac{b}{160} \times 3 = \dfrac{2.5}{16}$ $\qquad\qquad$ …(2)

72. (1) $\dfrac{\dfrac{500 \times 0.2}{1000} + \dfrac{17.1 \times 3}{342}}{0.6 \times 5} = \dfrac{1}{12} M.$

73.(1) $\dfrac{17.4}{87} = \dfrac{12.6}{110 + 16y} \times 2 \qquad \Rightarrow \qquad y = 1$

74. (15) $Mn_3O_4 \rightarrow MnO_4^- + Mn^{2+}$

$Mn_3O_4 \rightarrow 3MnO_4^- + 13e^{(-)}$

$Mn_3O_4 + 2e^{(-)} \rightarrow 3Mn^{2+}$

$$n_{eff} = \frac{2 \times 13}{2 + 13} = \frac{26}{15} \quad \Rightarrow \quad E = \frac{M}{26} \times 15$$

75. (3) $\quad$ 4m mol KI $\longrightarrow$ 2 m mole $e^{(-)}$

$\qquad$ 5m mol KI $\longrightarrow \frac{2}{4} \times 5$ m mole $e^{(-)}$

Atomic Structure

1.(ABD) Option (C) is postulate of Bohr's model

2.(B) $\quad$ Cu has $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ (z = 29)

3.(ABCD) Refer theory $\qquad$ **4.(ACD)** $\quad$ Refer theory

5.(A) $\quad$ Plum pudding model

6.(D) $\quad$ Sane atomic mass but different atomic numbers

7.(D) $\quad$ $3p \rightarrow n - \ell - 1$ (radial nodes) $= 3 - 1 - 1 = 1$

8.(C) $\quad$ $4d \rightarrow \ell$ (angular nodes)

9.(B) $\quad$ Refer theory

10.(B) $\quad$ Fe^{3+}, Mn^{2+} have same no. of electrons

11.(D) $\quad$ Pauli's Exclusion Principal

12.(CD) For an atom $\underset{Z}{\overset{A}{}} \underset{\substack{\downarrow \\ \text{symbol}}}{X}$; $\quad$ A : Mass number, $\;$ Z : Atomic Number ; $\quad$ For isotopes Z is same

13.(AD) Energy is governed by $(n + \ell)$ rule

14.(BC) As $n = \ell$ (is not allowed); $\; n < \ell$ (is not allowed) $\quad$ **15.(AC)** Both pairs have $10e^{\ominus}$s

16.(A) $\quad$ Isotopes have same number of electrons

17.(B) $\quad$ (R) is not correct explanation of (A)

18.(A) $\quad$ $\dfrac{hc}{\lambda} = 2.18 \times 10^{-18} \left(\dfrac{1}{1^2} - \dfrac{1}{2^2} \right)(1)^2$

$\qquad \dfrac{6.625 \times 10^{-34} \times 3 \times 10^8}{\lambda} = 2.18 \times \dfrac{3}{4} \times 10^{-18} \quad \Rightarrow \quad \lambda = \left(\dfrac{6.626 \times 4}{2.18} \right) \times 10^{-8} = 1.214 \times 10^{-7}\text{m}$

19.(B) $\quad$ Apply $(n + \ell)$ rule : For $\quad n_1 + \ell_1 = n_2 + \ell_2$

$\qquad\qquad\qquad\qquad\qquad\qquad n_2 > n_1$

$\qquad$ The electron with n_2 principal quainter number has more energy.

20.(C) $\quad$ Apply $\quad \dfrac{hc}{\lambda} = \dfrac{hc}{\lambda_1} + \dfrac{hc}{\lambda_2} \quad \Rightarrow \quad \dfrac{1}{355} = \dfrac{1}{680} + \dfrac{1}{\lambda_2} \quad \Rightarrow \quad \dfrac{680 - 355}{680 \times 355} = (\lambda_2)^{-1} \Rightarrow \lambda_2 = \dfrac{680 \times 355}{325} = 742.76$ nm

21.(B) $\quad$ For Helium ion, $E \propto \dfrac{Z^2}{n^2} \propto (2)^2 \left(\dfrac{1}{2^2} - \dfrac{1}{4^2} \right) = \left(\dfrac{1}{1^2} - \dfrac{1}{2^2} \right)$ for hydrogen atom

22.(D) $\quad$ $\dfrac{hc}{\lambda} \times N_A = 242 \times 10^3 \quad \Rightarrow \quad \lambda = \dfrac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{242 \times 10^3} = 494$ nm

23.(B) $\quad$ $\left[He^+ \right] = -19.6 \times 10^{-18} = E_n \left(\dfrac{Z^2}{1^2} \right) = E_n \left(\dfrac{2^2}{1^2} \right) \Rightarrow E_n = -4.9 \times 10^{-18}$

$\qquad \left[Li^{2+} \right] = -4.9 \times 10^{-18} \dfrac{(3)^2}{1^2} = -4.41 \times 10^{-17}$ J atom^{-1}

24.(C) $\Delta x \cdot \Delta P = \dfrac{h}{4\pi}$

$\Delta x \cdot \left(9.1 \times 10^{-31} \times \left(0.005 \times 10^{-2}\right) 600\right) \geq \dfrac{6.626 \times 10^{-34}}{4\pi}$ $\Delta x \cdot \left(9.1 \times 10^{-33} \times 3\right) \geq \dfrac{6.626 \times 10^{-34}}{4\pi}$

$\Delta x \geq \dfrac{6.626 \times 10^{-1}}{4\pi \times 3 \times 9.1}$ $\Rightarrow$ $\Delta x \geq 1.92 \times 10^{-3}$ m

25.(B) $n + \ell$ is greatest   **26.(A)**   As neutron emission only change A not Z.

27.(C) $\Delta v = (300 \times 0.001 \times 10^{-2} \ \text{m/s})$

$\Delta x \cdot \left(9.1 \times 10^{-31} \times 3 \times 10^{-3}\right) \geq \dfrac{6.63 \times 10^{-34}}{4\pi}$ $\Rightarrow$ $\Delta x \geq \left(\dfrac{6.63}{4\pi \times 9.1 \times 3}\right)$ $\Rightarrow$ $\Delta x \geq 1.92 \times 10^{-2}$ m

28.(D) $m\,v\,r = \dfrac{nh}{2\pi} = \dfrac{5}{2} \dfrac{h}{\pi} = \dfrac{2.5h}{\pi}$

29.(A) In single electron system energy is governed by principal quantum numbers only

30.(BC) Refer theory   **31.(C)** For 4f orbital $n = 4$, $\ell = 3$ **32.(B)** $Cr \rightarrow 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$
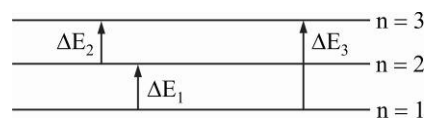
33.(B) Ist line $3 \rightarrow 2$, IInd line $4 \rightarrow 2$, IIIrd line $5 \rightarrow 2$

34.(D) Fe : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$; Fe^{2+} : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$

35.(B) $\ell = 0$ (s) Angular momentum $= 0$

36.(C) Second excited state $(n = 3)$: $E(n = 3) = -\dfrac{13.6}{(3)^2}(1)^2 = -1.51\,\text{eV}$

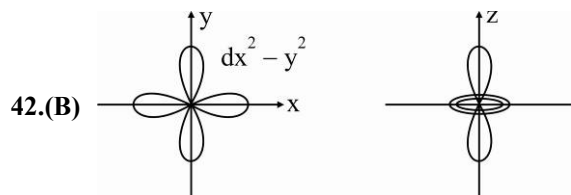**37.(A)** $\Delta E_1 + \Delta E_2 = \Delta E_3$ $\Rightarrow$ $h\nu_1 + h\nu_2 = h\nu_3$ $\Rightarrow$ $\nu_1 + \nu_1 = \nu_3$

38.(C) Number of waves in nth orbit $= n$

39.(D) K.E. $= h\nu - h\nu_0$

$h\nu = 1.5\,h\nu_0$ $\Rightarrow$ K.E. $= 0.5 h\nu_0$ $\Rightarrow$ $h\nu_0 = 13.6$ $\Rightarrow$ K.E. $= 13.6 \times 0.5 = 6.8$ eV

40.(D) $E_{n_1 \rightarrow n_2} = 13.6 \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

41.(D) Total energy $= -13.6(2)^2$; P.E. $= 2$T.E.$= -13.6 \times 2 \times (2)^2 = -108.8$ eV

42.(B)

43.(B) $Ti(22)$ $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^2 = \sqrt{n(n+2)} = \sqrt{2 \times 4} = \sqrt{8}$ B.M.   **44.(B)**   Refer theory

45.(C) $a_0 \longrightarrow$ Bohr's radius $\quad r = a_0\left(\dfrac{n^2}{z}\right)\left\{\begin{matrix} n = 2 \\ z = 1 \end{matrix}\right\}$

$m\,v\,r = \dfrac{n\,h}{2\pi} \quad \Rightarrow \quad mv\,a_0\dfrac{n^2}{z} = \dfrac{n\,h}{2\pi} \quad \Rightarrow \quad mv = \left(\dfrac{h\,z}{2\pi a_0 n}\right)(z=1)$

$mv = \left(\dfrac{h}{2\pi a_0 n}\right) \quad \Rightarrow \quad mv = \left(\dfrac{h}{4\pi a_0}\right)(n=2) \quad \Rightarrow \quad \dfrac{(mv)^2}{2m} = \dfrac{1}{2m}\times\left(\dfrac{h}{4\pi a_0}\right)^2 \quad \Rightarrow \text{ K.E.} = \left(\dfrac{h^2}{32\ m\pi^2 a_0^2}\right)$

46.(C) Use $(n + \ell)$ rule $\quad \therefore \quad$ Order of increasing energy is 3s, 3p, 4s, 3d.

47.(D) Number of d-electrons in $Fe^{2+} = 6$; Number of d-electrons in Fe = 6 (as in Fe^{2+}, e's are removed from 4s)
Number of p-electron is ($1s^2\ 2s^2\ 2p^6$) in Ne = 6 ; Number of s-electron in Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$)
Number of p-electrons in Cl = 11 ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$)

48.(A) Only one orbital, 3p has following set of quantum numbers, n = 3, $l = 1$ and $m_l = 0$.

49.(B) The electron is more tightly bound in the smallest allowed orbit.

50.(A) Orbital angular momentum (m) $= \sqrt{\ell(\ell+1)}\ \dfrac{h}{2\pi}$

For p-electrons ; $\ell = 1 \qquad$ Thurs, $m = \sqrt{\ell(\ell+1)}\ \dfrac{h}{2\pi} = \dfrac{\sqrt{2}h}{2\pi} = \dfrac{h}{\sqrt{2}\pi}$

51.(A) Correct order of filling for n = 6 in outermost will be : (Aufbau principle) : 6s 4f 5d 6p

52.(B) In an atom, for any value of n, the values of $l = 0$ to $(n-1)$. For a given value of l, the values of $m_l = -l$ to $+ l$ and the value of s = 1/2 or $-1/2$.

53.(C) From Heisenberg uncertainty principle

$\Delta p \cdot \Delta x \geq \dfrac{h}{4\pi} \quad \text{or} \quad m\Delta v \times \Delta x \geq \dfrac{h}{4\pi}$

or $\quad (m\Delta v)^2 \geq \dfrac{h}{4\pi} \qquad (\because \Delta x = \Delta p)$

or $\quad \Delta v \geq \dfrac{1}{2m}\sqrt{\dfrac{h}{\pi}}$

54.(C) Uncertainty in momentum $(m\Delta v) = 1 \times 10^{-18}$ g cm s^{-1}

Uncertainly in velocity, $(\Delta v) = \dfrac{1 \times 10^{-18}}{9 \times 10^{-28}} = 1.1 \times 10^9$ cm s^{-1}

55.(B) **(i)** represents an electron in 3s orbital.
(ii) is not possible as value of l varies from 0 to $(n-1)$ ..
(iii) represents an electron in 4f orbital.
(iv) is not possible as value of m varies from $-l$ to $+l$.
(v) is not possible as value of m varies from $-l$ to $+ l$, it can never be greater than l.

56.(A) $E_n = -13.6\left(\dfrac{Z^2}{n^2}\right)$; Hence 1st excited state is n = 2 : $KE = -E_n = -(-3.4)$ eV $= 3.4$ eV

57.(A) n = 3, $l = 2$, m = +2 (+2, +1, 0, -1, -2). It symbolizes one of the five d-orbitals

58.(C) $\lambda = \dfrac{h}{mv} = \dfrac{6.63 \times 10^{-27} \text{ erg sec}}{1g \times 10^4 \text{ cm/s}} = 6.63 \times 10^{-31} \text{ cm} = 6.63 \times 10^{-23} \text{ m}$

59.(A) Since both CO and CN^- have 14 electrons, therefore these are iso-electronic (i.e. having same number of electrons).

60.(A) The number of electrons in O^{2-}, N^{3-}, F^- and Na^+ is 10 each, but number of electrons in Mg^+ is 11.

61.(1)

	H^1	H^2	H^3
p	1	1	1 = 3
n	0	1	2 = 3

$\therefore \quad \dfrac{3}{3} = 1$

62.(20) $100 \times 8000 = W \times 4000 \quad \Rightarrow \quad W = 200$ **63.(32)** Total number of $e^- = 7 + 8 \times 3 + 1 = 32$

64.(1) $\dfrac{hc}{\lambda} = 1 + W; \dfrac{3hc}{\lambda} = 5 + W \Rightarrow W = 1 \text{ eV}$ **65.(27)** $kZ^2 = 36, 36\left[\dfrac{1}{1^2} - \dfrac{1}{2^2}\right] = 27 \text{eV}$

66.(5) $\Delta x_{min} = \dfrac{h}{4\pi.m.\Delta V} = \dfrac{6.626 \times 10^{-34}}{4\pi \times 10^{-6} \times \dfrac{3.313}{\pi} \times 10^{-3}} = 5 \times 10^{-26} \text{ m}$

67.(1) $\lambda = \dfrac{h}{\sqrt{3mkT}}, \lambda \propto m^{-1/2} T^{-1/2}$ **68.(45)** $n = 12 \text{ to } n = 3; \Delta n = 9; 9 \times \dfrac{10}{2} = 45$

69.(20) $3.6 \times 1.6 \times 10^{-13} = \dfrac{\left(9 \times 10^9\right)(Z)(2)\left(1.6 \times 10^{-19}\right)^2}{1.6 \times 10^{-14}}$

$Z = 20$

70.(12) Intensity of each beam $= 1.2 \times 10^{-3}$

Wattage of each beam $= 1.2 \times 10^{-3} \times 10^{-4} = 1.2 \times 10^{-7} \text{ W}$

$E_1 = \dfrac{12400}{4144} 3 \text{eV}, \quad E_2 = \dfrac{12400}{4972} = 2.5 \text{eV}$

$E_3 = \dfrac{12400}{6216} = 2 \text{eV};$

Only E_1 and E_2 can eject photoelectrons.

$N_1 = \dfrac{1.2 \times 10^{-7}}{2.5 \times 1.6 \times 10^{-19}}; N_2 = \dfrac{1.2 \times 10^{-7}}{3.0 \times 1.6 \times 10^{-19}}$

$\Rightarrow \quad N_1 + N_2 = 0.55 \times 10^{12} \text{ in 1 sec}$

$\therefore \quad \text{in 2 sec.} = 1.1 \times 10^{12}$

71.(25) $r_n = \dfrac{n^2 h^2}{4k\pi^2 \times 3e^2 \times 208 m_e}$

72.(80) $n_2 = 3, n_1 = 1$

$$\frac{1}{\lambda} = R_H \times 3^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right]$$

$$\Rightarrow \qquad \lambda = \frac{4}{5R_H} = 8 \times 10^{-8}\,m = 80\,nm$$

73.(10) No. of photoelectrons emitted $= \dfrac{90}{3} \times \dfrac{4000 \times 10^{-10}}{6.4 \times 10^{-34} \times 3 \times 10^8} = \dfrac{1}{1.6} \times 10^{20}$

$\therefore$ Magnitude of charge passing per second $= \dfrac{1}{1.6} \times 10^{20} \times 1.6 \times 10^{-19} = 10A$

74.(97)

75.(4) $E_{incident} = \dfrac{1240}{300} = 4.1\,eV$

So Li, Na, K, Mg will show.

Periodic Properties of Elements

1.(C) **2.(B)** Pb has most stable +2 state among the given (inert pair effect)

3.(C) $O^{2-} > F^- > Na^+ > Mg^{+2}$ **4.(D)** **5.(A)** Shielding effect : $s > p > d > f$

6.(A) 1st ionization enthalpies : Na < Mg > Al < Si **7.(C)**

8.(D) $I^- > I > I^+$ (anion are larger than parent ; cations are smaller) **9.(C)**

10.(A)
$$\left. \begin{array}{ll} I & \text{is Neon} \\ II & \text{is oxygen} \\ III & \text{is sodium} \\ IV & \text{is fluorine} \end{array} \right| \begin{array}{l} \text{Electron Affinity} \\ IV > II > III > I \end{array}$$

11.(BC) Suphur and Phosphorus can show covalency greater than 4. Ex : SF_6, PCl_5 etc.

12.(AC) Group 1 and 2 elements impart characteristic flame colour.

13.(AD) Sulphur has maximum electron affinity in its group. Chlorine has maximum electron affinity among halogens.

14.(ACD) **15.(BC)**

16.(BC) (Actually 1st ionization enthalpy follows B < C < N > O) and 1st electron gain enthalpy Cl > F > Br > I)

17.(AD) **18.(AC)** **19.(AC)** **20.(B)** **21.(A)** **22.(C)** **23.(B)**

24.(A) Alkali metal oxides are more basic $\therefore$ $K_2O > Na_2O > MgO > Al_2O_3$

25.(D) $O^{2-} > F^- > Na^+ > Mg^{+2} > Al^{+3}$ **26.(B)**

27.(C) Denser the cation, more will be the polarizing power. **28.(B)** Rb^+ is least solvated

29.(B) **30.(D)** **31.(C)** **32.(C)** **33.(C)**

**34.(C)** **35.(D)** **36.(D)** **37.(B)** **38.(B)** **39.(B)** **40.(ABCD)**

41.(D) Electron gain enthalpy becomes less negative from top to bottom in a group while it becomes more negative from left to right within a period.

42.(A) As positive charge on the cation increases, effective nuclear charge increases. Thus atomic size decreases.

43.(A) $Na \rightarrow Na^+ + e^-$; $\Delta H = 5.1\,eV$; $Na^+ + e^- \rightarrow Na$; $\Delta H = -5.1\,eV$.

44.(A) In going left to right across a period in the periodic table, the basicity (i.e. proton affinity) decreases as the electronegativity of the atom possessing the lone pair of electrons increases. Hence basicity of NH_2^- is higher than F^-. In moving down in a group, as the atomic mass increases, basicity decreases. Hence F^- is more basic than I^- and HO^- is more basic than HS^-. Hence among the given ionic species, NH_2^- has maximum proton affinity.

45.(A)

$X - X$ bond	$F - F$	$Cl - Cl$	$Br - Br$	$I - I$
Bond dissociation energy (kcal/mol)	38	57	45.5	35.6

The lower value of bond dissociation energy of fluorine is due to the high inter-electronic repulsion between non-bonding electrons in the 2p-orbitals of fluorine. As a result $F - F$ bonds is weaker in comparison to $Cl - Cl$ and $Br - Br$ bonds.

46.(B) Amongst isoelectronic ions, ionic radii of anions is more than that of cations. Further size of the anion increases with in $-ve$ charge and size of cation decreases with increases in +ve charge. Hence correct order is

$$O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}.$$
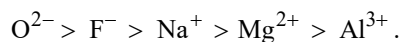
47.(D) Atomic volume is the volume occupied by one gram of an element. Within a period from left to right, atomic volume first decreases and then increases.

48.(2) Ti^{2+}, V^{3+} **49.(3)** 83, 54, 34

50.(9) $Fe^{+3}, Mn^{2+}, Co^{4+}, Co^{3+}, Cr^+, Fe^{2+}, Mn^{3+}, Cr^{3+}, V^{3+}$ **51.(4)** Sc, Pd, Os, Zr

52.(3) Se^{2-}, N^{3-}, P^{3-} **53.(6)** Li, Na, Mg, Rb, Sr, Ca   **54.(1)** Pt only   **55.(4)**

56.(9) $x = 4, y = 13$ **57.(9)** $a = 0, b = 5, c = 14$ **58.(0)**

59.(5) $x = 2(NO, N_2O); y = 3(MgO, SrO, K_2O)$ **60.(4)** $n = 3, \ell = 1$

61.(48) $7s, 7p, 6d, 5f$ **62.(32)**
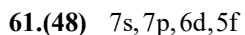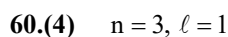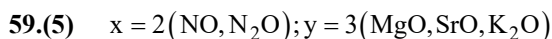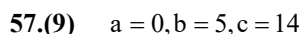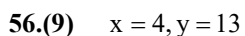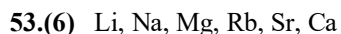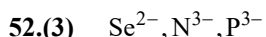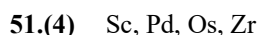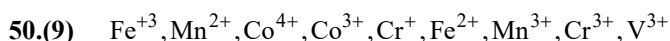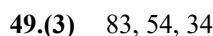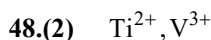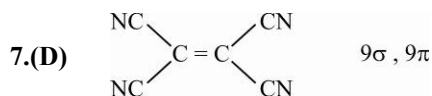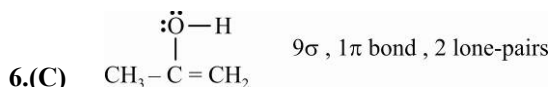
No. of orbitals $= 1 + 3 + 5 + 7 = 16$.
$16 \times 3 = 48$

Chemical Bonding - 1 & 2

1.(C) Apply Fajan's rule   **2.(AB)**

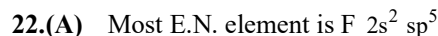**3.(D)** Te^{2-} largest size, loosely packed e^- **4.(D)** BF_3 sp^2, planar ; NF_3 sp^3, pyramidal

5.(ABCD)

6.(C) $CH_3 - \overset{\overset{\displaystyle :\ddot{O}-H}{|}}{C} = CH_2$ 9σ , 1π bond , 2 lone-pairs   **7.(D)** $(NC)(NC)C = C(CN)(CN)$ 9σ , 9π

8.(D) BCl_3 planar

Cl—B(—Cl)(—Cl) [structure]   [steric number = 3]

NCl_3 $:\ddot{N}$ (Cl)(Cl)(Cl) [structure]   Pyramid   [steric number = 4]

9.(B) $H_2C = CH - CH = CH_2$ All C are sp^2

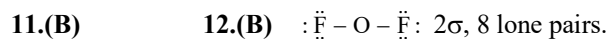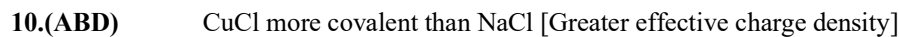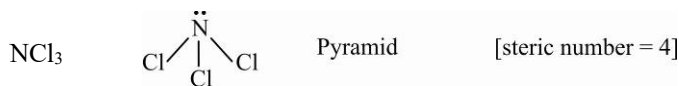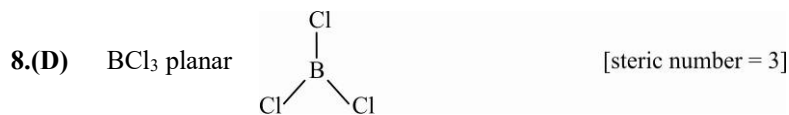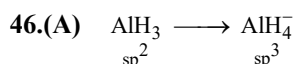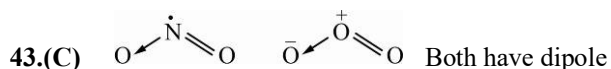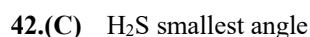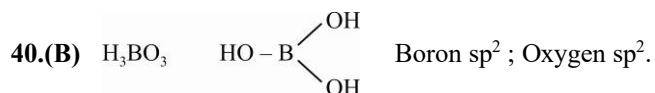**10.(ABD)**   CuCl more covalent than NaCl [Greater effective charge density]

11.(B)   **12.(B)** $:\ddot{F} - O - \ddot{F}:$ 2σ, 8 lone pairs.   **13.(B)** BF_4^- and NH_4^+ both sp^3, tetrahedral

14.(C)   **15.(B)** NO_2^+ sp ; NH_3^- sp^2 ; $\overset{+}{N}H_4$ sp^3 **16.(B)** $H_2O > HF > NH_3$

17.(D) $\bar{O} - \overset{+}{N}$ (with =O and O^-) 3σ, 1π, 0 lone pair   **18.(A)**   A tetrahedral shape for BH_4^-

19.(C) $H_2C=CH_2$ [structure] $C-H$ & $C=C$ are different   **20.(B)**

21.(D)   Valence shell used.   **22.(A)**   Most E.N. element is F $2s^2$ sp^5

23.(B)   [Ne] $3s^2 3p^2$ $\Rightarrow$ Mg (pseudo inert configuration)

24.(D) $H - O - H$ $\overset{\ominus}{O} - H$

Both bonds if cleaved one by one can never be of same strength. Successive H^+ donating ability of acids $\downarrow$se successively.

25.(B) CsI_3 : Cs^+ and I_3^- $\Rightarrow$ It is ionic.   **26.(C)** $SbCl_3$: Lowered bond angle

27.(C) PF_5 : bipyramidal ; BaF_5 : Square pyramidal   **28.(C)** $AlCl_3$ most covalent (Apply Fajan's Rule)

29.(D) IF_7 : pentagonal bipyramid   **30.(D)** XeF_2 : 3 lone pairs

31.(A) CaC_2 $C^- \equiv C^-$ $(1\sigma, 2\pi)$ **32.(B)** $F - H - - - - F$ strongest

33.(A) SF_4 axial bonds longer than equitorial   **34.(D)**   **35.(A)**

36.(A) SF_4 , CF_4 , XeF_4 **37.(D)** sp^3d^2 $\Rightarrow$ 12 angles at 90°
     1 lone pair $\downarrow$ 2 lone pairs
               0 lone pair

38.(C) BF_4^- : Regular tetrahedral   **39.(C)** $H_2C < NH_3 < SiH_4 < BF_3$

40.(B) H_3BO_3 $HO - B$ (—OH)(—OH)   Boron sp^2 ; Oxygen sp^2.   **41.(B)** XeF_2 linear ; CO_2 linear

42.(C) H_2S smallest angle   **43.(C)** $O - \dot{N} = O$ $\bar{O} - \overset{+}{O} = O$ Both have dipole

44.(C)   **45.(D)**   **46.(A)** $AlH_3 \longrightarrow AlH_4^-$
                                             sp^2 sp^3

47.(B) Fe^{+3} is more polarizing than Fe^{+2} $\therefore$ $FeCl_3$ more covalent

48.(A) II has high vapour pressure because of intra-H-bonding

49.(B) HCl has lowest boiling point **50.(C)** MX_3 ; zero dipole $\therefore$ sp^2

51.(D) $Be^{+2} < Mg^{+2} < Li^+ < Na^+$ **52.(D)** **53.(C)**

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \quad sp^3$$

54.(B)
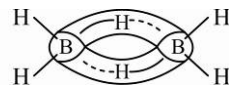
55.(C) NF_3 and H_3O^+ iso-structural ; NO_3^- and BF_3 iso-structural

56.(C) Unpaired e^- in KO_2 O_2^- (check MOT)

57.(B) NH_3 sp^3 ; $[PtCl_4]^{2-}$ dsp^2 ; PCl_5 sp^3d ; BCl_3 sp^2

58.(A) $H_3N \rightarrow BF_3$
$\quad\quad sp^3 \quad\quad sp^3$
tetrahedral   tetrahedral

59.(C) SF_2 2BP 2ℓp sp^3 ; SF_4 4BP 1ℓp sp^3d ; SF_6 6BP 0ℓp sp^3d^2

60.(C) B_2H_6

61.(D) $\begin{bmatrix} SO_4^{2-} & sp^3 \\ ClO_4^- & sp^3 \end{bmatrix}$ tetrahedral **62.(A)** **63.(D)**

64.(B) $O_2^- < O_2 < O_2^+$
$\quad\quad$ 1.5 2 2.5

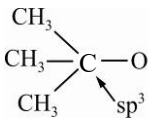**65.(AB)** C_2 and N_2 diamagnetic **66.(C)**

67.(B) Read the option (B) as $Li_2^- < Li_2^+ < Li_2$ (Li_2^{2-} has more electron in anti-bonding orbitals)
$\quad\quad$ Bond order 0.5 0.5 1

68.(A) **69.(A)** **70.(B)** $\underset{Para}{NO} \longrightarrow \underset{Diamagnetic}{NO^+}$ **71.(C)**

72.(B) Bond length $\propto \dfrac{1}{Bond\ order}$ **73.(D)** $O_2^+ > O_2 > O_2^- > O_2^{2-}$

74.(AB) Both 3

75.(AD) Both sp **76.(AB)** Both 14 e^-

77.(CD) Both are bent **78.(CD)** Check resonance

79.(AD) Check MOT **80.(CD)** Both 17e^- species

81.(C) In diamond and silicon carbide, central atom is sp^3 hybridised and hence, both are isostructural. NH_3 and PH_3, both are pyramidal and central atom in both cases is sp^3 hybridised. $SiCl_4$ and PCl_4^+, both are tetrahedral and central atom in both cases is sp^3 hybridised. In XeF_4, Xe is sp^3d^2 hybridised and structure is square planar while in XeO_5, Xe is sp^3 hybridised and structure is tetrahedral.
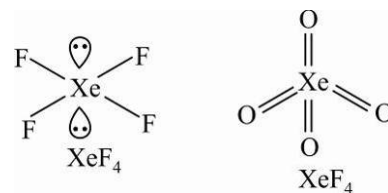
82.(B)

Species	Hybridistion	Shape	No. of e^-s
SO_3^{2-}	sp^3	Pyramidal	42
ClO_3^-	sp^3	Pyramidal	42
CO_3^{2-}	sp^2	Triangular planar	32
NO_3^-	sp^2	Triangular planar	32

83.(D) $\qquad\qquad O_2^- \ < \ O_2 \ < \ O_2^+$

Boiling point $\qquad$ 1.5 $\qquad$ 2.0 $\qquad$ 2.5

84.(A) $\qquad\qquad NO_3^- \qquad NO_2 \qquad NO_2^- \qquad NO_2^+$

Hybridisation $\quad sp^2 \qquad sp^2 \qquad sp^2 \qquad sp$
Bond angle $\qquad 120° \qquad 134° \qquad 115° \qquad 180°$

85.(A) Boron hydrides are electron deficient compounds.

86.(A) HCl is polar $(\mu \neq 0)$ and He is non-polar $(\mu = 0)$ gives dipole-induced dipole interaction.

87.(C) M.O. configuration of $O_2 \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \sigma 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$

$\Rightarrow \qquad$ Paramagnetic and B.O. $= \dfrac{10-6}{2} = 2$

$O_2^+ \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2p_z^2 \ \pi 2p_x^2 \ \pi 2p_y^2 \ \pi^* 2p_x^1 \qquad \Rightarrow \qquad$ Paramagnetic and Bond order $= \dfrac{10-5}{2} = 2.5$

$C_2 \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi 2p_x^2 \ \pi 2p_y^2 \ \Rightarrow$ Diamagnetic and Bond order $= \dfrac{8-4}{2} = 2$

$C_2^+ \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi 2p_x^2 \ \pi 2p_y^1 \ \Rightarrow$ Paramagnetic and Bond order $= \dfrac{7-4}{2} = 1.5$

$NO \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \sigma 2p_z^2 \ \pi 2p_x^2 \ \pi 2p_y^2 \ \pi^* 2p_x^1 \ \Rightarrow$ Paramagnetic and Bond order $= \dfrac{10-5}{2} = 2.5$

$NO^+ \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \sigma 2p_z^2 \ \pi 2p_x^2 \ \pi 2p_y^2 \ \Rightarrow$ Diamagnetic and Bond order $= \dfrac{10-4}{2} = 3$

$N_2 \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi 2p_x^2 \ \pi 2p_y^2 \ \sigma 2p_z^2 \ \Rightarrow$ Paramagnetic and Bond order $= \dfrac{10-4}{2} = 3$

$N_2^+ \Rightarrow \sigma ls^2 \ \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi 2p_x^2 \ \pi 2p_y^2 \ \sigma 2p_z^1 \ \Rightarrow$ Paramagnetic and Bond order $= \dfrac{9-4}{2} = 2.5$.

88.(D)

$\underset{\text{2 B.P. and 1 L.P.}}{H \overset{\ddot{O}}{\diagup}\diagdown H} \qquad \underset{\text{3 B.P. and 0 L.P.}}{Fl\diagdown\underset{F}{\overset{B}{|}}\diagup F} \qquad \underset{\text{2 B.P. and 2 L.P.}}{H\diagup\overset{\ddot{N}\overset{\centerdot\centerdot}{\,}^{(-)}}{\,}\diagdown H} \qquad \underset{\text{3 B.P. and 1 L.P.}}{Cl\diagup\underset{Cl}{\overset{\ddot{P}}{|}}\diagdown Cl}$

89.(D) Diatomic Species : $\qquad NO \qquad O_2^- \qquad C_2^{2-} \qquad He_2^+$

Bond order : $\qquad\qquad$ 2.5 $\qquad$ 1.5 $\qquad$ 3.0 $\qquad$ 0.5 $\qquad$ Thus increasing order : $He_2^+ < O_2^- < NO < C_2^{2-}$

90.(A) Ions : $\qquad\qquad NO_2^- \qquad NO_3^- \qquad NH_2^- \qquad NH_4^+ \qquad SCN^-$

Hybridisation : $\qquad sp^2 \qquad sp^2 \qquad sp^3 \qquad sp^3 \qquad sp$

91.(A) Increasing order of bond length is $C - H < C = C < C - O < C - C$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 107pm $\quad$ 134pm $\quad$ 141pm $\quad$ 154pm

92.(C) SF_4, I_3^- and PCl_5 all have central atom with sp^3d hybridisation ; whereas $[SbCl_5]^{2-}$ has sp^3d^2 hybridisation of Sb.

93.(D) Methanol can undergo intermolecular association through H-bonding as the $-OH$ group in alcohols is highly polarized.

$$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ ---&O-H&---&O-H&---&O-H&--- \end{array}$$
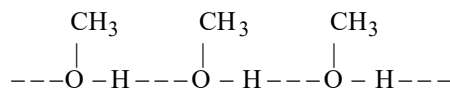
As a result, in order to convert liquid CH_3OH to gaseous state, the strong hydrogen bonds must be broken.

94.(D) For AB_5 molecules, there are three possible geometries i.e. planar pentagonal, square pyramidal and trigonal bipyramidal.

planar pentagonal $\quad\quad$ square pyramidal $\quad\quad$ trigonal bipyramidal
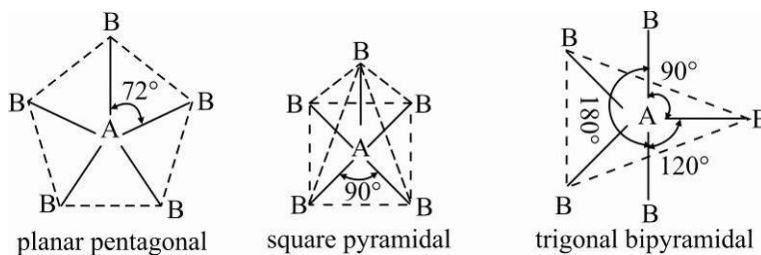
Out of these three geometries, it is only trigonal pyramidal shape in which bond pair-bond pair repulsions are minimum and hence this geometry is the most probable geometry of AB_5 molecule.

95.(B) Bond angle is maximum in NH_4^+ tetrahedral molecule with bond angle $109°$.

96.(B) In PO_4^{3-}, P atom has vacant d-orbitals, thus it can form $p\pi - d\pi$ bond. 'N' and 'C' have no vacant 'd' orbital in their valence shell, so they cannot form such bond.

97.(B) Diamagnetism is caused due to the absence of unpaired electrons. But in N^{2+}, there is unpaired electron. So, it is paramagnetic.
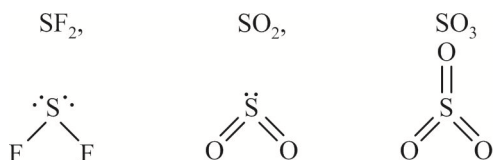
98.(A) The structure of CS_2 is linear and therefore it does not have permanent dipole moment. It is represented as $S = C = S$.

99.(B) The strength of interaction follow the order van der Waal's < hydrogen-bond < dipole-dipole < covalent. It is so because bond length of H-bond is larger than that of a covalent bond. And also covalent bond is strongest because the greater the extent of overlapping, the stronger is the bond formed.

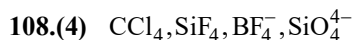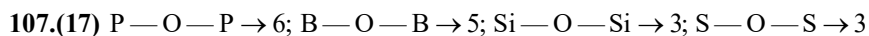**100.(C)** In NH_3 , $N - H$ bond is most polar and the shape is tetrahedral.
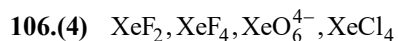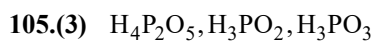
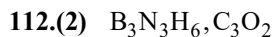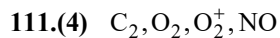**101.(4)** $ICl_2^-, XeO_3F_2, SF_4, SOF_4$

102.(3) Planar species are:

$$SF_2, \quad\quad\quad SO_2, \quad\quad\quad SO_3$$

103.(3) NO^+, CN^-, CO

104.(3) $(HPO_3)_n$ has n P—O—P linkages.

105.(3) $H_4P_2O_5, H_3PO_2, H_3PO_3$

106.(4) $XeF_2, XeF_4, XeO_6^{4-}, XeCl_4$

107.(17) $P-O-P \rightarrow 6; B-O-B \rightarrow 5; Si-O-Si \rightarrow 3; S-O-S \rightarrow 3$

108.(4) $CCl_4, SiF_4, BF_4^-, SiO_4^{4-}$

109.(1) (b) is only correct.

110.(5) Any existing species has $N_b < N_a$ electron.

111.(4) C_2, O_2, O_2^+, NO

112.(2) $B_3N_3H_6, C_3O_2$

113.(4)

	HOMO	**Symmetry**
B_2	$\pi 2p_x = \pi 2p_y$	u
N_2	$\sigma 2pz$	g
C_2	$\pi 2p_x = \pi 2p_y$	u
N_2^{2+}	$\pi 2p_x = \pi 2p_y$	u
O_2	$\pi * 2p_x = \pi * 2p_y$	g
O_2^{2-}	$\pi * 2p_x = \pi * 2p_y$	g
N_2^{2-}	$\pi * 2p_x = \pi * 2p_y$	g

114.(4) NO, ClO_2, OF, B_2

115.(3) $N_2^+ = (13)$ / Bond order $N_2^+ = \dfrac{9-4}{2} = 2.5$

[N_2^+ has one unpaired electron in $\sigma_{(2p)}$ (BMO)]

$O_2^- = (17)$ / Bond order $O_2^- = \dfrac{10-7}{2} = 1.5$

[O_2^- has one unpaired electron in $\pi *$]

OF (17) = Bond order (OF) = $\dfrac{10-7}{2} = 1.5$

[OF has one unpaired electron in $\pi *$]

States of Matter

1.(B) Refer theory $\quad$ **2.(C)** $\quad V = \left(\dfrac{nR}{P}\right)T \quad ; \quad$ Slope $\propto \dfrac{1}{P} \qquad \therefore \qquad P_1 < P_2 < P_3 < P_4$

3.(C) Refer theory from module on intermolecular forces.

4.(A) $\quad V = C \quad \Rightarrow \quad P \propto T \qquad \qquad \therefore \qquad T\uparrow,\ P\uparrow$

5.(D) $\quad \uparrow T_C$ implies case of liquefaction

$$\text{Hence} \quad \underset{154.3}{O_2} > \underset{126}{N_2} > \underset{33.2}{H_2} > \underset{5.3}{He} \qquad \text{Increasing order of liquefaction}$$

6.(B) $\quad F = \eta\, A\, \dfrac{dv}{dx} \quad$ (η : Viscosity coefficient) $\qquad$ Observe that its unit in SI system will be $\mathrm{Ns\,m^{-2}}$.

7.(A) $\quad PV = C$ at lowest temperature for ideal gases $\qquad$ **8.(C)** $\quad$ Viscosity $\uparrow$ with $\uparrow$ in intermolecular forces

9.(B) Refer theory $\qquad\qquad\qquad\qquad\qquad\qquad$ **10.(BC)** By kinetic theory of gases

11.(BC) Because at high pressure and low perpendicular interaction between the particles increases.

12.(BD) $\text{V . P} \propto \text{surface area} \propto \text{temperature} \qquad$ **13.(A)** $\quad$ Refer theory

14.(B) (R) is not a correct explanation of (A) but both statements are correct.

15.(C) At high altitude atmospheric pressure reduces

16.(A) Refer theory on liquefaction of gases on Andrew isotherms.

17.(D) Liquids tends to have minimum surface area in order to have minimum energy.

18.(B) At law $P \Rightarrow Vm - b \approx V_m$

$$\left(P + \dfrac{a}{V_m^2}\right)(V_m) = RT \quad \Rightarrow \quad Z = \dfrac{PV_m}{RT} = 1 - \dfrac{a}{RTV}$$

19.(C) $\quad C^* = \sqrt{\dfrac{2RT}{M_0}} \ ; \quad \overline{C} = \sqrt{\dfrac{8RT}{\pi M_0}} \ ; \ C = \sqrt{\dfrac{3RT}{M_0}}$

20.(C) $\quad$ At $\uparrow P \Rightarrow \left(P + \dfrac{a}{Vm^2}\right) \approx P$ although Vm is mall

$$P\,(Vm - b) = RT \qquad \Rightarrow \qquad Z = \dfrac{PVm}{RT} = 1 + \dfrac{Pb}{RT}$$

21.(D) $\quad T_C \propto \left(\dfrac{a}{b}\right)$

$\uparrow T_C$ means ease of liquefaction Cl_2 is larger in size as compared to $C_2H_6 \quad \therefore \quad \underset{(Cl_2)}{a} > \underset{C_2H_6}{a} \ \text{also} \ \underset{(Cl_2)}{b} < \underset{(C_2H_6)}{b}$

22.(D) By kinetic theory of gases.

23.(D) $\quad \underset{\substack{\downarrow \\ \text{Vapour} \\ \text{Pressure}}}{P} \times V = n \times R \times 300$

$$\left(\dfrac{26.7}{760}\right) \times 1 = n \times 0.0821 \times 300 \quad \Rightarrow \quad n = 1.42 \times 10^{-3}$$

24.(C)

(graph: curves T_1 and T_2 with $T_2 > T_1$, y vs Speed)
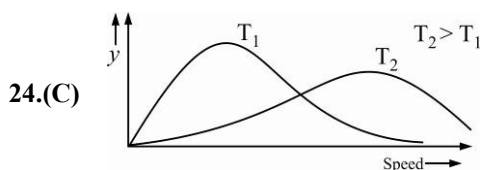
25.(C) K.E. of an atom $= \dfrac{3}{2} K_B T \quad \Rightarrow \quad$ K.E. $\propto$ T

26.(C) b $= 4 \times$ [Na $\times$ Volume of one particle]

27.(C)

(diagram: Straight line path, Collision points, Brownian Motion)
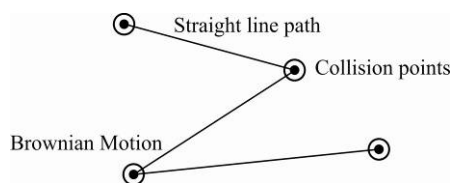
28.(D) Boyle's law, Avogadro's law, Charle's law are based on ideal gases which is explained by kinetic theory of gases.

29.(C) PV $=$ nRT $\qquad \Rightarrow \qquad \dfrac{P}{RT} = \left(\dfrac{n}{V}\right)$

30.(B) $\dfrac{V}{T} = \left(\dfrac{nR}{P}\right) \quad \Rightarrow \quad P\uparrow \dfrac{V}{T}\downarrow$

31.(C) Initially $\quad 2 \times 0.5 = n_1\, RT \qquad \dots(\alpha)$

$\qquad\qquad 1 \times 1 = n_2\, RT \quad \Rightarrow \quad n_1 = n_2$

Finally Let common $P_{\text{resence}} = P$

$\qquad P \times 2 = n_1^1\, RT \qquad \dots(\beta)$

$\qquad P \times 1 = n_2^1\, RT \quad \Rightarrow \quad \dfrac{n_1^1}{n_2^1} = 2 \quad \Rightarrow \quad n_2^1 = \dfrac{n_1^1}{2}$

Also $\quad n_1^1 + n_2^1 = 2n_1 \quad \Rightarrow \quad n_1^1 + \dfrac{n_1^1}{2} = 2n_1 \quad \Rightarrow \quad n_1^1 = \left(\dfrac{4n_1}{3}\right) \qquad \dots(\gamma)$

Re writing equation $(\alpha), (\beta)$ and (γ)

$\qquad P \times 2 = \left(\dfrac{4n_1}{3}\right) RT \qquad \Rightarrow \qquad 2 \times 0.5 = n_1\, RT$

$\qquad \dfrac{P}{0.5} = \dfrac{4}{3} \quad \Rightarrow \quad P = \dfrac{2}{3} = 0.67$

(diagram: two bulbs connected — bulb 1: 2L, 0.50 atm; bulb 2: 1L, 1.00 atm)
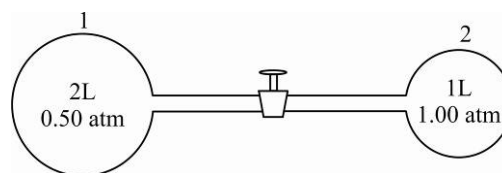
32.(CD) Units of Boltzmann's constant $J\,mol^{-2}\,K^{-1}$

33.(B) It is a polar molecule, thus more attractive forces among its molecules.

34.(D) C_P for monoatomic gas mixture of same volume $= \dfrac{5}{2} R$ and $C_V = \dfrac{3}{2} R \quad \therefore \quad \dfrac{C_P}{C_V} = \dfrac{5}{3} = 1.67$

35.(A) We know that from ideal equation : $V \propto \dfrac{T}{P}$

Given $T_1 = 15 + 273 = 288$; $P_1 = 1.5$ bar ; $T_2 = 25 + 273 = 298$, $P_2 = 1$ bar

$V_1 \propto \dfrac{288}{1.5}$ i.e. $V_1 \propto 192$ and $V_2 \propto \dfrac{298}{1} \Rightarrow \dfrac{V_2}{V_1} = \dfrac{298}{192} = 1.55 = 1.6$

36.(A) The average translational K.E. (E_T) of one molecule of an ideal gas will be given by $E_T = \dfrac{K.E.}{N_A} = \dfrac{3/2 RT}{N_A} = \dfrac{3}{2} KT$

where $\dfrac{R}{N_A} = $ Boltzmann constant $\Rightarrow E_T \propto T$. So, at constant temperature K.E. of molecules remains same.

37.(D) Mass of the gas = mass of the cylinder including gas – mass of empty cylinder.

So mass of a gas can be determined by weighing the container in which it is enclosed.

Thus, the statement (D) is wrong for gases.

38.(A) Temperature at which all molecular motion ceases is called absolute zero.

39.(A) According to Charles' law which states that "the volume of the given mass of a gas increases or decreases by $\frac{1}{273}$ of its volume at $0°C$ for each degree rise or fall of temperature at constant pressure".

$$V_t = V_0 \left(1 + \frac{t}{273}\right) \text{ at constant P and n.}$$

40.(B) $\dfrac{PV}{T} = \text{constant} \quad \Rightarrow \quad \dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2} \quad \Rightarrow \quad \dfrac{P_1 V_1}{P_2 V_2} = \dfrac{T_1}{T_2}$

41.(4) $3.2g\ O_2 = 0.1\ mol,$

$0.2g\ H_2 = 0.1 mol,$

Total $n = 0.2\ mol,$

$P = \dfrac{nRT}{V} = \dfrac{0.2 \times 0.0821 \times 273}{1.12} = 4\ atm$

42.(4) Suppose molecular masses of A and B are M_A and M_B respectively. Then their number of moles will be

$n_A = \dfrac{1}{M_A}, \quad n_B = \dfrac{2}{M_B}$

$P_A = 2 bar, P_A + P_B = 3\ bar$

i.e. $P_B = 1\ bar$

Applying the relation $PV = nRT$

$\therefore \qquad \dfrac{P_A}{P_B} = \dfrac{n_A}{n_B} = \dfrac{1/M_A}{2/M_B} = \dfrac{M_B}{2M_A}$

or $\qquad \dfrac{M_B}{M_A} = 2 \times \dfrac{P_A}{P_B} = 2 \times \dfrac{2}{1} = 4$
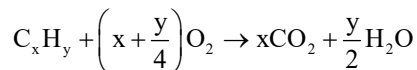
or $\qquad M_B = 4M_A$

43.(44) If t is the time taken for diffusion of each gas, then by Graham's law of diffusion

$\dfrac{r_x}{rCl_2} = \dfrac{127/t}{100/t} = \sqrt{\dfrac{M_{Cl_2}}{M_x}} = \sqrt{\dfrac{71}{M_x}}$

or $\qquad \dfrac{71}{M_x} = \left(\dfrac{127}{100}\right)^2$

or $\qquad M_x = 44\ u$

44.(56) The balanced equation for combustion

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

1 volume $\left(x + \frac{y}{4}\right)$ volume

$\therefore \qquad x + \frac{y}{4} = 6$ (by equation)

or $\qquad 4x + y = 24 \qquad\qquad\qquad\qquad …(1)$

Again $x = 4$ since evolved CO_2 is 4 times that of hydrocarbon

$\therefore \qquad 16 + y = 24 \qquad$ or $y = 8$ $\therefore$ formula of hydrocarbon C_4H_8

45.(40) $n_A = \dfrac{2.9}{M_A}$; $nH_2 = \dfrac{0.184}{2} = 0.092$

$$\frac{(PV)_A}{(PV)H_2} = \frac{(nRT)_A}{(nRT)_{H_2}}$$

$$1 = \frac{2.9}{M_A} \times \frac{(95 + 273)}{(17 + 273)} \times \frac{1}{0.092}$$

$$M_A = \frac{2.9 \times 368}{290 \times 0.092} = 40 \text{ g mol}^{-1}$$

46.(22) $\dfrac{P_1V_1}{P_2V_2} = \dfrac{n_1RT_1}{n_2RT_2} = \dfrac{n_1T_1}{n_2T_2}$

As, $V_1 = V_2$ & $T_1 = T_2$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$\frac{P_{H_2}}{P_{CO_2}} = \frac{n_{H_2}}{n_{CO_2}}$$

$$\frac{P_{H_2}}{1} = \frac{44/2}{44/44} = 22 \text{ atm}$$

47.(1) $P \propto \dfrac{1}{V}$

48.(16) $\dfrac{r_A}{r_B} = \sqrt{\dfrac{M_B}{M_A}}$

$$\frac{2}{1} = \sqrt{\frac{64}{M_A}}$$

$$M_A = 16 \text{ g / mole}$$

49.(3) $PV = nRT$

$$\frac{(PV)_i}{(PV)_f} = \frac{(nRT)_i}{(nRT)_f}$$

$$\frac{10V}{8V} = \frac{(15/MM)}{W/MM}$$

$$\frac{10}{8} = \frac{15}{W}$$

$$W = 12kg$$

Leaked gas $= (15-12) = 3 \ kg$

50.(327) $\left(\sqrt{\dfrac{2RT}{M}}\right)_{SO_2} = \left(\sqrt{\dfrac{2RT}{M}}\right)_{O_2}$

$$\left(\frac{T}{M}\right)_{SO_2} = \left(\frac{T}{M}\right)_{O_2}$$

$$\frac{T_{SO_2}}{64} = \frac{300}{32} \Rightarrow T_{SO_2} = 600K = 327°C$$

51.(3) $\text{rms}(\mu) = \sqrt{\dfrac{3RT}{M}}$

For atom, $\mu' = \left(\sqrt{\dfrac{3RT}{M}}\right)'$

$T' = 3T$ and $M = 3M'$

$$\frac{\mu'}{\mu} = \frac{\left(\sqrt{\dfrac{3RT}{M}}\right)'}{\left(\sqrt{\dfrac{3RT}{M}}\right)} = \sqrt{\frac{\dfrac{3R \times 3T}{M'}}{\dfrac{3RT}{3M'}}} = \sqrt{9} = 3$$

$\mu' = 3\mu$

52.(500) Let the initial number of moles in vessel be 5 at 27°C, i.e., 300K. Moles of air left at new temperature

$$= 5 - \frac{2}{5} \times 5 = 3$$

Pressure and volume remaining the same,

$$n_1 RT_1 = n_2 RT_2$$

$$5 \times 300 = 3 \times T_2 \Rightarrow T_2 = 500K$$

53.(32) $\dfrac{r_X}{r_Y} = \dfrac{\dfrac{V_X}{t_X}}{\dfrac{V_Y}{t_Y}} = \dfrac{\dfrac{40}{20}}{\dfrac{80}{20}} = \dfrac{1}{2} \Rightarrow \sqrt{\dfrac{M_X}{M_Y}} = \dfrac{r_Y}{r_X} \Rightarrow \dfrac{M_X}{M_Y} = 4$

$$M_Y = \frac{128}{4} = 32$$

54.(400) $T_C = \dfrac{8}{3}\dfrac{P_C V_C}{R} = \dfrac{8}{3} \times \dfrac{40 \times 3}{0.8} = 400K$

55.(3) $PM = \rho RT \qquad \Rightarrow \qquad \dfrac{(PM)_{given}}{(PM)_{STP}} = \dfrac{(\rho RT)_{given}}{(\rho RT)_{STP}}$

$\dfrac{2}{1} = \dfrac{5.46 \times 300}{\rho \times 273} \Rightarrow \rho = 3g\ dm^{-3}$

Thermochemistry & Thermodynamics

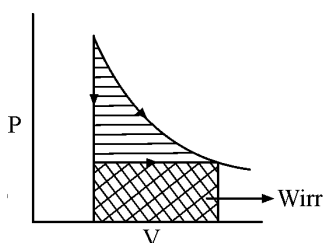**1.(C)** Closed system allows heat exchange but not mass between system and surrounding.
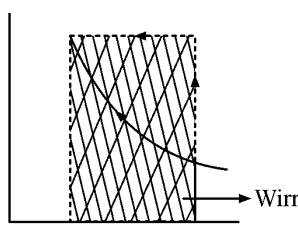
2.(C) Specific heat is constant　　　　　　　**3.(B)**

4.(C) For adiabatic process, $q = 0 \Rightarrow w = \Delta U$　　　　Free expansion $\Rightarrow \quad w = 0,\ \Delta U = 0 \Rightarrow \Delta T = 0$

5.(B)

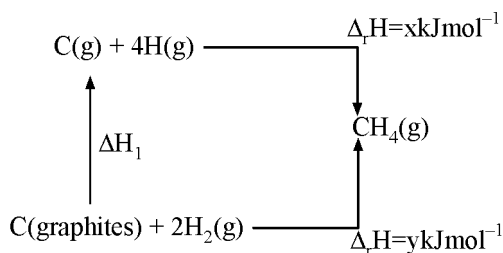Expansion (– ve work)　　　　　　　Compression (+ve work)

6.(C) $\Delta S_{system} + \Delta S_{surrounding} \geq 0$

7.(C) $C(graphite) + \dfrac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta_r H = y\ kJ\ mol^{-1}$

$CO(g) + \dfrac{1}{2}O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta_r H = z\ kJmol^{-1}$

$C(graphite) + O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta_r H\ \ y + z = x$

8.(C) Thus $y = \Delta H_1 + x \Rightarrow x > y$ since $\Delta H_1 = +ve$ and x and y are negative.

9.(C) Enthalpy of formation can be +ve or –ve　　　**10.(A)**

11.(B) For spontaneous process ΔG should be negative　　**12.(AD)**

Chemical Rxn

13.(AB)

Heat is flowing out of system. So, it is –ve. If indicates that system is losing energy.
So $\Delta H = \Delta H_f - \Delta H_i = -ve$

14.(CD) Flow of heat from warmer body to colder body is spontaneous. In general dissipation of energy is spontaneous process.

15.(CD) $w_1 = -nR \times 300 \times \ln 10$; $w_2 = -nR \times 600 \times \ln 10$

$\dfrac{w_1}{w_2} = \dfrac{1}{2} \Rightarrow w_2 = 2w_1$ 　　　　　 Also for ideal gases $\Delta U = U(T) \quad \Rightarrow \quad$ for isothermal process $\Delta U = 0$

16.(AC) $\Delta_r H = \sum \Delta H(\text{Pr oduct}) - \sum \Delta H \,(\text{Reactant})$

If $\Delta_r H = -ve \Rightarrow \sum \Delta H(\text{products}) < \sum \Delta H(\text{Reactants})$

Since energy of product is reduced it means. Some energy is evolved for the system

17.(B) 　　　　　　**18.(A)** $\Delta_C H = q_p = q_r + \Delta H_g RT = -1364.47 - \dfrac{1 \times 8.314 \times 298}{1000}$ 　　 $\Delta_C H = -1366.95 \text{ kJ / mol}$

19.(A) $q = 208 \text{ J}$ since system absorbs head

$w = -nRT \ln \dfrac{v_2}{v_1} = -0.04 \times 8.314 \times 310 \times \ln\left(\dfrac{375}{50}\right) = -207.7J \approx -208J$

20.(C) For (A) : $\Delta G = \Delta H - T\Delta S$ 　 For adiabatic process OR for a free expansion of a gas ; $\Delta H = 0 \quad \therefore$

$\dfrac{\Delta G_{\text{system}}}{\Delta S_{\text{system}}} = -T$

For (C) : $\Delta G = -nRT \ell nK \Rightarrow \Delta G = \Delta H - T\Delta S$

21.(A) $\Delta S = nR \ln \dfrac{v_f}{v_i} = 2 \times 8.314 \times \ln 10 = 38.3 \text{ J / K}$

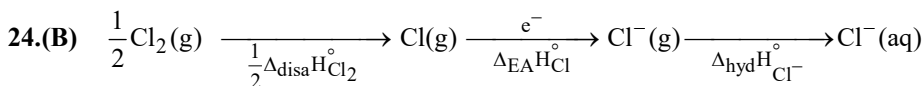**22.(D)** $PbO_2 + Pb \longrightarrow 2PbO, \ \Delta G° < 0 \Rightarrow$ spontaneous

$SnO_2 + S_n \longrightarrow 2SnO, \ \Delta G° > 0 \Rightarrow$ non-spontaneous

Thus 　 O.S. for lead $= +2$; 　 O.S for tin $= +4$

23.(B) $\Delta G = \Delta H - T\Delta S$

For spontaneous $\Delta G < 0 \Rightarrow \quad T > \dfrac{\Delta H}{\Delta S}$

But at equilibrium $\Delta G = 0 \Rightarrow \Delta H - T_e \, \Delta S = 0 \quad \Rightarrow \quad T_e = \dfrac{\Delta H}{\Delta S}$ 　　　　　 Thus $T > T_e$

24.(B) $\dfrac{1}{2}Cl_2(g) \xrightarrow[\frac{1}{2}\Delta_{disa}H^°_{Cl_2}]{} Cl(g) \xrightarrow[\Delta_{EA}H^°_{Cl}]{e^-} Cl^-(g) \xrightarrow[\Delta_{hyd}H^°_{Cl^-}]{} Cl^-(aq)$

Thus energy involved in $\dfrac{1}{2}Cl_2(g) \longrightarrow Cl^-(g)$ is : $\dfrac{1}{2}\Delta_{diss}H^°_{Cl_2} + \Delta_{EA}H^°_{Cl} + \Delta_{hyd}H^°_{Cl^-} = -610 \text{ kJ / mol}$

25.(A) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$ for spontaneous process

For isolated system $\Delta S_{\text{surrounding}} = 0$ 　　　 Thus $\Delta S_{\text{system}} \geq 0$

26.(A) For isolated system $q = 0$

For ideal gas $\Delta U = nC_v\Delta T = nC_v(T_f - T_i)$; 　　　 For reversible process $\Delta U_{rev} = W_{rev}$

For irreversible process $\Delta U_{irr} = W_{irr}$ 　　　　 ; 　　　 But for same expansion $|W_{rev}| > |W_{irr}|$

$$|\Delta U_{rev}| > |\Delta U_{irr}|$$

$$|\Delta T_{fer}| > |\Delta T_{irr}| \implies (T_f)_{irr} > (T_f)_{rev}$$

27.(B) At const T and P, $\Delta S = nr \ln \dfrac{V_f}{V_i}$

Since work is done by system $V_f > V_i$ $\implies$ $\Delta S > 0$ Also $dG = dH - Tds$

For ideal gas $dU = 0$ at constant T $\implies$ $q = W = -ve$ and $dH = q \implies dG = -ve$

Thus $(ds) > 0$ and $(dG) < 0$

28.(B) $C_p - C_v = R$

Cp = Heat transfer at constant V + energy transferred to surrounding as work.

Thus $C_p - C_v = R = $ energy transferred to surrounding as mechanical work.

29.(C) Since ΔH is negative, increasing temperature equilibrium will shift on reverse direction and solubility will decrease.

30.(B) Using Gibb's Helmholtz equation : $\Delta G = \Delta H - T\Delta S$

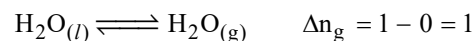During adsorption of a gas, entropy decreases i.e. $\Delta S < 0$

For spontaneous adsorption, ΔG should be negative, which is possible when ΔH is highly negative.

31.(A) $\Delta H = (E_a)_f - (E_a)_b = 0$.

32.(A) $\Delta_{vap}H° = 40.66 \, kJ \, mol^{-1}$

$T = 100 + 273 = 373$ K, $\Delta E = ?$

$\Delta H = \Delta E + \Delta n_g RT \implies \Delta E = \Delta H - \Delta n_g RT$

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ $\Delta n_g = 1 - 0 = 1$

$\Delta E = \Delta H - RT = (40.66 \times 10^3) - (8.314 \times 373) = 37559$ J/mol or 37.56 kJ/mol

33.(C) For free expansion of an ideal gas under adiabatic condition $q = 0, \Delta T = 0, w = 0$.

34.(D) Gas phase reaction : $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$. It is a dissociation reaction, hence $\Delta H = +ve$. Also one mole of PCl_5 is dissociated into two moles of PCl_3 and Cl_2 in the same phase. Therefore, $\Delta S = S_{product} - S_{reactant} \implies \Delta S = +ve$.

35.(C) The criteria for spontaneity of a process in terms of ΔG is as follows :

* If ΔG is negative, the process is spontaneous.
* If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.
* If ΔG is zero, the system is in equilibrium.
  The process does not occur.

36.(C) $\Delta G = \Delta H - T\Delta S$

$\Delta G = -ve$ for spontaneous reaction

When $\Delta S = +ve, \Delta H = +ve$ and $T\Delta S < \Delta H \implies \Delta G = -ve$

When randomness favours and energy factor do not favour then spontaneity depends upon the temperature.

37.(A) For spontaneous process, ΔS_{Total} i.e., $\Delta S_{system} + \Delta S_{surrounding}$ should be positive.

38.(C) The entropy of a substance increases with increase in temperature. However at absolute zero the entropy of a pure crystalline substance is taken as zero, which is also called as third law of thermodynamics.

39.(B) Since a catalyst affect equally both forward and backward reactions, therefore it does not affect equilibrium constant of reaction.

40.(C) If more trans-2-pentene is added, then its concentration in right hand side will increase. But in order to maintain the constant K, concentration of cis-2-pentene will also increase. Therefore more cis-2-pentene will be formed.

41.(810) Since, the external pressure is greatly different form the pressure of N_2 and thus, process is irreversible.

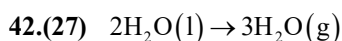$$\therefore \quad W = -P_{ex}\left(V_2 - V_1\right)$$

$$W = -1 \times \left(V_2 - V_1\right)$$

Given, $V_1 = 2L$ $V_2 = ?$ $T = 273K$, $P_1 = 5atm$, $P_2 = 1atm$ $\therefore$ $P_1 V_1 = P_2 V_2$

$$\therefore \quad V_2 = \frac{2 \times 5}{1} = 10L$$

$$\therefore \quad W = -1 \times \left(10 - 2\right) = -8L - atm = -810J$$

$$\therefore \quad W \times \left(-1\right) = 810J$$

42.(27) $2H_2O(l) \rightarrow 3H_2O(g)$

$$\Delta n_g = 3 - 0 = 3$$

$$\because \quad \Delta H = \Delta U + \Delta n_g RT$$

$$\Delta U = \Delta H - \Delta n_g RT$$

$$30 - 3 \times .0821 \times 500 \times 10^{-3}$$

$$\Delta U = 27 \text{ kcal}$$

43.(33) For adiabatic process

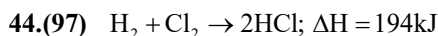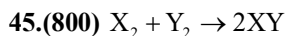$TV^{\gamma - 1} = \text{constant}$

For poly atomic gas

$$\gamma = \frac{4}{3} = 1.33 \quad \left(\gamma = \frac{C_p}{C_v}\right)$$

$$n = 1.33 - 1 = 0.33$$

$$\therefore \quad n \times 100 = 33$$

44.(97) $H_2 + Cl_2 \rightarrow 2HCl$; $\Delta H = 194kJ$

$$\therefore \text{ Heat of formation of } HCl = \frac{194}{2} + 97kJ$$

45.(800) $X_2 + Y_2 \rightarrow 2XY$

$$\Delta H = \left(BE\right)_{x-x} + \left(BE\right)_{y-y} - 2\left(BE\right)_{x-y}$$

If BE of $\left(x - y\right) = a$, then BE of $\left(x - x\right) = a$

and BE of $\left(y - y\right) = \dfrac{a}{2}$

$\Delta H_f \left(x - y\right) = -200kJ$

$$\therefore \quad 400 = \frac{a}{2} \quad \text{or } a = +800kJ$$

The bond dissociation energy of $x_2 = 800 \, kJ/mol$

46.(5) The neutralization of a strong acid by a strong base is represented by

$$H^{\oplus}(aq) + \overset{\ominus}{O}H \rightarrow H_2O(I) \quad \Delta H = -55.6 kJ........(i)$$

We have to calculate:

$$CH_3COOH \rightarrow CH_3COO^{\ominus} + H^{\oplus} \qquad \Delta H = ?$$

Given:

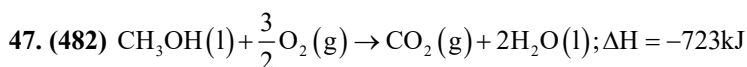$$CH_3COOH + \overset{\oplus}{O}H \Rightarrow CH_3COO^{\ominus} + H_2O; \Delta H_2 = -50.6............(ii)$$
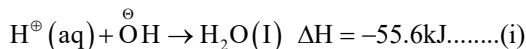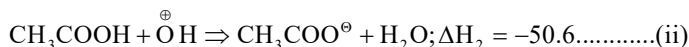
Subtract equation (i) from equation (ii), we get

$$\Delta H = \Delta H_2 - \Delta H_1$$

$$= -50.6 - (-55.6) = 5.0 \text{ kJ mol}^{-1}$$

47. (482) $CH_3OH(l) + \dfrac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \Delta H = -723 kJ$

By burning with $\dfrac{3}{2}O_2(g)$ heat evolved $= -723 kJ$

$\therefore$ By burning with 1 mole $O_2(g) = \dfrac{-723 \times 2}{3} = 482$ kJ

48.(150) $\because$ 150 kJ energy required for muscular work to walk a distance of one km. (Given)

$\therefore$ 750 kJ energy required for work to walk of 5 km distance. Enthalpy of combustion is $3000 \, kJ \, mol^{-1}$.

Glucose provide 30% energy of its mass.

Molecular weight of glucose $= 180$

Weight of glucose required for work to 5 km (750 kj energy)

$$= \dfrac{180}{3000} \times 750 \times \dfrac{100}{30} = 150 \text{ g}$$

49.(300) $\dfrac{\Delta H_{fusion}}{T_{mp}} = \Delta S_{fusion}$

$$\dfrac{600}{T} = 2$$

$$T = 300K$$

50.(0) From $\Delta S_{fu} = \dfrac{\Delta H_{fu}}{T_f}$

$$T_f = \dfrac{1.435 \times 1000}{5.26} = 272.81 \simeq 273K$$

In $\,^{\circ}C = 0$

51.(0) Form $\Delta G_r = \Delta H_r - T\Delta S_r$

$$\Delta G_r = 40.63 - \dfrac{373.4 \times 108.8}{1000} = 0$$

52.(1) $\because \Delta G^0 = -2.303 RT \log K$

$\therefore$ $\log K = \dfrac{4.606 \times 1000}{2.303 \times 2 \times 500} = 2 = \log 100$

$$\therefore \quad K = 1 \times 10^2$$

$$\therefore \quad x = 1$$

53.(5) Net work done $= W_A + W_B = 25 - 20 = 5$ unit

54.(2) From $q_p = q_v + \Delta n_g RT$

$$(q_v - q_p) = \Delta n_g RT$$

$$\Rightarrow \quad xRT = (-2)RT$$

$$x = 2$$

55. (0) From first law of thermodynamics,

$$\Delta U = Q + W$$

For isothermal process, $\Delta T = 0$

Hence, $\Delta U = 0$

Chemical & Ionic Equilibrium

1.(D) $\Delta G^\circ = -RT \ln Keq$ **2.(C)** **3.(ACD)**

4.(A) On cooling reaction goes in exothermic direction. **5.(D)** **6.(C)**

7.(D) $Ag^+ + 2NH_3 \rightleftharpoons \left[Ag(NH_3)_2 \right]^+$ **8.(A)**

9.(B) Higher bp $\Rightarrow$ lower vapor pressure

10.(ACD) $T\uparrow \Rightarrow K_{eq}\uparrow \Rightarrow$ reaction goes forward it is endothermic

11.(AD) Melting point and freezing point are same **12.(A)** **13.(B)** Common ion effect

14.(A) Weak acid weak base salt solution is acidic if $K_a > K_b$; Basic if $K_b > K_a$ **15.(D)**

16.(C) He does to react with any of gases present Addition of inert gas at constant pressure decreases the dissociation of PCl_5.

17.(B) $K_p = K_c (RT)^{\Delta n_g}$ **18.(D)** $[H^+]$ is changed from 10^{-1} to 10^{-2} Ten times dilution is required.

19.(A) $\underset{0.5-x}{C} + \underset{}{CO_2} \rightleftharpoons \underset{2x}{2CO} \quad \Rightarrow \quad x = 0.3\,atm$ **20.(A)** In III $H_2PO_4^-$ is acting like base **21.(A)**

22.(C) $\underset{0.034-x}{H_2CO_3} \rightleftharpoons \underset{x}{H^+} + \underset{x-y}{HCO_3^-}$; $\underset{x-y}{HCO_3^-} \rightleftharpoons \underset{x+y}{H^+} + \underset{y}{CO_3^{2-}}$ Neglecting H^+ from second step and $x - y \approx x$

23.(B) When ppt starts $[Ag^+][Br^-] = K_{sp}(AgBr)$ **24.(B)** When ppt begins $[Mg^{2+}][OH^-]^2 = 10^{-11}$

25.(C) HCO_3^- is weakest. Check individual options. **26.(C)** Use $pH = 7 + \dfrac{1}{2}(pK_a - pK_b)$

27.(A) Remove H^+ **28.(A)** **29.(D)**

30.(C) On decreasing temperature reaction goes in exothermic direction. On increasing pressure reaction goes where number of gas particles decreases.

31.(C) NH_3 can extract proton from H_2O **32.(ABD)** pH of HCl would be 6.97 approx. Use Faradays law for (D)

33.(A) HCl is a strong acid and dissociates completely into ions in aqueous solution.

34.(D) Acidic buffer is a mixture of a weak acid and its salt with a strong base. $HClO_4$ is strong acid.

35.(B)

Salt	K_{SP}	Solubility
Ag_2CrO_4	$1.1 \times 10^{-12} = 4s^3$	$s = \sqrt[3]{\dfrac{K_{SP}}{4}} = 0.65 \times 10^{-4}$
$AgCl$	$1.8 \times 10^{-10} = s^2$	$s = \sqrt{K_{SP}} = 0.71 \times 10^{-6}$
$AgBr$	$5 \times 10^{-13} = s^2$	$s = \sqrt{K_{SP}} = 0.7 \times 10^{-6}$
AgI	$8.3 \times 10^{-17} = s^2$	$s = \sqrt{K_{SP}} = 0.9 \times 10^{-8}$

Solubility of Ag_2CrO_4 is highest thus, it will be precipitated at last.

36.(C) Na_2CO_3 which is a salt of NaOH (strong base) and H_2CO_3 (weak acid) will produce a basic solution with pH greater than 7.

37.(A) BF_3 is Lewis acid (e^- pair acceptor).

38.(B) $pH = pK_a + \log\dfrac{[Salt]}{[Acid]}$ $\Rightarrow$ $5 = -\log K_a + \log\dfrac{[Salt]}{[Acid]}$ $[\because pK_a = -\log K_a]$

$5 = -\log[1 \times 10^{-4}] + \log\dfrac{[Salt]}{[Acid]}$ $\Rightarrow$ $1 = \log\dfrac{[Salt]}{[Acid]}$ $\Rightarrow$ $\dfrac{[Salt]}{[Acid]} = 10 = 10:1$

39.(C) $N_2 + O_2 \rightleftharpoons 2NO \; ; \; K_1 \; ; \quad 2NO + O_2 \rightleftharpoons 2NO_2 \; ; \; K_2$

$NO_2 \rightleftharpoons \dfrac{1}{2}N_2 + O_2 \; ; \; K = ?$

$K_1 = \dfrac{[NO]^2}{[N_2][O_2]} \; ; \; K_2 = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$ $\Rightarrow$ $K = \dfrac{[N_2]^{1/2}[O_2]}{[NO_2]} = \sqrt{\dfrac{[N_2][O_2] \times [NO]^2[O_2]}{[NO]^2 \times [NO_2]^2}} = \sqrt{\dfrac{1}{K_1 K_2}}$

40.(D) $2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$

$\quad\quad\; 2 \quad\quad\quad\quad\; 0 \quad\quad\; 0 \quad$ (initially)

$\; 2(1-x) \quad\quad\quad 2x \quad\quad x \quad$ (at equilibrium)
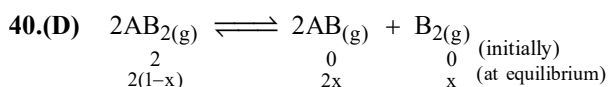
Amount of moles at equilibrium $= 2(1 - x) + 2x + x = 2 + x$

$K_p = \dfrac{[p_{AB}]^2[p_{B_2}]}{[p_{AB_2}]^2} = \dfrac{\left(\dfrac{2x}{2+x} \times P\right)^2 \times \left(\dfrac{x}{2+x} \times P\right)}{\left(\dfrac{2(1-x)}{2+x} \times P\right)^2} = \dfrac{\dfrac{4x^3}{2+x} \times P}{4(1-x)^2}$ $\Rightarrow$ $K_p = \dfrac{4x^3 \times P}{2} \times \dfrac{1}{4}$ $(\because 1 - x \approx 1 \,\&\, 2 + x \approx 2)$

$x = \left(\dfrac{8K_p}{4P}\right)^{1/3}$ $\Rightarrow$ $x = \left(\dfrac{2K_p}{P}\right)^{1/3}$

41.(A) The cation of group II are precipitated as their sulphides.

    *   Solubility product of sulphide of group II radicals are very low.

    *   Therefore, even with low conc. of S^{2-} ions, the ionic product exceeds the value of their solubility product and the radical of group II gets precipitated.

* The low conc. of S^{2-} ions is obtained by passing H_2S gas through the solution of the salt in the presence of dil. HCl which suppresses degree of ionisation of H_2S by common ion effect.

$$H_2S \rightleftharpoons \boxed{2H^+} + S^{2-}$$
$$\boxed{H^+} + Cl^-$$
common ion
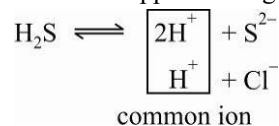
Note: Solubility product of group IV radicals are quite high.

* It is necessary to suppress the conc. of S^{2-} ions, otherwise radicals of group IV will also get precipitated along with group II radicals.

42.(B) CH_3COOH (weak acid), NaOH (strong base). After neutralisation, the salt (CH_3COONa) formed dissociates in water giving free OH^- ions. Thus pH will be greater than 7.

43.(D) $\underset{\text{Weak acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Conjugate base}}{CH_3COO^-} + H^+$
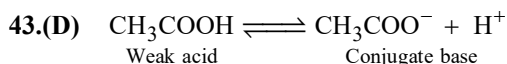
As CH_3COOH is the weakest acid, so its conjugate base (CH_3COO^-) is the strongest base. H_2SO_4, HCl, HNO_3 are strong acids, so their conjugate bases are weak.

44.(A) Vapour pressure is directly related to temperature. Greater is the temperature, greater will be the vapour pressure. So to keep it constant, temperature should be constant.

45.(C) Na_2CO_3 is salt of strong base NaOH and weak acid. $NaHCO_3$ however is also having an acidic H so less basic than Na_2CO_3.

46.(B) For precipitation : $I.P \geq K_{sp}$

To initiate the precipitation : $I.P. = K_{sp}$ $\Rightarrow$ $[Mg^{2+}][OH^-]^2 = K_{sp}$

$\Rightarrow$ $[OH^-] = \sqrt{\dfrac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\dfrac{1 \times 10^{-11}}{0.1}} = 10^{-5} M$ $\Rightarrow$ $pOH = 5 \Rightarrow pH = 9$

47.(A) First find solubility in mol/L. (x mol/L)

$$CaC_2O_4(s) + aq \rightleftharpoons \underset{x}{Ca^{2+}(aq)} + \underset{x}{C_2O_4^{2-}(aq)}$$
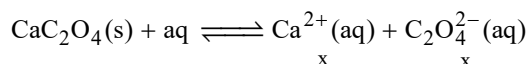
$\Rightarrow$ $K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = x^2$ $\Rightarrow$ $x = 5 \times 10^{-5}$ mol/L

Solubility in g/L $= (5 \times 10^{-5}) \times 128 = 0.0064 g$

48.(B) mmol of CH_3COOH = 10 ; mmol of CH_3COONa = 10

$$pH = pK_a + \log\dfrac{[CH_3COONa]}{[CH_3COOH]} = pK_a + \log\dfrac{10/V}{10/V} = pK_a = 4.76$$

49.(B) $pH = pK_a + \log\dfrac{[CH_3COONa]}{[CH_3COOH]}$

Now $\dfrac{[CH_3COONa]}{[CH_3COOH]} = 10$ $\Rightarrow$ pH increase by 1.

50.(B) $K_a = C_1\alpha_1^2 = C_2\alpha_2^2$; $\alpha_2 = 2\alpha_1$ $\Rightarrow$ $C_1\left[\dfrac{\alpha_1}{\alpha_2}\right]^2 = C_2$ $\Rightarrow$ $C_2 = 0.1 \times \left[\dfrac{1}{2}\right]^2 = \dfrac{0.1}{4}$

Since concentration is decreased to 1/4m, the volume is increased to 4 times which means volume is 200 mL. So 900 mL H_2O is added.
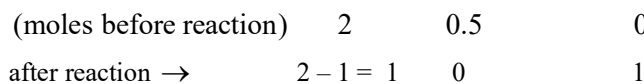
51.(16) $\Delta H = \Delta E + \Delta nRT$

or $\qquad -\Delta nRT = \Delta E - \Delta H = 1200$

or $\qquad \Delta n = \dfrac{-1200}{2 \times 300} = -2$

$\dfrac{K_p}{K_c} = (RT)^{\Delta n} = (0.0821 \times 300)^{-2} = (24.63)^{-2}$

or $\qquad \dfrac{K_p}{K_c} = \dfrac{1}{(24.63)^2} = 1.648 \times 10^{-3}$

or $\qquad \dfrac{K_p}{K_c} \times 10^4 = 16.48 \simeq 16$

52.(2)
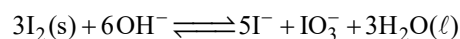$$2NO \;+\; O_2 \;\longrightarrow\; 2NO_2$$

(moles before reaction) $\quad 2 \qquad 0.5 \qquad\qquad 0$

after reaction $\rightarrow \qquad 2-1=1 \qquad 0 \qquad\qquad 1$

$\Delta n = |\,2.5 - 2\,| = 0.5$

Change in pressure

$\Delta P = \dfrac{\Delta nRT}{V} = 0.5 \times \dfrac{1}{12} \times \dfrac{300}{6.25}$ atm

$= 2$

53.(8) Balanced equation is –

$3I_2(s) + 6OH^- \rightleftharpoons 5I^- + IO_3^- + 3H_2O(\ell)$

$\Delta G^\circ = 5 \times (-50) + (-123.5) + 3 \times (-233) \times -0 - 6 \times (-150) = -172.5 \ KJ/mol$

Now, $\quad \Delta G^\circ = -RT \ln k$

$\Rightarrow \qquad -172.5 = -\dfrac{25}{3} \times 300 \times 2.3 \times 10^{-3} \log K \qquad \Rightarrow \qquad \log K = 30$

$\Rightarrow \qquad 10^{30} = \dfrac{[I^-]^5 \times [IO_3^-]}{[OH^-]^6} = \dfrac{10^{-5} \times 10^{-1}}{[OH^-]^6}$

$\Rightarrow \qquad [OH^-] = 10^{-6} \qquad\qquad \Rightarrow \qquad pOH = 6 \qquad \Rightarrow \qquad pH = 8$
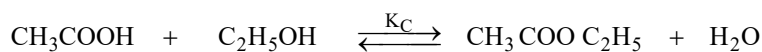
54.(2)
$$CH_3COOH \;+\; C_2H_5OH \;\underset{}{\overset{K_C}{\rightleftharpoons}}\; CH_3COO\,C_2H_5 \;+\; H_2O$$

Initially : $\qquad 0.1 \text{ mol} \qquad 0.1 \text{ mol} \qquad\qquad 0 \qquad\qquad 0$

At equilibrium: $(0.1-x)\text{mol} \qquad (0.1-x)\text{mol} \qquad\qquad x \qquad\qquad x$

In 10 ml solution at equilibrium moles of CH_3COOH present $= 0.1\,(0.1-x) \equiv 0.1\,(0.1-x)$ moles of NaOH

$\therefore \qquad 0.1\,(0.1-x) = 80 \times 10^{-4} = 8 \times 10^{-3}$

or $\quad 0.01 - 0.1\,x = 0.008 \qquad\qquad$ or $\qquad x = 0.02$

$K_C = \dfrac{x^2}{(0.1-x)^2} = \dfrac{(0.02)^2}{(0.08)^2} = \dfrac{1}{4^2} = \dfrac{1}{16}$

$= 32\,K_C = 32 \times \dfrac{1}{16} = 2$

55.(36) $\log K_p = \dfrac{-\Delta_r H^0}{2.303\ RT} + C$

Slope of the plot is, $\dfrac{-\Delta_r H^0}{2.303\ R} = 5 \times 10^3$

$\Delta_r H^0 = -5 \times 2.303 \times 8.314$ kJ/mol

$\Delta_r H^0 = -95.736$ kJ/mol

$\Delta_r S^0 = 250 - 250 - 100 = -0.1$ kJ/mol

$\Delta_r G^0 = -95.736 + 298\ (0.1)$ kJ/mol

$\Delta_r G^0 = -65.936$ kJ/mol

$\log K_p = \dfrac{65.936 \times 10^3}{8.314 \times 298 \times 2.303} = 11.556$

or $\quad K_p = 3.597 \times 10^{11} = 35.97 \times 10^{10} \simeq 36 \times 10^{10}$

56.(10) $Ka_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$; $Ka_2 = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

$Ka_1 \times Ka_2 = \dfrac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]} = 10^{-18}$

$\therefore \quad \dfrac{10^{-10} \times [CO_3^{2-}]}{10^{-2}} = 10^{-18}$

$[CO_3^{2-}] = 10^{-10}$

$\therefore \quad -\log[CO_3^2] = 10$

57.(900) $\because \quad \alpha$ is negligible w.r.t. 1

$K_a = C_1\alpha_1^2 = C_2\alpha_2^2$

$\therefore \quad C_2 = C_1\left(\dfrac{\alpha_1}{\alpha_2}\right)^2$

$= 0.2 \times \dfrac{1}{4} = 0.05$

$C_1V_1 = C_2V_2$

$300 \times 0.2 = 0.05 \times V_2$

$V_2 = 1200$ ml

Volume of H_2O added $= 1200 - 300$

$= 900$ ml

58.(4) $(OH^-) = (OH^-)_{NaOH} + (OH^-)_{Mg(OH)_2}$

$= 0.1 + 2s \approx 0.1$ M $(2s \ll 0.1)$

$K_{SP}[Mg(OH)_2] = [Mg^{2+}](0.1)^2$

$Mg^{2+} = 4 \times 10^{-10}$ M

59.(1) For acid buffer,

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 5 + \log\frac{0.1}{0.01} = 6$$

$$\begin{array}{ccccccc} A^- & + & H_2O & \rightleftharpoons & HA & + & OH^- \\ C_2(1-h) & & & & C_1 + C_2h & & C_2h \\ \simeq & & & & \simeq & & \end{array}$$
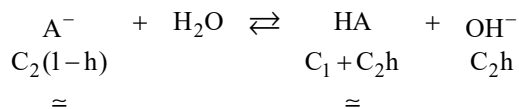
$\therefore \quad \dfrac{C_2h \times C_1}{C_2} = K_h = \dfrac{K_W}{K_a}$

$\therefore \quad h = \dfrac{K_W}{K_a C_1} = \dfrac{10^{-14}}{10^{-5} \times 10^{-2}} = 10^{-7}$

$\therefore \quad h \times 10^7 = 1$

60.(8) $Mg(OH)_2 \xrightleftharpoons{} \underset{x}{Mg^{2+}} + \underset{2x+3y}{2OH^-}$

$Al(OH)_3 \xrightleftharpoons{} Al^{3+} + 3OH^-$
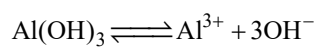
Now $x \gg y$ because K_{sp} of $Mg(OH)_2 \gg K_{sp}$ of $Al(OH)_3$

$\Rightarrow \quad x \times (2x)^2 = 4 \times 10^{-12} \Rightarrow \quad x = 10^{-4}$ …(i)

And $y \times (2x)^3 = 1 \times 10^{-33}$

$\Rightarrow \quad y = \dfrac{10^{-33}}{8x^3} = \dfrac{10^{-33}}{8 \times 10^{-12}} = \dfrac{10^{-21}}{8}$ …(ii)

$\dfrac{x}{y} = \dfrac{10^{-4}}{10^{-21}} \times 8 = 8 \times 10^{17}$

So answer $\Rightarrow 8 \times 10^{+17} \times 10^{-17} = 8$

61.(2) $\underset{c(1-h)}{Fe^{3+}} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} \underset{ch}{Fe(OH)^{2+}} + \underset{ch}{H^+}; \; K_h = 6.5 \times 10^{-3}$

$K_h = 6.5 \times 10^{-3} = \dfrac{ch^2}{(1-h)} = \dfrac{c \times (0.5)^2}{(0.5)} = c \times 0.5$

or $\quad c = 13 \times 10^{-3} (M)$

$[H^+] = ch = 13 \times 10^{-3} \times \dfrac{1}{2} = 6.5 \times 10^{-3}$

or $\quad pH = 3 - \log 6.5 \times 2.187 \simeq 2$

62.(11)
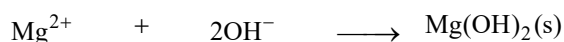
$$\begin{array}{ccccc} Mg^{2+} & + & 2OH^- & \longrightarrow & Mg(OH)_2(s) \\ 10 \times 10^{-3}\,mol & & 20 \times 10^{-3}\,mol & & - \\ - & & - & & 10 \times 10^{-3}\,mol \end{array}$$

$$\begin{array}{ccccc} Mg(OH)_2(s) & \longrightarrow & Mg^{2+} & + & 2OH^- \\ & & s & & 2s \end{array}$$
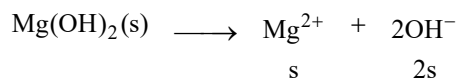
Where s is the solubility of $Mg(OH)_2$ in the resulting solution

$\therefore \quad 4s^3 = 12 \times 10^{-12}$

$\therefore \qquad s = (3)^{1/3} \times (10^{-12})^{1/3} = 1.44 \times 10^{-4} (M)$

$\therefore \qquad [OH^-] = 2s = 2.88 \times 10^{-4} (M)$

or $\qquad pOH = 4 - \log 2.88 = 4 - 0.459 = 2.541$

$\therefore \qquad pH = 14 - pOH = 14 - 2.541 = 11.459$

63.(93) In the resulting solution, $[Ca^{2+}] = \dfrac{10^{-5}}{2} (M)$

In order to observe the precipitation of $CaCO_3$ required $[Ca^{2+}] = 7 \times 10^{-5} (M)$

$\therefore \qquad \dfrac{7 \times 10^{-5}}{10^{-5/2}} = \dfrac{200}{V}$ where V is the final volume of solution in ml

or $\qquad \dfrac{200}{V} = 14 \qquad\qquad\qquad V = \dfrac{200}{14} ml$

$\therefore \qquad$ % reduction in volume $= \dfrac{(200 - 200/14)}{200} \times 100$

$= \left(1 - \dfrac{1}{14}\right) \times 100 = \dfrac{13}{14} \times 100 = 92.856 \simeq 93\%$

64.(15) For the precipitation of ZnS, required $[S^{2-}]$

$= \dfrac{10^{-21}}{10^{-2}} = 10^{-19} (M)$

$[H^+]^2 [S^{2-}] = 10^{-22}$

or $\qquad [H^+]^2 = \dfrac{10^{-22}}{[S^{2-}]} = \dfrac{10^{-22}}{10^{-19}} = 10^{-3} = 10 \times 10^{-4}$

or $\qquad [H^+] = (10)^{1/2} \times 10^{-2} (M) \qquad$ or $\qquad \log [H^+] = \dfrac{1}{2}\log 10 - 2$

or $\qquad pH = 2 - \dfrac{1}{2}\log 10 = 2 - \dfrac{1}{2} = \dfrac{3}{2}$

$\therefore \qquad$ (minimum pH) $\times 10 = 3/2 \times 10 = 15$

65.(31) $Ag_2CrO_4(s) \rightleftharpoons \underset{2s_1 + 2s_2}{2Ag^+} + \underset{s_1}{CrO_4^{2-}}$

$Ag_2C_2O_4(s) \rightleftharpoons \underset{2s_2 + 2s_1}{2Ag^+} + \underset{s_2}{C_2O_4^{2-}}$
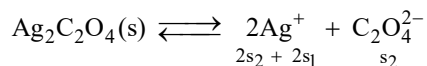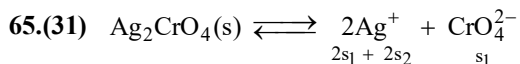
$\therefore \qquad 4(s_1 + s_2)^2 \times s_1 = 9 \times 10^{-12}$

$\qquad\qquad 4(s_1 + s_2)^2 \times s_2 = 6 \times 10^{-12}$

or $\qquad \dfrac{s_1}{s_2} = 3/2 \, s_2 \qquad$ or $\qquad s_1 = 3/2 \, s_2 \qquad \therefore \qquad 4 \times \left(\dfrac{5}{2}\right)^2 \times s_2^3 = 6 \times 10^{-12}$

or $\qquad s_2^3 = \dfrac{6 \times 10^{-12}}{25} = 24 \times 10^{-14} = 240 \times 10^{-15}$

or $\qquad s_2 = (240)^{1/3} \times 10^{-5} = 6.214 \times 10^{-5} (M)$

$\qquad\qquad s_1 = 6.214 \times 10^{-5} \times \dfrac{3}{2} = 9.321 \times 10^{-5} (M)$

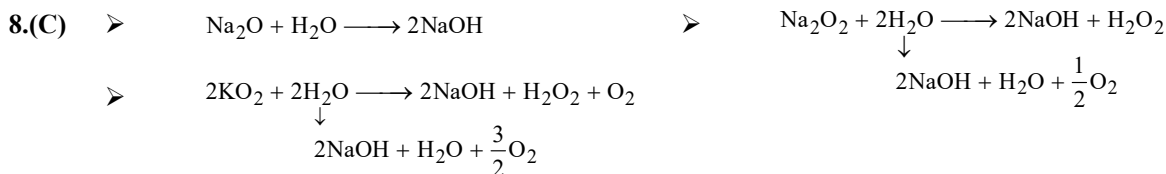$\therefore \qquad [Ag^+] = 2(6.214 + 9.321) \times 10^{-5}$

$\qquad\qquad = 31.07 \times 10^{-5}$

or $\qquad [Ag^+] \times 10^5 = 31.07 \simeq 31$

Hydrogen, s & p-Block Elements & Compounds

1.(AB) On combustion with excess of air, sodium forms peroxide, Na_2O_2 and some superoxide, NaO_2. (*Read NCERT*)

2.(D) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. (*Read NCERT*).

3.(D) Read NCERT (S-block Elements)

4.(C) Which of the following shows an increase in solubility down the group : [Read option (A) as follows]
(A) Alkali metals hydroxide

5.(B) More the electropositive character of the cation, more will be the thermal stability. (Read NCERT, S-Block Elements)

6.(A) Clearly O_2^- (in KO_2) has odd number electrons and hence will be paramagnetic. Check yourself about the diamagnetic nature of O_2^{2-} (in Na_2O_2 & PbO_2) from molecular orbital theory and of O_3 through its Lewis structure.

7.(ABC) *Remember the correct statements as fact.*

8.(C)
➤ $Na_2O + H_2O \longrightarrow 2NaOH$

➤ $\begin{array}{l} Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2 \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad 2NaOH + H_2O + \dfrac{1}{2}O_2 \end{array}$

➤ $\begin{array}{l} 2KO_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2 + O_2 \\ \qquad\qquad\qquad \downarrow \\ \qquad 2NaOH + H_2O + \dfrac{3}{2}O_2 \end{array}$
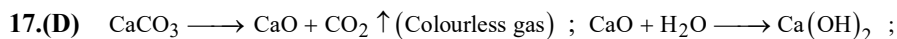
9.(A) Fact   **10.(BC)** Alkali carbonate (except Li_2CO_3) are V. stable & NH_4^+ behaves as Alkali metal ions.

11.(BD) Read NCERT (S-Block Elements)   **12.(A)** Remember as a fact

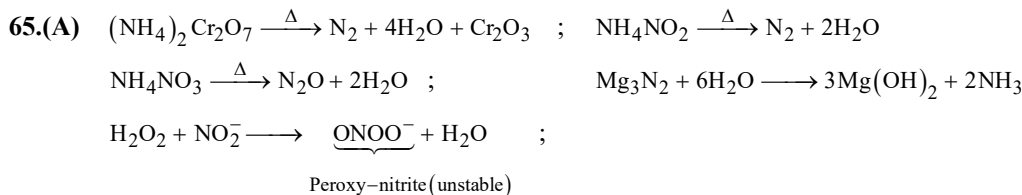**13.(D)** Read NCERT (Hydrogen Chapter), Section 9.4.3, page 279.   **14.(B)** Read option (B) as $Ca(OD)_2$

15.(C) Fact : $\rightarrow$ Apart from Borax, microcosmic salt $\left[Na(NH_4)HPO_4\right]$ is also for bead test.

16.(B) Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ make common salt hygroscopic because they are deliquescent (absorb moisture easily from the atmosphere).   [Read NCERT (s-Block Elements)]
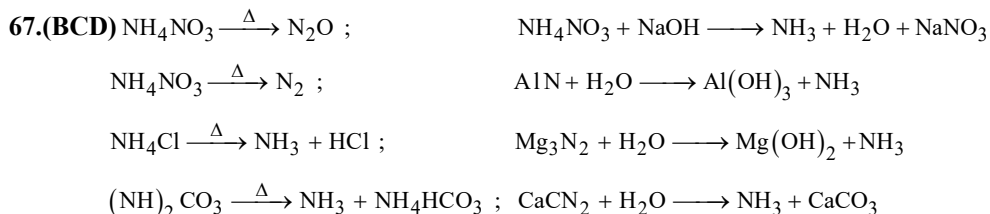
17.(D) $CaCO_3 \longrightarrow CaO + CO_2 \uparrow$ (Colourless gas) ; $CaO + H_2O \longrightarrow Ca(OH)_2$;

$Ca(OH)_2 + CO_2$(excess) $\longrightarrow Ca(HCO_3)_2$; $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$

18.(D) Read NCERT (s-Block Elements)   **19.(C)** $2Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{} + 2H_2O$
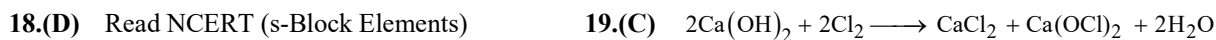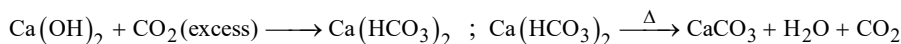
20.(D) Fact   **21.(AC)**

22.(C) ➢ Magnesium is a highly <u>flammable</u> metal, but, while it is easy to ignite when powdered or shaved into thin strips, it is difficult to ignite in mass or bulk. Once ignited, it is difficult to extinguish, being able to burn in <u>nitrogen</u> (forming <u>magnesium nitride</u>), <u>carbon dioxide</u> (forming <u>magnesium oxide</u>, and <u>carbon</u>), water (forming magnesium oxide and hydrogen) and sulphur dioxide (forming <u>magnesium oxide</u>, and <u>sulphur</u>).

➢ Also Read NCERT (S-Block Elements), section 10.6.6.

23.(D) Read NCERT (S-Block Elements), Section 10.1.6   **24.(BD)** Read NCERT (Hydrogen Chapter), Section 9.6.6

25.(D) Alums <u>crystallize</u> in regular <u>octahedral</u> (fact).   **26.(B)**   **27.(D)**

28.(D) NCERT (Hydrogen), Section 9.5.2/Page 280   **29.(C)**   **30.(B)**

31.(A) NCERT (Hydrogen), Section 9.5.3/Page 281   **32.(A)** NCERT (Hydrogen), Section 9.6.7/Page 284

33.(A) NCERT (Hydrogen), Section 9.5.3/Page 281   **34.(CD)** NCERT (Hydrogen), Section 9.1/Page 277

35.(AB) NCERT (Hydrogen), Section 9.3.2/Page 278

36.(AC) NCERT (Hydrogen), Section 9.8/Page 286 & table 9.3/Page 282

Fact : Hydrogen bonds with deuterium are slightly stronger then the ones involving normal hydrogen.

37.(AB)

38.(CD) NCERT (Hydrogen)/Section 9.6.1, 9.6.2 & 9.6.3 (Page 281-283)

Fact : Water though dissolves ionic compounds and partially covalent compounds but still it is called as "universal solvent" as it dissolved more substances than any ether liquid.

39.(AB) "Hardness" from NCERT (Hydrogen)

40.(BC) NCERT (Hydrogen), Section 9.5.2/Page 280   **41.(AD)** NCERT(Hydrogen), Section 9.5.2, Page 280

42.(C)   **43.(A)** NCERT (s-Block), Section 10.1.6/Page 294   **44.(C)** NCERT (s-Block), Section 10.1.6, Page 294

45.(AB) NCERT (s-Block), Section 10.7 (Page 301), & Section 10.3.2 Page 278

46.(B) NCERT (s-Block), Section 10.2.2, Page 295   **47.(A)** NCERT (s-Block), Section 10.6.6, Page 300

48.(D) NCERT (s-Block), Section 10.7, Page 301   **49.(A)** NCERT (s-Block), Section 10.2.3, Page 295

50.(A) NCERT (s-Block), Section 10.7, Page 301

51.(BD) NCERT (s-Block), Section 10.1.2 & 10.1.4 Page 292

52.(AC) NCERT (s-Block), Section 10.4   **53.(A)** NCERT (s-Block), Section 10.7, Page 301

54.(D) Volume strength of $H_2O_2 = N_{H_2O_2} \times 5.6 = 1 \times 5.6 = 5.6$ V

55.(AC) NCERT (s-Block), Section 10.7, Page 301   **56.(AB)** NCERT (s-Block), Section 10.8, Page 302

57.(ABC) NCERT (s-Block Elements), Section 10.3, Page 296

58.(B) Fact : Silica & diamond are electrical insulators, however graphite conducts electricity   **59.(B)**

60.(D) ➢ Recall 'Inert pair effect'.   ➢ Read NCERT (p-Block Elements-XIth) Section 11.6, Page 315

61.(C) Read NCERT (p-Block Elements-XIth), Section 11.8.4, Page 321

62.(D) Read NCERT (p-Block Elements), Section 11.3.1, Page 312   **63.(B)**

64.(ABD) $Na_2B_4O_7 \xrightarrow{HCl} H_3BO_3 \xrightarrow{\Delta} B_2O_3 \xrightarrow[\Delta\,(Reduction)]{Mg\,/\,Al\,/\,C} B$

65.(A) $(NH_4)_2 Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$; $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$; $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

$H_2O_2 + NO_2^- \longrightarrow \underline{ONOO^-} + H_2O$;

$\qquad\qquad\qquad\qquad$ Peroxy$-$nitrite(unstable)

66.(D)

67.(BCD) $NH_4NO_3 \xrightarrow{\Delta} N_2O$; $NH_4NO_3 + NaOH \longrightarrow NH_3 + H_2O + NaNO_3$

$NH_4NO_3 \xrightarrow{\Delta} N_2$; $AlN + H_2O \longrightarrow Al(OH)_3 + NH_3$

$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$; $Mg_3N_2 + H_2O \longrightarrow Mg(OH)_2 + NH_3$

$(NH)_2 CO_3 \xrightarrow{\Delta} NH_3 + NH_4HCO_3$; $CaCN_2 + H_2O \longrightarrow NH_3 + CaCO_3$

68.(AD) $\qquad$ **69.(A)** Read XIIth NCERT (p-Block Elements), Section 7.5 (Page 174) $\qquad$ **70.(C)**

71.(D) Lower the oxidation state, the better is the reducing character. $\qquad$ **72.(C)** Fact $\qquad$ **73.(D)**

74.(D) Read XIIth NCERT (p-Block Elements), Section 7.5 (Page 175) $\qquad$ **75.(B)**

76.(B) Read XIIth NCERT (p-Block Elements), Section 7.5 (Page 175) $\qquad$ **77.(A)** $\qquad$ **78.(A)**

79.(B) XIth NCERT (p-Block), Section 11.6/Page 315 $\qquad$ **80.(B)** Read NCERT.

81.(A) XIth NCERT (p-Block), Section 11.8.6/Page 322 $\qquad$ **82.(B)** XIth NCERT (p-Block), Section 11.8.4/Page 322

83.(AB) XIth NCERT (p-Block), Section 11.1.2/Page 309 $\qquad$ **84.(B)** $\qquad$ **85.(AB)**

86.(BC) ➢ NCERT XIth (p-Block), Section 11.7.2 and 11.7.3 (Page 318)
$\qquad$ ➢ Fullerenes don't have dangling bonds $\qquad$ ➢ $\qquad$ Graphite is slippery and soft.

87.(ABD) $\qquad$ **88.(BD)** $:\overset{\frown}{\ddot{O}} = C = \overset{\frown}{\ddot{O}}: \longleftrightarrow :\overset{\oplus}{\ddot{O}} \equiv C - \overset{\ominus}{\ddot{O}}:$
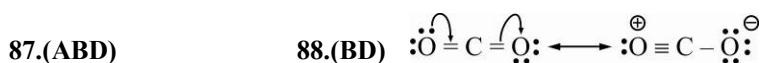
89.(C) $\qquad$ **90.(A)** $\qquad$ **91.(A)** For isoelectronic species, we count valence electrons.

92.(B) NCERT (Solids), Section, 1.3.4 (Page 5) and Table 1.2 (Page 6) $\qquad$ **93.(C)**

94.(C) NCERT XIth (Hydrogen), Section 9.3.2 $\qquad$ **95.(A)** NCERT XIIth (p-Block), Section 7.1

96.(D) NCERT XIIth (p-Block), Section 7.14 (Page 187)

97.(C) O^{2-} donates electron pair to H^+ (from $H-OH$) $\qquad$ **98.(D)** $\qquad$ **99.(B)**

100.(C) Read NCERT XIIth (p-Block Elements), Section 7.1.7 (Page 168) $\qquad$ **101.(A)** $\qquad$ **102.(C)**

103.(B) $\qquad$ **104.(C)**

105.(D) $Br_2 + \overset{-}{O}H(dil) \longrightarrow Br^- + BrO^-$; $Br_2 + \overset{-}{O}H(conc) \longrightarrow Br^- + BrO_3^-$
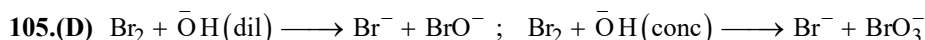
106.(C) Recall inert pair effect. $\qquad$ **107.(D)** $\qquad$ **108.(C)** Recall Fajan's rules.
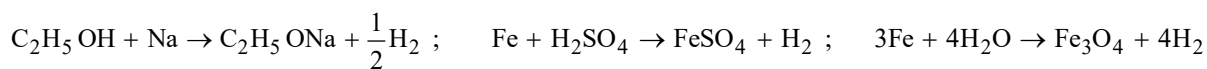
109.(C) $\qquad$ **110.(D)** Read NCERT (p-Block Elements)

111.(C) Read NCERT (p-Block Elements) $\qquad$ **112.(A)**

113.(C) Read XIIth NCERT (p-Block Elements), Section 7.23.5 Page 205 uses   **114.(B)**   **115.(C)**

116.(A) Heavy water is used for slowing down the speed of neutrons in nuclear reactors, hence used as moderators. Boiling point of heavy water is greater (374.42 K) than that of ordinary water (373 K), hence heavy water is more associated. Dielectric constant of ordinary water is greater than that of heavy water, hence ordinary water is a better solvent.

117.(A) Copper is a noble metal, as it lies below hydrogen in the electrochemical series. Therefore it can't displace hydrogen from dilute HCl. While iron and sodium lie above H in the electrochemical series, so they can liberate H_2 either from steam or H_2SO_4 solution.

$$C_2H_5OH + Na \rightarrow C_2H_5ONa + \frac{1}{2}H_2 \ ; \qquad Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \ ; \qquad 3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

118.(B) Hardness of water, due to the presence of chlorides and sulphates of Ca and Mg is called permanent hardness. Hence hard water will consist of Mg^{2+} and Cl^- ions .

119.(B) When ice melts, its molecules move into the holes or open spaces and comes closer to each other than they were in solid state. Thus, ice has lower density than water and there is contraction in volume.

120.(B) $\begin{array}{c} H \\ | \\ O-O \\ | \\ H \end{array}$ is the true structure.

121.(C) Solubility of alkaline earth metal sulphates decreases down the group because hydration energy decreases.

122.(B) The hydration enthalpy of $BeSO_4$ is higher than its lattice energy. Within group 2, the hydration energy decreases down the group while lattice energy is almost the same.

123.(C) Alkali metals are highly electropositive and halogens are electronegative. Thus for the halides of a given alkali metal, the ovalent character decreases with increase in electronegativity of halogens.

$\therefore$ Order of covalent character of halides is : MI > MBr > MCl > MF.

124.(A) The alkali metal ions exist as hydrated ions $M^+(H_2O)_x$ in the aqueous solution. The degree of hydration, however, decreases with the ionic size as we move from Li^+ to Cs^+. In other words, Li^+ ion is most highly hydrated. e.g. $[Li(H_2O)_6]^+$. Since the mobility of ion is inversely proportional to the size of their hydrated ions, therefore, amongst the alkali metal ions, lithium has the lowest ionic mobility.

$$Rb^+_{(aq)} > K^+_{(aq)} > Na^+_{(aq)} > Li^+_{(aq)}.$$
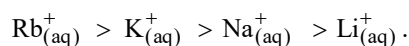
125.(C) Only 'Na' imparts golden colour to Bunsen flame, therefore, A = Na, B = H_2, C = NaOH, D = Zn.

$$\underset{(A)}{2Na} + 2H_2O \rightarrow \underset{(C)}{2NaOH} + \underset{(B)}{H_2} \ ; \quad \underset{(D)}{Zn} + \underset{(C)}{2NaOH} \rightarrow Na_2ZnO_2 + \underset{(B)}{H_2} \ ; \quad \underset{(D)}{Zn} + H_2SO_4 \rightarrow ZnSO_4 + \underset{(B)}{H_2}$$
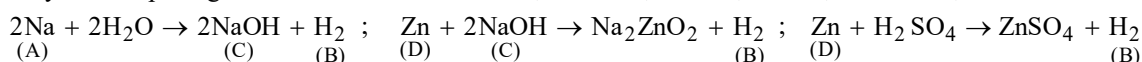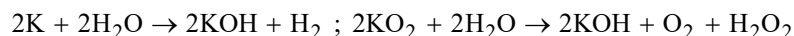
126.(B) As we move down the group from $BeSO_4$ to $BaSO_4$ the enthalpy of hydration of the positive ion becomes smaller due to increase in ionic size. Salts of heavier metal ions are less soluble than those of lighter ions.

127.(C) The pair which gives the same gaseous product is Ca and CaH_2.

Reactions : $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2 \ ; \quad CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$
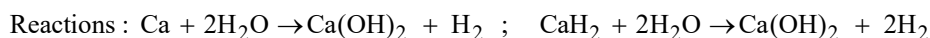
K gives H_2 while KO_2 gives O_2 and H_2O_2.

$$2K + 2H_2O \rightarrow 2KOH + H_2 \ ; \ 2KO_2 + 2H_2O \rightarrow 2KOH + O_2 + H_2O_2$$

Na gives H_2, while Na_2O_2 gives H_2O_2.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \ ; \ Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$$

Ba gives H_2 while BaO_2 gives H_2O_2.

$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2 \; ; \; BaO_2 + 2H_2O \rightarrow Ba(OH)_2 + H_2O_2 .$$

128.(D) The alkali metals are larger in size and have smaller nuclear charge thus they have low ionization energy in comparison to alkaline earth metals. The alkaline earth metals have fully filled (ns^2) s-orbital and have more nuclear charge.

29.(A) In group 13 elements, stability of +3 oxidation state decreases down the group while that of +1 oxidation state increases due to inert pair effect.

Hence, stability of +1 oxidation state increases in the sequence : Al < Ga < In < Tl.

130.(A) Me_3SiCl can form only dimer, whereas other can form polymers.

131.(D) SiO_4^{4-} ortho-silicate is basic unit of silicates.

132.(C) Pyrosilicate contains two units of SiO_4^{4-} joined along a corner containing oxygen atom.
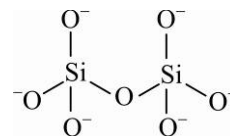
133.(ABD) Al reacts with NaOH to give sodium meta-aluminate.

134.(C) Hydrolysis of substituted chlorosilanes yields corresponding silanols which undergo polymerisation. Out of the given chlorosilanes, only $(CH_3)_2SiCl_2$ will give linear polymer on hydrolysis followed by polymerisation.

Dimethyl dichlorosilane   Dimethyl silanol
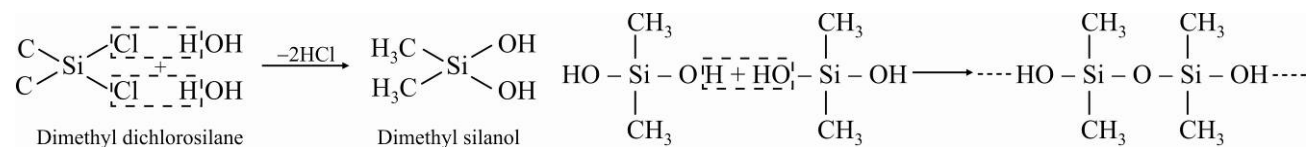
135.(D) $SeO_2 \rightarrow$ acidic oxide ; $Al_2O_3 \rightarrow$ amphoteric ; $Sb_2O_3 \rightarrow$ amphoteric ; $Bi_2O_3 \rightarrow$ basic oxide

136.(B) There is no lone pair on boron in BCl_3 hence no repulsion place. There is a lone pair on nitrogen in NCl_3 hence repulsion takes place. Therefore BCl_3 is planar molecule but NCl_3 is pyramidal molecule.

137.(A) Carbon has no d-orbitals, while silicon contains d-orbitals in its valence shell which can be used for bonding purpose.

138.(C) H_3BO_3 is a weak monobasic acid. We know that $B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$. Therefore it is a weak monobasic acid.

139.(40) 48 mg of $MgSO_4$ present in $10^3 g$ of water

$10^6 g$ water contains $MgSO_4 \qquad = 48 \times 10^3$

$\qquad\qquad\qquad\qquad\qquad\qquad\quad = 48$ g

$\therefore \qquad 120$ g of $MgSO_4 \equiv 100$ g of $CaCO_3$

$\Rightarrow \qquad 48$ g $MgSO_4 \equiv \dfrac{100}{120} \times 48 = 40$ ppm

140.(262)

$$2NaCr(OH)_4 + 2NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$
$\qquad\qquad$ (A) $\qquad\qquad\qquad\qquad\qquad\qquad$ (B)

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow H_2SO_4$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad Na_2Cr_2O_7$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (C)
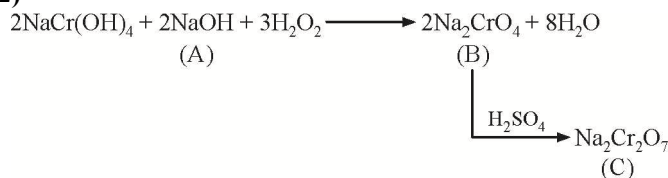
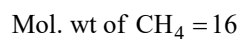Mol wt of $Na_2Cr_2O_7 \qquad = (23 \times 2) + (52 \times 2) + (16 \times 7)$
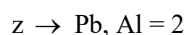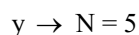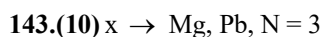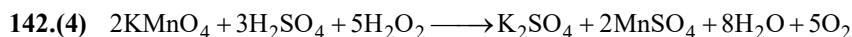
$$= 46 + 104 + 112$$
$$= 262$$

141.(5) $N_1 = \dfrac{10}{5.6}$, $N_2 = \dfrac{15}{5.6}$, $N_3 = \dfrac{20}{5.6}$

$$\left(\dfrac{10}{5.6} \times \dfrac{1}{2}\right) + \left(\dfrac{15}{5.6} \times \dfrac{1}{2}\right) + \left(\dfrac{20}{5.6} \times \dfrac{1}{2}\right) = N_T \times 4.5$$

$\Rightarrow \qquad N_T = 0.8928 \text{ N}$

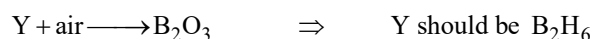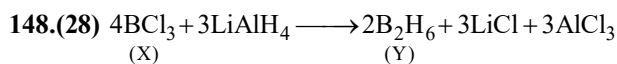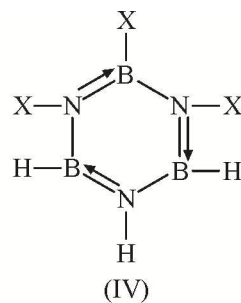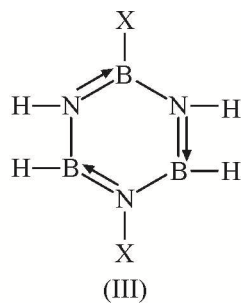Volume strength $= 5.6 \times 0.8928 \approx 5$

142.(4) $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

143.(10) $x \rightarrow$ Mg, Pb, N = 3

$\qquad$ $y \rightarrow$ N = 5

$\qquad$ $z \rightarrow$ Pb, Al = 2

144.(42) $\underset{(X)}{Be_2C + 2H_2O \rightarrow 2BeO + CH_4}$

$\qquad$ $\underset{\qquad\qquad\qquad\quad(Y)}{CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2}$

$\qquad$ Mol. wt of $CH_4 = 16$

$\qquad$ Mol wt of $C_2H_2 = 26$

$\qquad \therefore \qquad$ Sum of mol. wt. $= 16 + 26 = 42$

145.(9) $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

146.(8) $CaC_2 \quad + \quad N_2 \quad \longrightarrow \quad CaCN_2 \quad + \quad C$
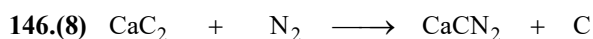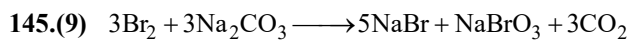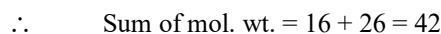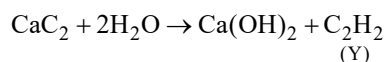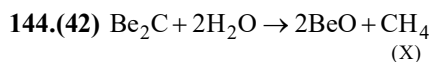
$\qquad$ 64 g $\qquad\qquad\qquad\qquad$ 80 gm

$\qquad$ 6.4 g $\qquad\qquad\qquad\qquad = \dfrac{80}{64} \times 6.4 = 8$ gm

147.(4)

(I) $\qquad\qquad$ (II) $\qquad\qquad$ (III) $\qquad\qquad$ (IV)

148.(28) $\underset{(X)}{4BCl_3} + 3LiAlH_4 \longrightarrow \underset{(Y)}{2B_2H_6} + 3LiCl + 3AlCl_3$

$\qquad$ $Y + air \longrightarrow B_2O_3 \qquad \Rightarrow \qquad$ Y should be B_2H_6
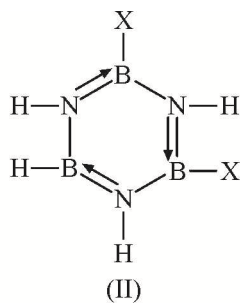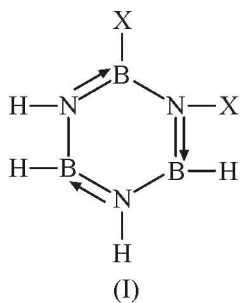
$\qquad$ % of H_2 in $B_2H_6 = \dfrac{6}{28} \times 100 \simeq 21.72$

149.(68) $Na_2B_4O_7 \cdot 10H_2O$
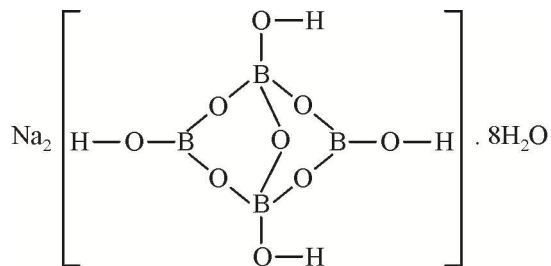
L.p = 17 × 2 = 34
B.p = 34
Total = 34 + 34 = 68

150.(2) Borax has two tetrahedral and two triangular units joined together.
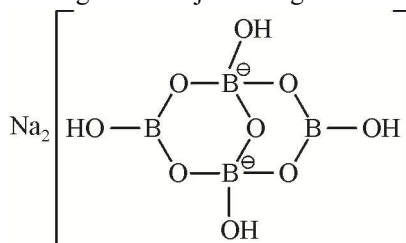
151.(6) $(Si_2O_7)^{6-}$

**152.(4)** Clark's method is used for removal of temporary hardness.

153.(3) Superoxide (O_2^-) ion is stable only in the presence of large cations such as K, Rb, Cs etc.

IOC & GOC

1.(A) Numbering of carbon chains follows lowest locant rule whereas sequence of writing groups chain follows alphabetical order.

2.(D) Priority of –COOH group is more than –CO– group, so numbering starts from carbonyl carbon atom in the carboxylic group. Thus name is 4-oxopentaoic acid.

3.(B) In aromatic compounds, numbering starts from the carbon atom at which group with alphabetical priority is attached. Out of –Cl (chloro), –NO₂ (Nitro) and –CH₃ (methyl) groups, –Cl has highest priority. After that numbering follows in such a way that other group get lowest number.
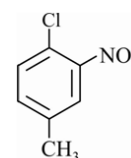
1-chloro-3-methyl-2-nitrobenzene

4.(C) The percentage of s-character in hybridization increases electronegativity of carbon atom. In $CH_3 - CH_2 - C \equiv \overset{*}{C}H$, said carbon atom is sp-hybridized, so, it most electronegative due to 50% (highest) s-character.

5.(ABD)
Functional isomerism is possible for compounds containing functional group. Alkyl halides cannot show functional isomerism since these are side chain (on groups).

6.(A) Resonance dominates hyperconjugation, so carbocation containing resonance effects is more stable.
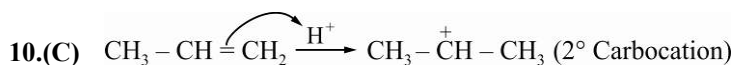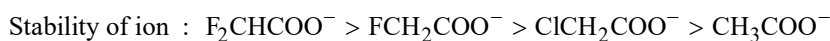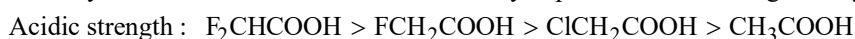
$$(CH_3 - \overset{+}{C}H - \overset{\cdot\cdot}{O} - CH_3) \longleftrightarrow (CH_3 - CH = \overset{+}{O} - CH_3)$$

$CH_3 - \overset{+}{C}H - CH_3$ contains six α-hydrogen and $CH_3 \overset{+}{C}H - CH_2 - OCH_3$ contains five α-hydrogen,

So, $CH_3 \overset{+}{C}HCH_3$ (I) is more stable than (III) so, correct order is II > I > III.

7.(B) Longest carbon chain is six carbon atoms, 3rd & 4th position is occupied by methyl groups. Thus IUPAC name is 3, 4-Dimethylhexane.

8.(A) In Grignard reagent, CH_3CH_2MgCl, $C - Mg$ bond is ionic bond due to which carbon atom is negativity charged and it shows $+I$ effect. $-I$ group will make carbon atom more positively charged. Thus CH_3CH_2Cl contains more positively charged carbon atom due to more $-I$ effect of $-Cl$.
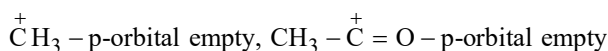
9.(D) Carboxylate ion is most stable of it is formed by deprotonation of strongest conjugate acid.
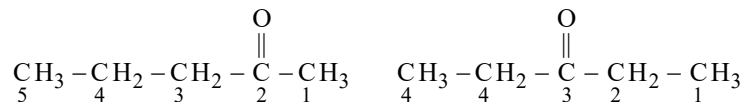Acidic strength : $F_2CHCOOH > FCH_2COOH > ClCH_2COOH > CH_3COOH$

Stability of ion : $F_2CHCOO^- > FCH_2COO^- > ClCH_2COO^- > CH_3COO^-$

10.(C) $CH_3 - CH = CH_2 \xrightarrow{H^+} CH_3 - \overset{+}{C}H - CH_3$ (2° Carbocation)

11.(AD) $H - C \equiv C - C \equiv C - H$, only sp-hybridized carbon atoms.

$CH_2 = CH - CH = CH_2$, only sp^2-hybridized carbon atoms.
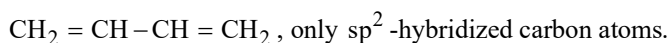
12.(BC) There should be an empty orbital to accept electron pair, for a species to be electrophile.

$AlCl_3 - $ p-orbital, $SO_3 - $ d-orbital empty $\qquad\qquad NO_2^+ - $ p-orbital empty

$\overset{+}{C}H_3 - $ p-orbital empty, $CH_3 - \overset{+}{C} = O - $ p-orbital empty

13.(B) For positive isomerism, parent carbon chain should contain same carbon atoms.

$$\underset{5}{C}H_3 - \underset{4}{C}H_2 - \underset{3}{C}H_2 - \overset{\overset{\displaystyle O}{||}}{\underset{2}{C}} - \underset{1}{C}H_3 \qquad \underset{4}{C}H_3 - \underset{4}{C}H_2 - \overset{\overset{\displaystyle O}{||}}{\underset{3}{C}} - \underset{2}{C}H_2 - \underset{1}{C}H_3$$

Only position of ketonic group is different in the compounds

14.(AC)
$$CH_3 - CH_2 - CH_2 - \overset{\overset{\displaystyle O}{||}}{C} - CH_3 \qquad CH_3CH_2\overset{\overset{\displaystyle O}{||}}{C}CH_2CH_3$$

Position isomers.

$CH_3 - CH_2 - CH_2 - CH_2 - CHO \qquad (CH_3)_2CH - CH_2 - CHO$
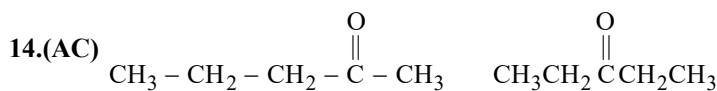
Different Chain, some functional group $\qquad \Rightarrow \qquad$ Chain isomers.
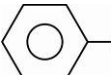
15.(A) Answer can be either (A) or (C) but the question says "Nucleophile is species that **should have**". So, it should have a pair of electrons to donate. It may or may not have a negative charge.

16.(AB) Hyperconjugation observed in two cases.
    * Delocalization of σ-electrons into empty p-orbital * Delocalization of σ-electrons into empty π^* orbitals.

17.(B) Both statements are true but reason is not correct explanation of A.

18.(A) **I.** $CH_2 = CH - \overset{+}{C}H_2 - Alkyl \rightarrow resonance$ **II.** $CH_3 - \overset{+}{C}H - CH_3 - isopropyl \rightarrow only\ hyperconjugation$

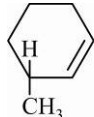**III.** $-\overset{+}{C}H_2 - benzyl \rightarrow resonance$ Correct order should be $III \approx I > II$

However, In case of comparison between I and III, usually we take III > I.

19.(B) RSH is more than ROH but RS^- is more nucleophilic because sulphur atom contains more diffused electron density, so, approachability of RS^- at back side of $C-X$ bond is more due to which it is stronger nucleophile.

20.(D) Basicity of given anions is reverse of acidity of their conjugate acids. Acidic order of conjugate acids

$RCOOH > HC \equiv CH < NH_3 < RH \quad \Rightarrow \quad$ basic strength $RCOO^- < HC \equiv C^- < \overset{-}{N}H_2 < R^-$

21.(BC) Contains one asymmetric carbon atom $CH_2 = CH - \overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}} - CH_2CH_3$ Contains one asymmetric carbon atom

22.(C) Electron withdrawing group stabilize the carbanions $\overset{-}{C}Cl_3 \rightarrow$ very high $-I$ effect : $C_6H_5\overset{-}{C}H_2 \rightarrow$ Resonance effect

Thus order is $\overset{-}{C}Cl_3 > C_6H_5\overset{-}{C}H_2 > (CH_3)_2\overset{-}{C}H > (CH_3)_3 C^-$

23.(C) Geometrical isomers

Thus total of 4-stereoisomers are possible.

Shows optical isomerism also   Shows optical isomerism also
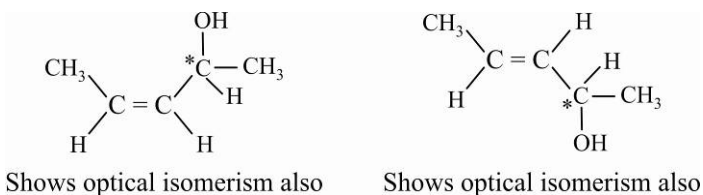
24.(A)

25.(ABD) Compound containing chiral carbon atom rotates plane of polarised light. In the case when more than one chiral centres exist, overall chirality should exist.
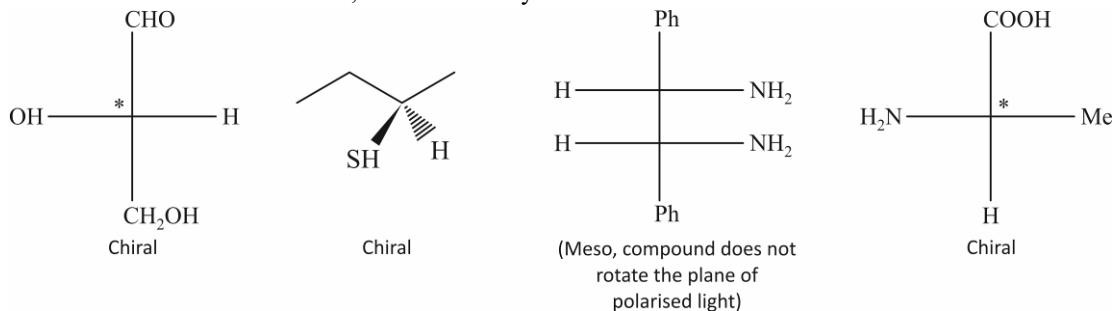
26.(B) 1° halides one most reactive and 3° halides are least reactive in S_N2 reaction because steric hindrance increases from 1° to 3° at back side of $C-X$ bond.
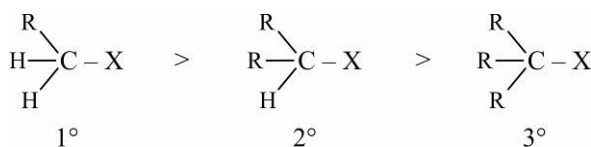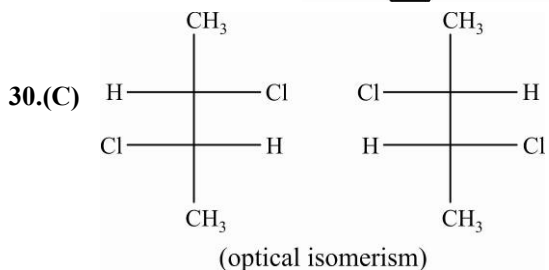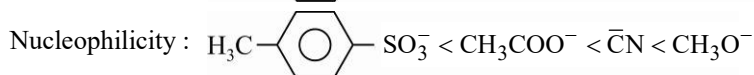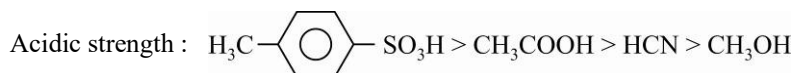

27.(A) Resonance effect containing free radicals are more stable than hyperconjugation effect.

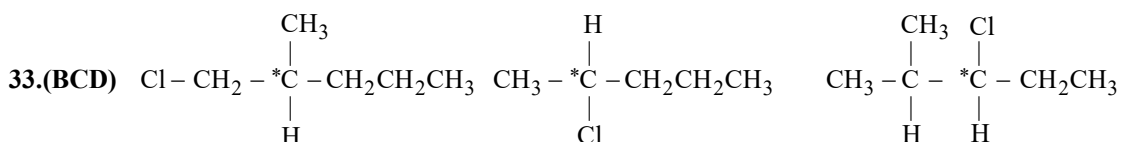$(C_6H_5)_3 C° > (C_6H_5)_2 C°H > (CH_3)_3 C° > (CH_3)_2 C°$

28.(D) Free radicals one chemically reactive species due to unpaired electron.

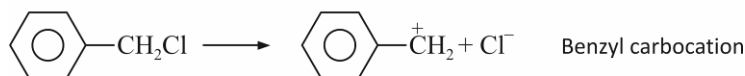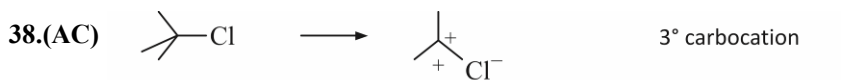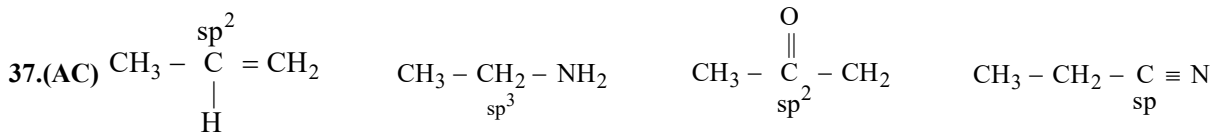**29.(B)** Nucleophilicity is the reverse of the stability of anions, i.e. reverse of the acidity of conjugate acids
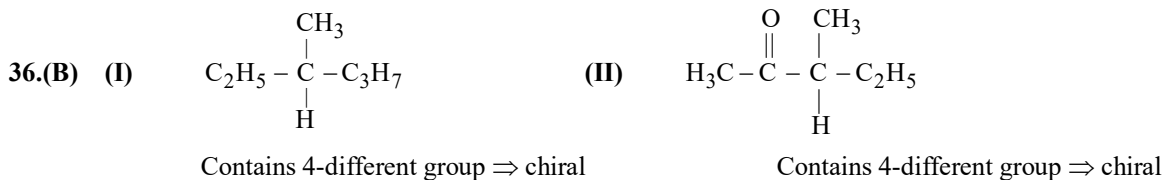
Acidic strength : $H_3C-\langle\bigcirc\rangle-SO_3H > CH_3COOH > HCN > CH_3OH$

Nucleophilicity : $H_3C-\langle\bigcirc\rangle-SO_3^- < CH_3COO^- < \overline{C}N < CH_3O^-$

30.(C)

```
      CH₃              CH₃
       |                |
 H ——— | ——— Cl   Cl ——— | ——— H
       |                |
Cl ——— | ——— H    H ——— | ——— Cl
       |                |
      CH₃              CH₃
```
(optical isomerism)

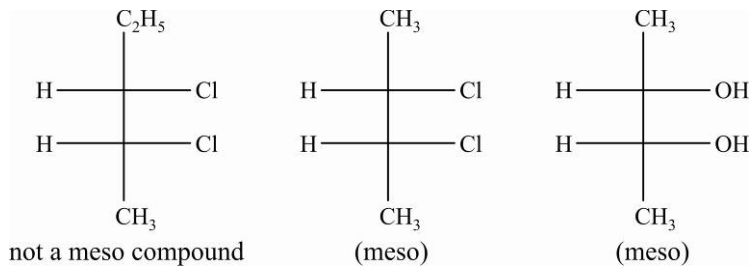**31.(ABD)** Acetonitrile is $CH_3 - C \equiv N$ which contains sp^3 & sp hybridised carbon atoms. Other compounds contain group in which carbon is sp^2 hybridised carbon atom.

32.(D) In gaseous sate, $d \propto M$, C_2H_5OH & CH_3OCH_3 contains same molecular mass, so same density for both.
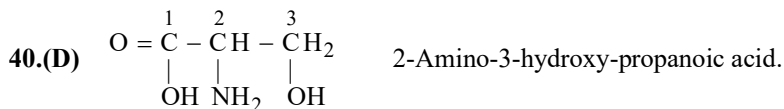
33.(BCD)

$$Cl - CH_2 - \overset{CH_3}{\underset{H}{\overset{|}{*C}}} - CH_2CH_2CH_3 \quad CH_3 - \overset{H}{\underset{Cl}{\overset{|}{*C}}} - CH_2CH_2CH_3 \quad CH_3 - \overset{CH_3}{\underset{H}{\overset{|}{C}}} - \overset{Cl}{\underset{H}{\overset{|}{*C}}} - CH_2CH_3$$

34.(C)

35.(BD) At least two chiral centers should be in the compound with environment around chiral carbon atoms.

```
     C₂H₅             CH₃              CH₃
      |                |                |
H ——— | ——— Cl   H ——— | ——— Cl   H ——— | ——— OH
      |                |                |
H ——— | ——— Cl   H ——— | ——— Cl   H ——— | ——— OH
      |                |                |
     CH₃              CH₃              CH₃
not a meso compound   (meso)           (meso)
```

36.(B) **(I)** $C_2H_5 - \overset{CH_3}{\underset{H}{\overset{|}{C}}} - C_3H_7$ **(II)** $H_3C - \overset{O}{\overset{||}{C}} - \overset{CH_3}{\underset{H}{\overset{|}{C}}} - C_2H_5$

Contains 4-different group $\Rightarrow$ chiral   Contains 4-different group $\Rightarrow$ chiral

37.(AC) $CH_3 - \overset{sp^2}{\underset{H}{\overset{|}{C}}} = CH_2$ $CH_3 - CH_2 - \underset{sp^3}{NH_2}$ $CH_3 - \underset{sp^2}{\overset{O}{\overset{||}{C}}} - CH_2$ $CH_3 - CH_2 - \underset{sp}{C} \equiv N$

38.(AC)

```
  >—Cl  ⟶  >·⁺        3° carbocation
              + Cl⁻
```

$\langle\bigcirc\rangle-CH_2Cl \longrightarrow \langle\bigcirc\rangle-\overset{+}{C}H_2 + Cl^-$ Benzyl carbocation
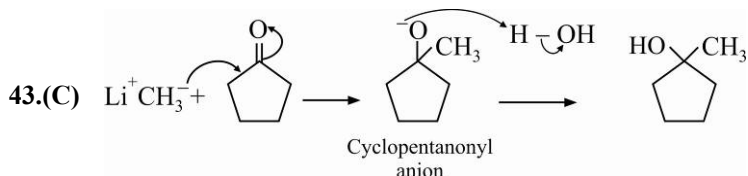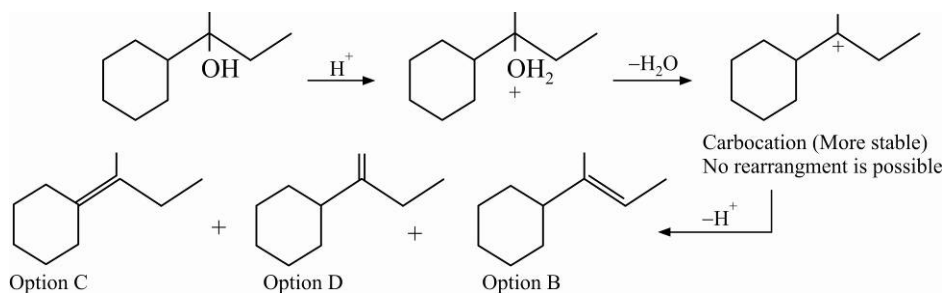
$1°$ carbocation is not formed because stability is very low.

39.(D) **S**tructure I should be treated as 2-butene, hence it will show only geometric isomerism. Structure II should be treated as 2-butanol, hence it will show only optical isomerism. However, it is a single choice question, in that case (D) is correct answer. Both types of isomerism studied under stereoisomerism.
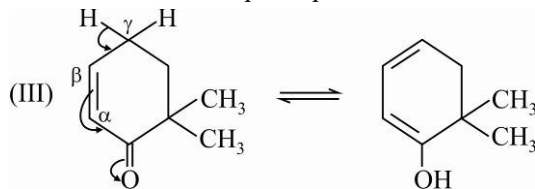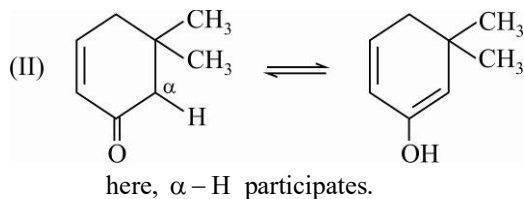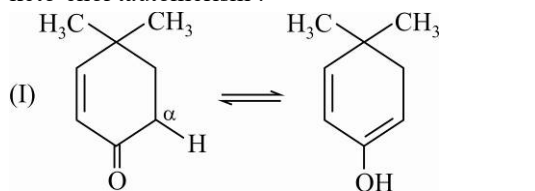
40.(D)

$$\overset{1}{O = C} - \overset{2}{C}H - \overset{3}{C}H_2$$
$$\quad\ |\qquad |\qquad\ |$$
$$\ \ OH\quad NH_2\quad OH$$

2-Amino-3-hydroxy-propanoic acid.

41.(D) Nucleophiles are electron rich species hence, they are Lewis bases.

42.(A)

Carbocation (More stable)
No rearrangment is possible

Option C   Option D   Option B

43.(C)

Cyclopentanonyl anion

44.(D) There are four double bonds. Hence, no. of $\pi-$ electrons $= 2 \times 4 = 8$.

45.(B) keto-enol tautomerism :

(I)

Here, $\alpha - H$ participates.

(II)

here, $\alpha - H$ participates.

(III)

here, $\gamma - H$ participates (p-tautomerism) and it is induced in presence of base.

46.(A) Mass of organic compound $= 0.25$ g
Experimental values (at STP) :

$V_1 = 40$ mL ; $V_2 = ?$; $T_1 = 300$ K ; $T_2 = 273$ K ; $P_1 = 725 - 25 = 700$ mm ; $P_2 = 760$ mm

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad \Rightarrow \qquad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{700 \times 40 \times 273}{300 \times 760} = 33.52 \, mL$$

22400 mL of N_2 at STP weighs = 28 g

$\therefore$ 33.52 mL of N_2 at STP weighs $= \dfrac{28 \times 33.52}{22400} = \dfrac{33.52}{8} = 0.0419 \, g$

% of N $= \dfrac{\text{Mass of nitrgoen at STP}}{\text{Mass of organic compound taken}} \times 100 = \dfrac{0.0419}{0.25} \times 100 = 16.76\%$
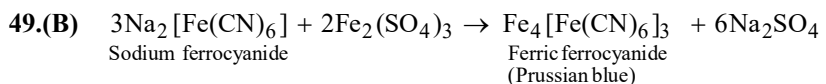
47.(A) $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2 SO_4$

10 mL of 1 M H_2SO_4 = 10 m mol. $[\because M \times V_{(mL)} = mmol]$

NH_3 consumed = 20 mmol

Acid used for the absorption of ammonia $= 20 - 10 \, mmol = 10 \, mL$ of 2 N (or 1 M) H_2SO_4

$$\% \text{ of N} = \frac{1.4 \times N \times V}{W} = \frac{1.4 \times 2 \times 10}{0.75} = 37.33\% \, .$$
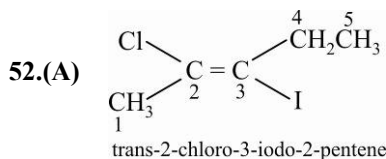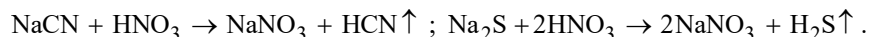
48.(C)   Aromatic species has a close loop of delocalizable $(4n + 2)\pi$ electrons. In this species d-electron is not part of close loop. So this species contain 6 delocalizable electrons in 6p-orbitals.

49.(B) $\underset{\substack{\text{Sodium ferrocyanide}}}{3Na_2[Fe(CN)_6]} + 2Fe_2(SO_4)_3 \rightarrow \underset{\substack{\text{Ferric ferrocyanide} \\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4 \, .$

50.(B)   Similar to Question 46. Find V_{N_2} .

$$\% N = \frac{V_{N_2}(STP)}{8 \times W_{org. \, compound}} \times 100 \qquad \Rightarrow \qquad \% \text{ of N} = \frac{46.099}{8 \times 0.35} = 16.46$$

51.(A)   In case of Lassaigne's test of halogens, it is necessary to remove sodium cyanide and sodium Sulphide from the sodium extract if nitrogen and sulphur are present. This is done by boiling the sodium extract with conc. HNO_3.

        $NaCN + HNO_3 \rightarrow NaNO_3 + HCN\uparrow$; $Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S\uparrow$.

52.(A)

trans-2-chloro-3-iodo-2-pentene

53.(A)   Ortho-cresol is the most reactive towards electrophilic reagents (in S_E reaction). The reason for this is the $-CH_3$ group (+I effect) and $-OH$ group (+R/+M effect) which increase the electron density on the benzene ring.

54.(C) H_3O^+ is not electrophile as it has no vacant orbital.

55.(A)   In case of different nucleophiles, but present in the same group in the periodic table, then larger is the size, higher is the nucleophilicity. Hence the decreasing order of nucleophilicity of the halide ions is :

        $I^- > Br^- > Cl^- > F^-$.

56.(B)   Sublimation method is used for those organic substances which pass directly from solid to vapour state on heating and vice-versa on cooling, e.g. benzoic acid, naphthalene, camphor, anthracene, etc. Naphthalene is volatile and benzoic acid is nonvolatile due to the formation of the dimer.

57.(B)   Carboxylic acid is much stronger than water and alcohol. Since the carboxylate ion after the removal of proton is stabilised by resonating structures. The $-OH$ in alcohols is almost neutral. Acetylene is also weakest acid.

58.(C) Tollen's reagent is solution of ammoniacal silver nitrate and used for the detection of $-CHO$ group. Aldehydes reduce Tollen's reagent and itself get oxidised to give Ag^+ ions to Ag powder which forms the silver coloured mirror in the test tube. So this test is also known as silver mirror test.

$$R - CHO + [Ag(NH_3)_2]^+ \rightarrow R - COO^- + Ag\,(Powder)\,.$$
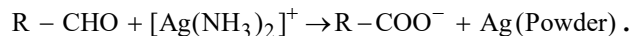
59.(D) Carboxylic acid dissolve in $NaHCO_3$ but phenols do not being very weak acids.
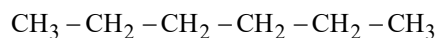
60.(A)

or
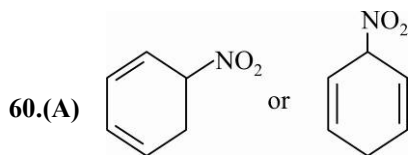
Hence it is homocyclic (as the ring system is made of one type of atoms, i.e., carbon) but not aromatic.
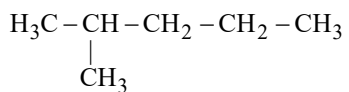
61.(4) The compound has one chiral centre. Therefore, $2^n = 2^1 = 2$ optically active compounds are possible. Also, two geometrical isomers (cis and trans) are possible. So, total of four isomers are possible.
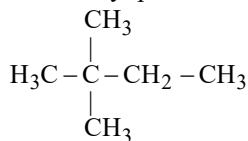
$$CH_3 - \overset{H}{C} = \overset{H}{C} - \overset{H}{\underset{CH_3}{C}} - OH$$
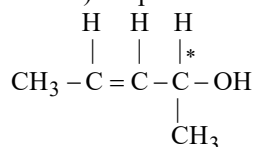
62.(5) Structural isomers refers to the compounds that have same molecular formula but different arrangement of atoms or groups within the molecule. Based on this, following are the structural isomers for C_6H_{14} :
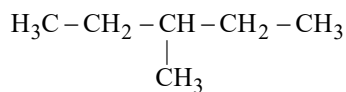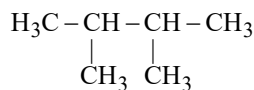
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$
n-Hexane

$$H_3C - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - CH_3$$
2-Methyl pentane

$$H_3C - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$$
3-Methyl pentane

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - CH_3$$
2,2-Dimethyl butane

$$H_3C - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_3$$
2,3-Dimethyl butane

63.(7) There are seven chiral centres present in the given compound.
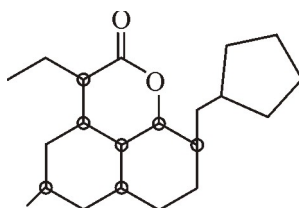
64.(8) When molecule is asymmetric, no. of geometrical isomers is given by 2^n where n is no. of double bonds.

65.(7) (I) $\quad CH_3 - CH_2 - CH_2 - CH_2 - OCH_3$

(II&III) $\quad CH_3 - CH_2 - \underset{*}{\overset{\overset{CH_3}{|}}{CH}} - OCH_3$

(IV) $\quad CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_2 - OCH_3$

(V) $CH_3 - \underset{\underset{OCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$
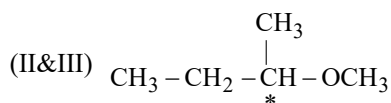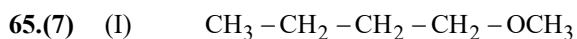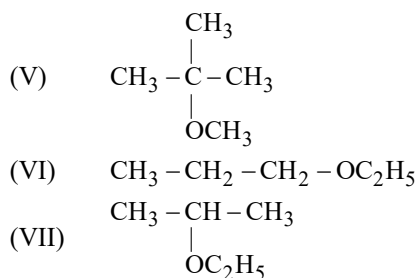
(VI) $CH_3 - CH_2 - CH_2 - OC_2H_5$

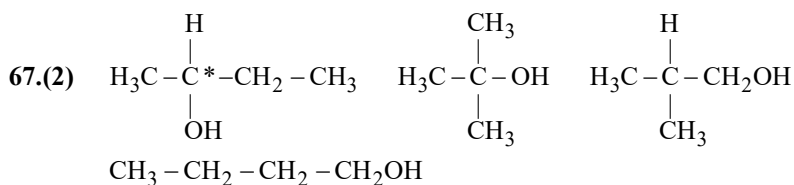(VII) $CH_3 - \underset{\underset{OC_2H_5}{|}}{CH} - CH_3$
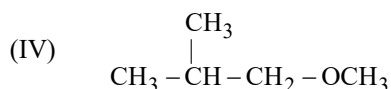
66.(11) Triple bonds = 1
Double bonds = 6
Rings = 3
Due to each triple bond, there are 2 degree of unsaturation while due to double bond & ring there is 1 degree of unsaturation each. So in total D.U. = 2 + 6 + 3 = 11

67.(2) $H_3C - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}* - CH_2 - CH_3$ $H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH$ $H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} - CH_2OH$

$CH_3 - CH_2 - CH_2 - CH_2OH$

68.(3) There are three derivatives for formula $C_6H_3Cl_3$.
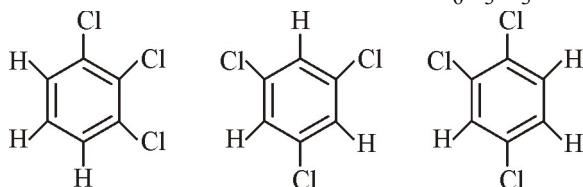
69.(8) There are 8 chiral carbon atoms present.
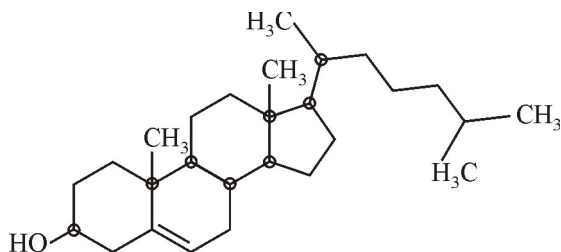
70.(2) The resonating structures are

71.(6) $CH_3 - CH_2 - CH_2 - CH = CH_2$ $CH_3 - CH_2 - CH = CH - CH_3$
　　　　　1-Pentene　　　　　　　　　　　　2-Pentene
$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH - CH_3$ $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH = CH_2$ $CH_3 - \underset{\overset{||}{CH_2}}{C} - CH_2 - CH_3$
3-Methylbut-2-ene　　　　3-Methylbutene　　　　　2-Methylbut-1-ene
2-Pentene can show geometrical isomerism also. So in total there are 6 isomers.
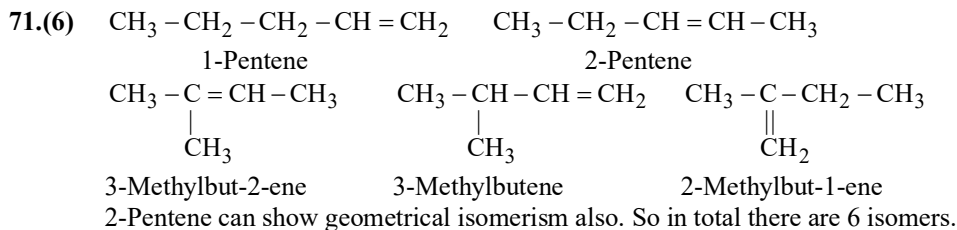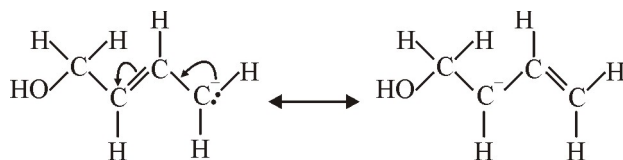
72.(3) Three isomers are possible for disubstituted benzene.
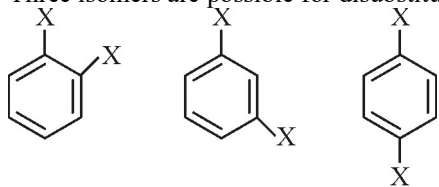
73.(4) $a = 2^n$ where a = number of optically active isomers and n = number of asymmetric carbon atoms

As n = 2, so $a = 2^2 = 4$.

74.(7)

$$H - \overset{\overset{\displaystyle C-C}{|}}{\underset{\underset{\displaystyle C-C-C}{|}}{\textcircled{C}}} - C \longrightarrow \text{Chiral carbon}$$

75.(9) (a)

$$\overset{Br}{\underset{Br}{\overset{|}{\underset{|}{C-C-C-C}}}} \quad (1,1)$$

(b)

$$\overset{Br}{\underset{Br}{\overset{|}{\underset{|}{C-\overset{}{C}-C-C}}}} \quad (2,2)$$

(c)

$$\underset{Br \quad Br}{\overset{|}{\underset{|}{C-C-C-C}}} \quad (1,3)$$

(d)

$$\underset{Br \;\; Br}{\overset{|}{\underset{|}{C-C-C-C}}} \quad (1,2)$$

(e)

$$\underset{Br \;\; Br}{\overset{|}{\underset{|}{C-C-C-C}}} \quad (2,3)$$

(f)

$$\underset{Br \qquad\quad Br}{\overset{|}{\underset{|}{C-C-C-C}}} \quad (1,4)$$

(g)

$$\overset{Br}{\underset{C \;\; Br}{\overset{|}{\underset{|}{C-C-C}}}} \quad (1,1)$$

(h)

$$\overset{Br}{\underset{C-Br}{\overset{|}{\underset{|}{C-C-C}}}} \quad (1,3)$$

(i)

$$\overset{Br \;\; Br}{\underset{C}{\overset{|}{\underset{|}{C-C-C}}}} \quad (1,2)$$

Class XI | Chemistry

| **Hydrocarbons** |

1.(C) $CH_3CCl_3 \xrightarrow{\text{Ag powder}} CH_3 - C \equiv C - CH_3$
2−butyne

2.(D)

$\xrightarrow{AgNO_3}$ white ppt

(A) $\xrightarrow[\text{[O]}]{\text{Oxidation}}$

$\xrightarrow{\Delta}$

3.(C)

$\xrightarrow[\text{SbCl}_5]{\text{toluene}}$

$\longrightarrow$ Recemization

2° benzyl
carbocation

4.(B)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_2CH_3 \xrightarrow[h_2]{Cl_2}$$

$ClCH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$　　$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - CH_2CH_3$　　$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - \overset{\underset{\displaystyle Cl}{|}}{C}H - CH_3$　　$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_2CH_2Cl$

(I)　　　　　　**(II)**　　　　　　**(III)**　　　　　　**(IV)**

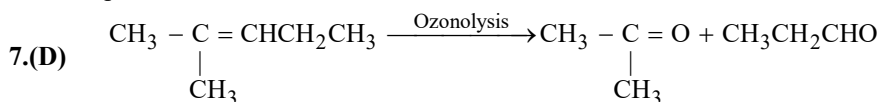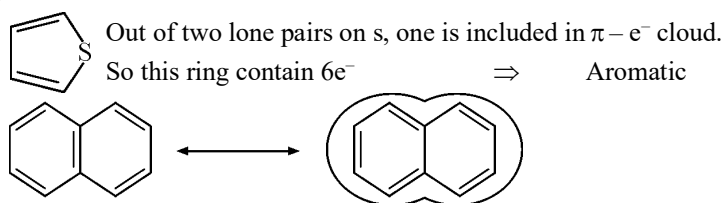Four structural isomers are produced but (I) and (III) contains chiral centre, so, two isomers are chiral compound,

5.(B) Dissolved metal reduction produces trans isomer and heterogeneous catalyst produces cis isomer

6.(B) $CH_2 = CH-$ group should exist on the hydrocarbon which on oznonolysis will produce formaldehyde as one product.

7.(D) $CH_3 - \overset{\underset{\displaystyle CH_3}{|}}{C} = CHCH_2CH_3 \xrightarrow{\text{Ozonolysis}} CH_3 - \overset{\underset{\displaystyle CH_3}{|}}{C} = O + CH_3CH_2CHO$

8.(BCD) $(4n + 2)\ \pi\ e^-$ rule

Out of two lone pairs on s, one is included in $\pi - e^-$ cloud.
So this ring contain $6e^-$　　　　$\Rightarrow$　　　Aromatic

 $\longleftrightarrow$

Consider one ring and count e–s on the perimeter of its
It contains $10e^-$ which are according $(4n + 2)\ \pi\ e^-s$　　$\Rightarrow$　　　Aromatic

$\overset{\displaystyle\bigcirc}{N-H} \quad \Rightarrow \quad$ Contains $6e^-s \Rightarrow$ Aromatic

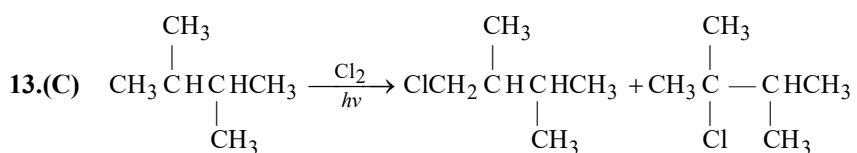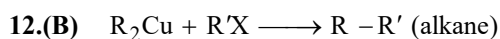$\Rightarrow \quad 4x\ e^-s \Rightarrow$ Not Aromatic
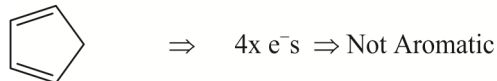
9.(ABCD) All the given alkynes will give corresponding alkene on reaction with sodium in liquid ammonia due to partial hydrogenation of triple bond.

Note : If we use $NaNH_2$, then only $CH_3CH_2C \equiv CH$ and $PhC \equiv CH$ containing acidic hydrogen will react.

10.(CD) $CH_3MgX + CH_3C \equiv CH \longrightarrow CH_4 + CH_3C \equiv C^-MgX$

11.(C)

12.(B) $R_2Cu + R'X \longrightarrow R - R'$ (alkane)

13.(C)

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H\overset{}{C}HCH_3 \xrightarrow[hv]{Cl_2} ClCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3 + CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

(Only two structural isomers are formed). Stereoisomers are ignored.

14.(C) At lower temperature, thermodynamic controlled products are formed. Thus, 1-bromo-2-butene is formed
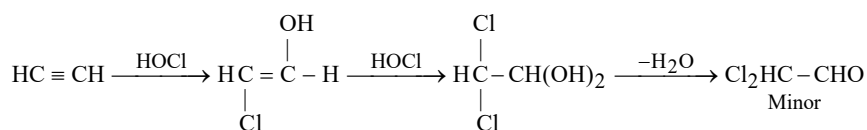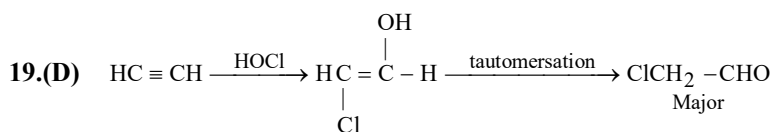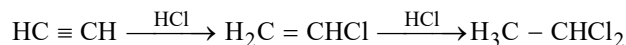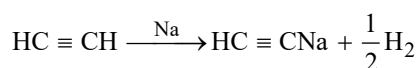
15.(D) Zn-Hg/HCl reduces butan-2-one, other compounds requires strong reducing agents

16.(D) Isobutene has lowest surface area, so, contains lowest boiling point.

17.(D) Butene-1 is non polar in nature, so, non-polar catalyst is best to reduce it.

$$CH_3CH_2CH = CH_2 \xrightarrow{Pd/H_2} CH_3CH_2CH_2CH_3$$
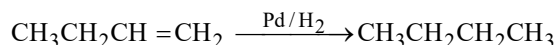
18.(ABC) Acetylene is weakly acidic in nature due to which it cannot react with NaOH.
HCl reacts with triple bond.

$$HC \equiv CH \xrightarrow{Na} HC \equiv CNa + \frac{1}{2}H_2$$

$$HC \equiv CH \xrightarrow{AgNO_3} HC \equiv CAg \text{ (silver mirror)}$$

$$HC \equiv CH \xrightarrow{HCl} H_2C = CHCl \xrightarrow{HCl} H_3C - CHCl_2$$

19.(D)

$$HC \equiv CH \xrightarrow{HOCl} \underset{\underset{\displaystyle Cl}{|}}{H}C = \overset{\overset{\displaystyle OH}{|}}{C} - H \xrightarrow{\text{tautomersation}} \underset{\text{Major}}{ClCH_2 - CHO}$$

$$HC \equiv CH \xrightarrow{HOCl} \underset{\underset{\displaystyle Cl}{|}}{H}C = \overset{\overset{\displaystyle OH}{|}}{C} - H \xrightarrow{HOCl} \underset{\underset{\displaystyle Cl}{|}}{H}C - CH(OH)_2 \xrightarrow{-H_2O} \underset{\text{Minor}}{Cl_2HC - CHO}$$
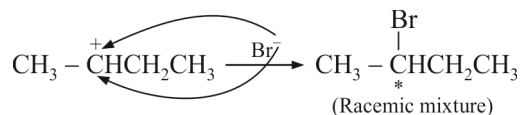
20.(C) CH_3MgI contains $C - Mg$ bond

21.(D) n-pentane : Highest molar mass and highest surface area ; n-butane : Lowest molar mass and lowest surface area n-pentane > 2-methylbutane > 2, 2-dimethylpropane > n-butane
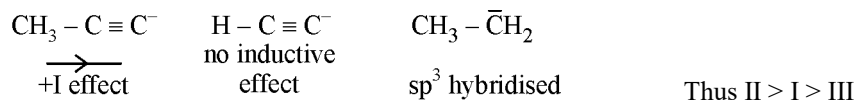
22.(A) $F_2 > Cl_2 > Br_2 > I_2$

23.(B)

24.(A) $CH_2 = CHCH_2CH_3 \xrightarrow{HBr} CH_3 - \overset{+}{C}HCH_2CH_3(\text{major}) + \overset{+}{C}H_2CH_2CH_2CH_3 \text{ (minor)}$

$CH_3 - \overset{+}{C}HCH_2CH_3 \xrightarrow{Br^-} CH_3 - \underset{*}{\overset{Br}{\underset{|}{C}}HCH_2CH_3}$
(Racemic mixture)

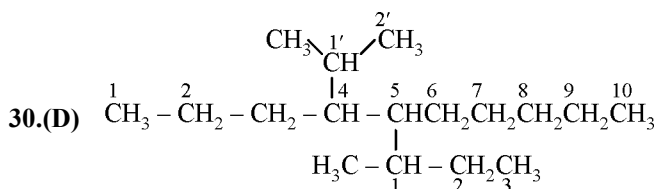**25.(ABC)** Each carbon connected by double bond should contain two different group individually.

26.(C) Stronger acid reacts faster.

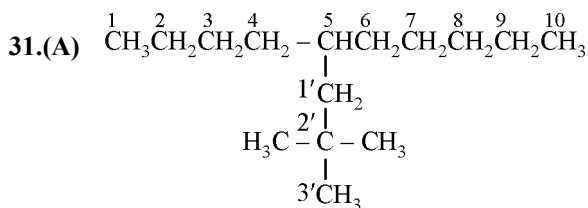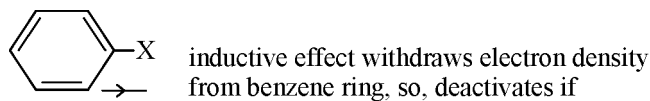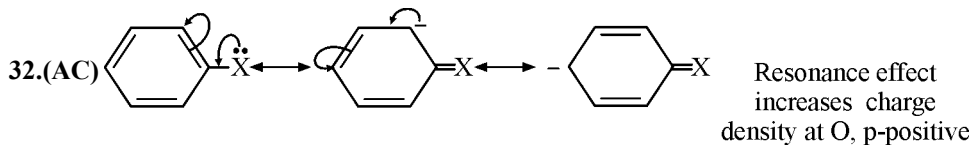**27.(B)** sp hybridized carbon atom is more electronegative so, negative charge is more stable on if

$CH_3 - C \equiv C^- \qquad H - C \equiv C^- \qquad CH_3 - \bar{C}H_2$

$\xrightarrow{\text{+I effect}} \qquad \text{no inductive effect} \qquad sp^3 \text{ hybridised}$

Thus II > I > III

28.(ABC) Factual

29.(BCD) Factual

30.(D)

$$\overset{CH_3}{\underset{1'}{\diagdown}}\overset{\overset{2'}{CH_3}}{\underset{CH}{\diagup}}$$

$\overset{1}{C}H_3 - \overset{2}{C}H_2 - \overset{}{C}H_2 - \overset{4}{C}H - \overset{5}{C}H\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_2\overset{10}{C}H_3$

$H_3C - \underset{1}{C}H - \underset{2}{C}H_2\underset{3}{C}H_3$

4-(1methylethyl)-5-(1-methylpropyl)-decane

31.(A) $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2 - \overset{5}{C}H\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_2\overset{10}{C}H_3$

$\underset{}{\overset{1'}{C}H_2}$

$H_3C - \overset{2'}{\underset{|}{C}} - CH_3$

$\overset{3'}{C}H_3$

5-(2', 2' - dimethylpropyl) - decane

32.(AC)

Resonance effect increases charge density at O, p-positive

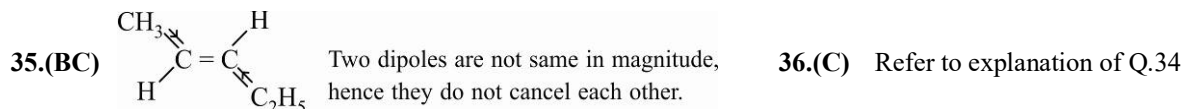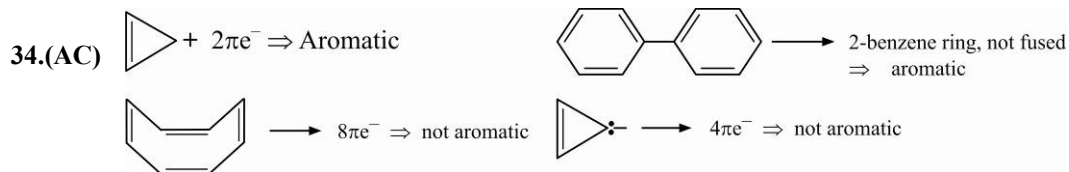inductive effect withdraws electron density from benzene ring, so, deactivates if

33.(ABC) (A) $CH_3 - \overset{..}{\overset{..}{O}} \overset{+}{C}H_3 \longleftrightarrow CH_3 - \overset{+}{O} = CH_2$ Resonance effect

$CH_3 - \overset{+}{C}H_2$ hyperconjugation . Thus $CH_3O\overset{+}{C}H_2$ is more stable then $CH_3\overset{+}{C}H_2$

**(B)** $CH_3 - \overset{+}{C}H - CH_3$ (2° carbocation) is less stable than $CH_3 - O - \overset{+}{C}H_2$ because of resonance.

(C) $CH_2 = CH - \overset{+}{C}H_2$ is more stable than $CH_3CH_2 - \overset{+}{C}H_2$ (1° carbocation) because of resonance.

(D) Vinyl carbocation are less stable than normal carbocation $\underset{sp^2}{CH_2 = \overset{+}{C}H} < CH_3 - \overset{+}{C}H_2$

34.(AC) $+ 2\pi e^- \Rightarrow$ Aromatic

2-benzene ring, not fused $\Rightarrow$ aromatic

$8\pi e^- \Rightarrow$ not aromatic

$4\pi e^- \Rightarrow$ not aromatic

35.(BC) Two dipoles are not same in magnitude, hence they do not cancel each other.
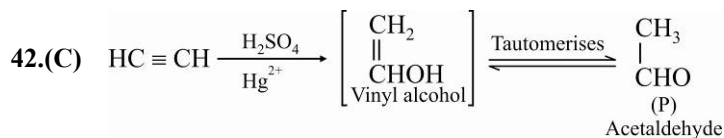
36.(C) Refer to explanation of Q.34

37.(C) More branching means lesser surface area which results in lesser molecular forces of attraction (Van der waals forces) and hence lower boiling point.

38.(C)

(A)   1-Chloro-1-methylcyclohexane   (B)

39.(C)
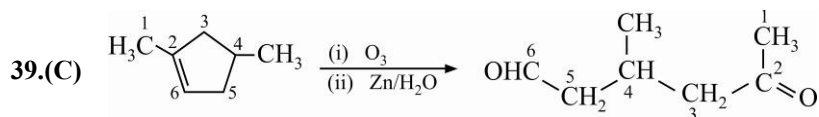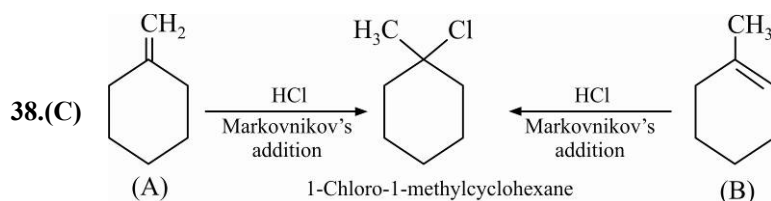
40.(C) $-CH_3$ group is o, p-directing. Because of crowding, no substitution occurs at the carbon atom between the two $-CH_3$ groups in m-Xylene, even though two $-CH_3$ groups activate that position.
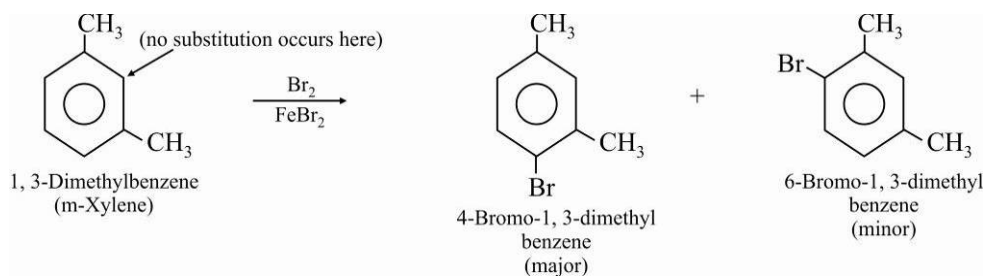

41.(D) The molecules which do not satisfy Huckel rule or $(4n + 2)\pi - \text{electron}$ rule are said to be non-aromatic. The compound (d) has total $4\pi e^-$. It does not follow $(4n + 2)$ rule. So it is non-aromatic compound. All other compounds (a, b, c) are planar and have $6\pi e^-$, so they are aromatic.

42.(C) $HC \equiv CH \xrightarrow[\text{Hg}^{2+}]{\text{H}_2\text{SO}_4} \begin{bmatrix} CH_2 \\ \parallel \\ CHOH \\ \text{Vinyl alcohol} \end{bmatrix} \xrightleftharpoons{\text{Tautomerises}} \begin{array}{c} CH_3 \\ | \\ CHO \\ (P) \\ \text{Acetaldehyde} \end{array}$
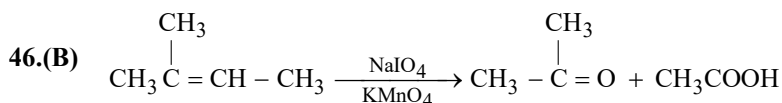
However, acetaldehyde does not give Victor Meyer test. It will give Tollen's test, Brady's test along with iodoform test.

43.(A) Maleic acid shows geometrical isomerism (Fumaric acid) and not optical isomerism.

44.(D)
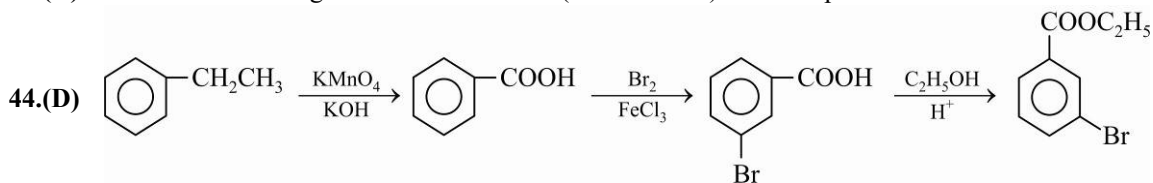
**45.(D)** The conformation (D) is most stable because of intermolecular H-bonding.

46.(B)

47.(B) Effect of substituents : Presence of electron withdrawing groups $(-NO_2, -X, -CN)$ increase the acidity of phenols while the presence of electron releasing groups $(-NH_2, -CH_3)$ decrease the acidity of phenols. Hence the order of decreasing acidity is : p-nitrophenol > phenol > p-cresol.

48.(A) Due to –I effect of F atom, CF_3 in benzene ring deactivates the ring and does not favour electrophilic substitution. While $-CH_3$ and $-OCH_3$ via hyperconjugation and resonance effect respectively favour electrophilic substitution in the benzene ring at 'ortho' and 'para' position. The +M effect of $-OCH_3$ is more than +H effect of $-CH_3$, therefore correct order for electrophilic substitution is (A).

49.(C) The branching of chain increases the octane number of a fuel. High octane number means better fuel.

50.(AD)
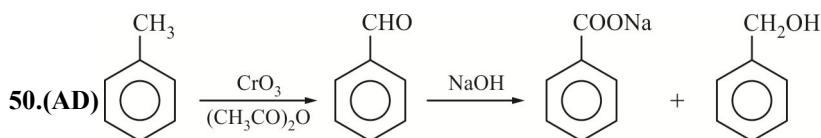
51.(6) One unhybridized orbital on each carbon involved in double bond and two on each carbon involved in triple bond.

52.(2)

53.(3)
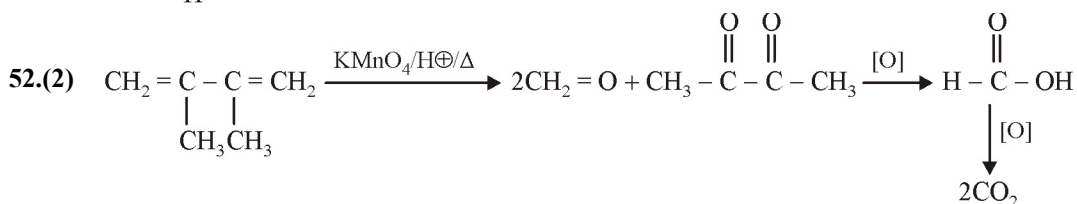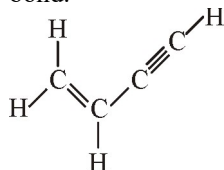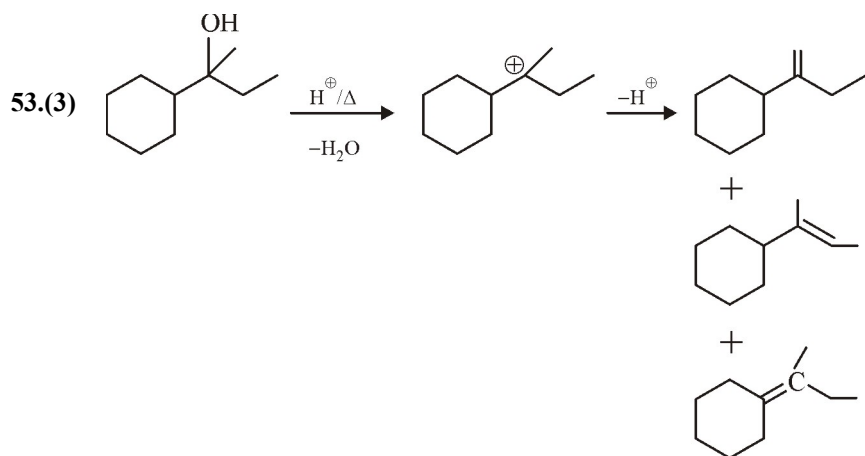
54.(4) The reaction involved is

55.(1)
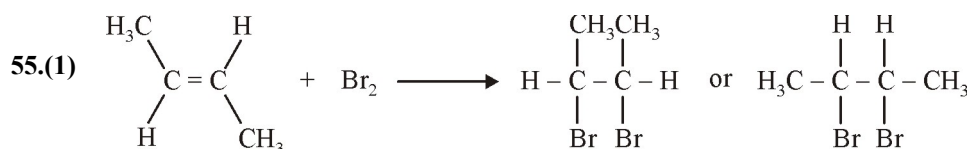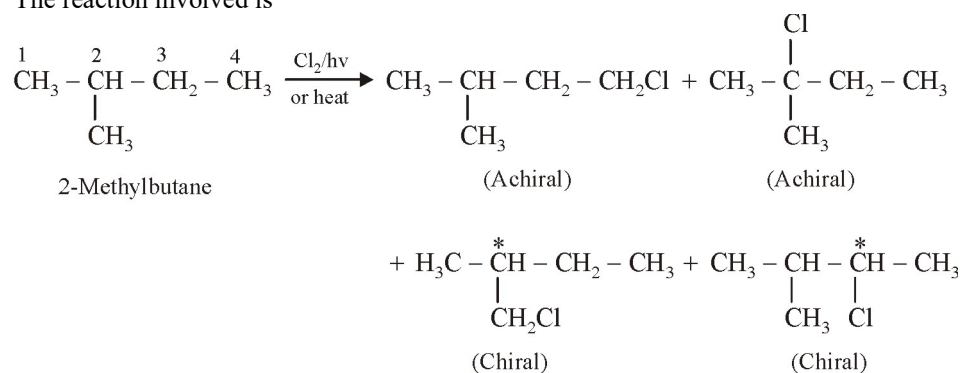
The compound obtained is a meso compound. Meso compounds are those which are superimposable on their mirror image even though they contain chiral centres.

Hint : Symmetric Trans compound on anti-addition gives meso compound.

56.(8)

Total = 2 + 4 + 1 + 1 = 8

57.(0) The reaction is

$$H_3C - CH = CH - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH - \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} - CH = CH - CH_3 \xrightarrow{O_3}$$

Zn/H$_2$O

$$H_3C - CH = O \quad + \quad O = CH - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = O$$
Achiral   Achiral

$$+ \quad O = CH - \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} - CH = O \; + \; CH_3 - CH = O$$
Achiral   Achiral

58.(3)

$$C - C \equiv C - C - C - C \xrightarrow{Li / Liq.NH_3} \underset{CH_3}{\overset{H}{>}} C = C \underset{H}{\overset{C_3H_7}{<}}$$

$$C - C \equiv C - \underset{\underset{C}{|}}{C} - C \xrightarrow{Li / Liq.NH_3} \underset{CH_3}{\overset{H}{>}} C = C \underset{H}{\overset{\overset{H}{\underset{}{C}}\overset{CH_3}{<}}{\underset{CH_3}{<}}}$$

$$C - C - C \equiv C - C - C \xrightarrow{Li / Liq.NH_3} \underset{C_2H_5}{\overset{H}{>}} C = C \underset{H}{\overset{C_2H_5}{<}}$$
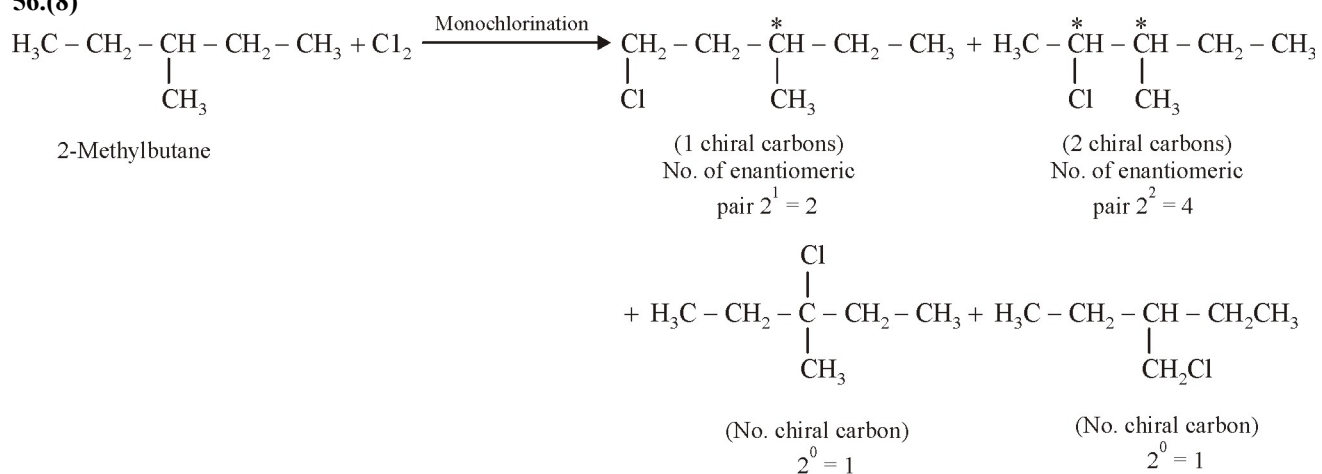
Total 3 trans alkene can be formed.

59.(3)

$$\xrightarrow{O_3/Zn} 2CH_3 - \overset{\overset{O}{\parallel}}{C} - CHO + CHO - CHO$$

$$\xrightarrow{O_3/Zn} CH_3 - \overset{\overset{O}{\parallel}}{C} - \overset{\overset{O}{\parallel}}{C} - CH_3 + 2CHO - CHO$$

3 different product can be formed

60.(4)

$$\text{Alkyne (given)} \xrightarrow[\text{H}_2]{\text{Lindlar cataylst}} \text{Alkene}$$

$$x \times 10 \qquad\qquad\qquad\qquad x \times 10 + 2$$

$$\text{(A)} \qquad\qquad\qquad\qquad\qquad \text{(B)}$$

(Molar mass = 36.5) $\Big|$ HCl

$$\text{(D)} \xleftarrow[\text{Wurtz reaction}]{\text{Na}} \text{(C)}$$

(Mol. mass = 86 given) $(x \times 10 + 2 + 36.5)$

Calculated mass of (D) $= 2(10 \times x + 2 + 36.5) - 2 \times 35.5 = 20x + 6$

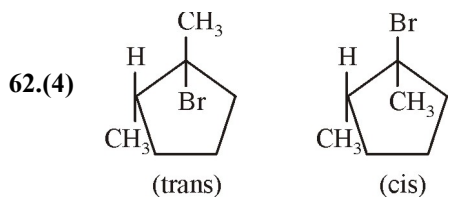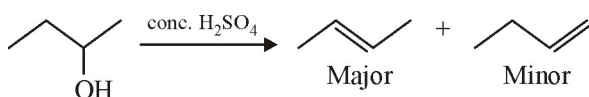(After Wurtz reaction, deduct two chlorine atoms)
Therefore, Mol. mass calculated = Mol. Mass given
$20x + 6 = 86$

$$x = \frac{86 - 6}{20} = 4$$

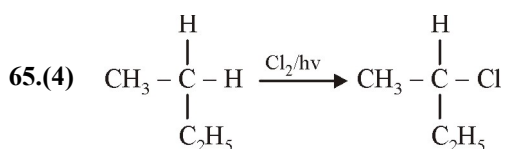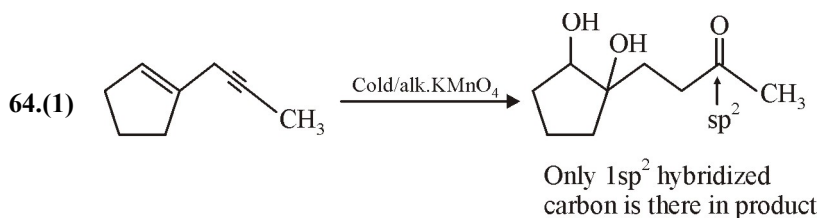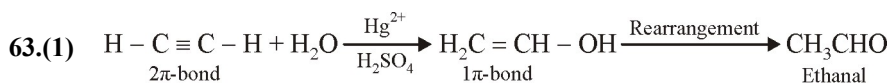Therefore, the alkyne is propyne with molecular mass 40.

61.(3) The total number of possible products is three 2-butene can exist in cis form as well as trans form so total 3 product could be possible.

62.(4)

(trans)   (cis)

Since both of them lack symmetry both have enantiomeric pair
Hence total no. of isomers are 4.
Note: Only 3° product is formed because Br$_2$ is highly selective.

63.(1)

$$H - C \equiv C - H + H_2O \xrightarrow[\text{H}_2\text{SO}_4]{\text{Hg}^{2+}} H_2C = CH - OH \xrightarrow{\text{Rearrangement}} CH_3CHO$$

2π-bond   1π-bond   Ethanal

64.(1)

Only 1sp^2 hybridized carbon is there in product

65.(4)

$$CH_3 - \underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}} - H \xrightarrow{Cl_2/hv} CH_3 - \underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{C}} - Cl$$
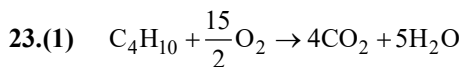
Minimum 4 carbons are required

Environmental Chemistry

21.(5) Water is considered as pure if its BOD is less than 5 ppm.

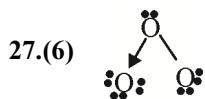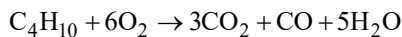**22.(5)** Fe is co-ordinated to 5 groups and 6th site is free to which CO links if present.

23.(1) $C_4H_{10} + \dfrac{15}{2}O_2 \rightarrow 4CO_2 + 5H_2O$ **24.(3)**   **25.(4)**   **26.(8)**

  $C_4H_{10} + 6O_2 \rightarrow 3CO_2 + CO + 5H_2O$

27.(6)   **28.(5)**

29.(5) CO_2 and other green house gases are methane, water vapour, nitrous oxide, CFC's and ozone.

30.(5)   **31.(7)**

32.(1) $Zn = 5\,ppm$

  $Fe = 0.2\,ppm$

  $= (5 \times 0.2) = 1$

33.(4) A-Hydroxyapatite $\left[3Ca_3(PO_4)_2 \cdot Ca(OH)_2 \right]$

  B-harder fluorapatite $\left[3(Ca_3PO_4) \cdot CaF_2 \right]$

  $|A - B| = 17(2) - 19(2) = 4$

34.(5) $CF_2Cl_{2(g)} \xrightarrow{\;UV\;} \overset{\bullet}{Cl}_{(g)} \quad + \quad \overset{\bullet}{C}F_2Cl_{(g)}$

  (Diamagnetic)   (P)   (P)

  $\overset{\bullet}{Cl} + O_{3(g)} \longrightarrow Cl\overset{\bullet}{O}_{(g)} \quad + \quad O_{2(g)}$

                (D)   (P)

  $Cl\overset{\bullet}{O} + O_{(g)} \longrightarrow \overset{\bullet}{Cl}_{(g)} \quad + \quad O_{2(g)}$

  (P)   (P)   (P)   (P)

35.(6) $N_2 + O_2(g) \xrightarrow{\;1400K\;} 2\overset{+2}{N}O(g)$

  $2NO_{(g)} + O_2(g) \longrightarrow 2\overset{+4}{N}O_2(g)$