DAV CENTENARY PUBLIC SCHOOL, PASCHIM ENCLAVE, NEW DELHI-87

Solutions to Final Step - B | Chemistry

The Solid State

1.(B) Crystalline solid's physical properties depends on the directions of measurement, so they are not isotropic.

2.(B) Quartz glass (SiO_2) is super cooled liquid, so it is amorphous.

3.(D) In anti-ferromagnetic substances magnets are aligned in opposite direction.

4.(A) Since glass is amorphous, its refractive index is same in all direction

5.(A) I_2 is non-polar molecule, so in solid state I_2 molecules are held by London dispersion forces.

6.(AC) Graphite and diamond both are network solid **7.(C)**

8.(C) Lattice point is occupied by one atom, ion or molecule. **9.(B)**

10.(B) For p-type semiconductor, that are formed by doping IIIA group element with IV group element in neutral form.

11.(B) In face centered unit cell, 8 tetrahedral void exist on the body diagonals.

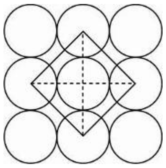
12.(AB) Schottky as well as Frenkel defects are observed in AgBr crystal.

13.(B) hcp and ccp both are closest packing, so, they are most efficient.

14.(C) The packing efficiency of BCC is 68%, so empty space is 32%. **15.(ABC)**

16.(AD) In NaCl and ZnS, both cation and anion has same coordination number

17.(C) For 2D packing coordination number is 4.



18.(D) Doping creates holes or extra electrons which are helpful for electrical conductivity.

19.(B) Electron rich impurity leaves extra electrons which creates n-type semi-conductor

20.(ACD) **21.(ABC)**

22.(A) In ferromagnetic solids, all magnets are aligned in same direction (direction of external magnetic field)

23.(A) In Frenkel defect, specie slips into void, so, it is also called dislocation defect.

24.(D) In ccp, 8 tetrahedral voids are inside unit cell, they are not shared by other unit cell.

25.(A) In fcc, spheres are in contact with each other at surface diagonal. Thus edge length $(a) = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r$

In bcc, spheres are in contact with each other at body diagonal. Thu edge length $(a) = \frac{4r}{\sqrt{3}}$

In simple cubic, spheres are in contact at edge thus a = 2r

26.(C) $2r_{Cs^+} + 2r_{Cl^-} = a\sqrt{3} \quad \Rightarrow \quad r_{Cs^+} + r_{Cl^-} = \frac{a\sqrt{3}}{2}$

27.(B) Let the fraction of M^{3+} is x

$$x \times 3 + (0.98 - x) \times 2 = 2 \;\Rightarrow\; 3x + 1.96 - 2x = 2 \;\Rightarrow\; x = 0.04 \qquad \text{So} \qquad \% = \frac{0.04}{0.98} \times 100 = 4.08\%$$

28.(D) For bcc, $\sqrt{3}a = 4r$ $\quad r = \frac{\sqrt{3}\times 351}{4} = 151.98 \approx 152$ pm

29.(D) For regular fcc with A at center and B at face centred point formula $\Rightarrow$ AB_3 losting one face point decreases efficiently 1/2of B. Thus formula $\Rightarrow AB_{3-\frac{1}{2}} = A_2B_5$

30.(A) The mass of one unit cell $= 4\times\frac{58.5}{6.02\times10^{23}}$ gm $\quad$ Thus number of unit cells $= \frac{6.02\times10^{23}}{4\times58.5} = 2.58\times10^{21}$ cells

31.(D) $r_+ + r_- = \frac{a}{2} = 254 \quad r_- = 254 - 110 = 144$ pm

32.(B) Packing efficiency of fcc and bcc are 74% and 68% respectively, so empty spaces are 26% and 32%.

33.(C) Number of atoms of Na(bcc type) = 2 and Number of atoms of Mg (fcc type) = 4

34.(A) Forumula: $X_{(8\times2/3)}Y_4 \equiv X_{4/3}Y \equiv X_4Y_3$

35.(D) The effective no of atoms in fcc are 4, so, volume $= \frac{4}{3}\pi r^3 \times 4 = \frac{16}{3}\pi r^3$

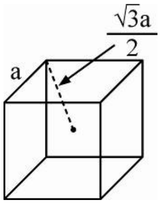
36.(B) Empirical formula = AB_3
Since corner contributes 1/8th part of ion and surface center contributes 1/2 part of ion to the unit cell.

37.(B)

38.(C) Packing efficiency of bcc lattice $= 68\%$

Hence, empty space $= 32\%$

39.(D) The distance between the body centered atom and one corner atom is $\frac{\sqrt{3}a}{2}$ i.e. half of the body diagonal.



40.(D) Diamond is like ZnS (Zinc blende).
Carbon forming ccp (fcc) and also occupying half of tetrahedral voids.

Total number of carbon atoms per unit cell $= \underset{\text{(Comers)}}{8\times\frac{1}{8}} + \underset{\text{(Free centrered)}}{6\times\frac{1}{2}} + \underset{\text{(Tetrahedral void)}}{4} = 8$

41.(A) Number of octahedral voids is same as number of atoms.

42.(D) Number of atoms in ccp $= 4 = O^{2-}$

Number of tetrahedral $= 2\times N = 2\times4$

Number of A^{2+} ions $= 8\times\frac{1}{4} = 2$

Number of octahedral volts = Number of B^+ ions $= N = 4$

Ratio, $\quad O^{2-} : A^{2+} : B^+ = 4 : 2 = 2 : 1 : 2$

Formula of oxide $= AB_2O_2$

43.(C) Packing fraction for a cubic unit cell is given by $f = \frac{z\times\frac{4}{3}\pi r^3}{a^3}$ where $a =$ edge length, $r =$ radius of cation and anion.

44.(C) For Simple cubic : $r = a/2$; $\quad$ For Body centered : $r = a\sqrt{3}/4$
r = radius of sphere

For Face centered : $r = \frac{a}{2\sqrt{2}}$ $\quad\therefore\quad$ Ratio of radii of the three will be $\frac{a}{2} : \frac{a\sqrt{3}}{4} : \frac{a}{2\sqrt{2}}$

45.(B) F-centres are the sites where anions are missing and instead electron are present. They are responsible for colours.

46.(7) For ZnS structure, $(Z_{\text{eff}}$ of $\text{ZnS} = 4)$

Number of $B^{\ominus} = 4$ /Unit cell (corner + face centre)

Number of $A^{\ominus} = 4$ /Unit cell (in alternate TVs)

Number of $B^{\ominus}$ ion removed

$= 4$ (Two from each face centre) $\times \frac{1}{2}$ (per face centre share) $= 2$

Number of $Br^{\ominus}$ ion left $= 4 - 2 = 2$ /unit cell

Number of Z^{2-} ions entering in place of $B^{\ominus} = 1$

[To maintain electrical neutrality, $2B^{\ominus} = 1\ Z^{2-}$]

Formula $= A_4B_2Z_1$

$\therefore \quad x + y + c = 4 + 2 + 1 = 7$

47.(2) Consider one face of unit cell as shown below:

Number of atoms on one face

$= 4(\text{corners}) \times \frac{1}{8}(\text{Per corner share}) + 1(\text{face center}) \times \frac{1}{2}(\text{face center share})$

$= \frac{1}{2} + \frac{1}{2} = 1/\text{ per face}$

Given number of atoms on all faces $= 6 \times 10^{30}$

Given number of atoms on one face $= \frac{1}{6} \times 6 \times 10^{30} = 10^{30}$ atoms

Number of unit cells at one face of crystal $= \frac{6 \times 10^{30}}{6} = 10^{30}$

So, number of unit cells at the edge of crystal $= \sqrt{10^{30}} = 10^{15}$

Now, edge length of unit cell $= \frac{4}{\sqrt{2}} \times 50$ nm

Edge length of cubical crystal $= \frac{4}{\sqrt{2}} \times 50 \times 10^{15}$ nm

So, area of face of crystal $= \left(\frac{4}{\sqrt{2} \times 50 \times 10^{15}}\right) \text{nm}^2$

$= \frac{16}{2} \times 25 \times 10^2 \times 10^{30} = 2 \times 10^{34}\,\text{nm}^2 = 2 \times 10^{-18+34}\,\text{m}^2 = 2 \times 10^{16}\,\text{m}^2$

$\therefore \quad A \times 10^{16}\,\text{m}^2 = 2 \times 10^{16}\,\text{m}^2$

$A = 2$

48.(2) Void volume = 0.22/unit volume of unit cell

$0.11A = 0.22 \Rightarrow A = 2$

49.(2) Figures A and D

50.(8) Diameter of $\text{Cs} = 2 \times 2.6 = 5.2\text{Å} = 5.2 \times 10^{-8}\,\text{cm}$

Number of atoms in 2.50 cm row $= \frac{2.50}{5.2 \times 10^{-8}} = 0.48 \times 10^8 = 4.8 \times 10^7$ Cs atoms

$\therefore$ Moles of Cs atoms $= \dfrac{4.8 \times 10^{7}}{6 \times 10^{23}} = 0.8 \times 10^{-16}$

$\therefore$ $x \times 10^{-17} = 8 \times 10^{-17} \Rightarrow x = 8$

51.(4) **a.** Number of X atoms $= 8 \times \dfrac{1}{8} = 1 / \text{unt cell}$

Number of Y atoms $= 1 / \text{unit cell}$

Number of O atoms $= 12 \times \dfrac{1}{4} = 3 / \text{unt cell}$

Formula is: $XYO_3 \Rightarrow X_aY_bO_c$

b. Number of O atoms missing from two edge centers

per unit cell $= 2 \times \dfrac{1}{4} = \dfrac{1}{2} / \text{unt cell}$

Number of O atoms left $= 3 - \dfrac{1}{2} = 2.5 / \text{unit cell}$

Formula is $XYO_{2.5} \Rightarrow X_2Y_2O_5 \Rightarrow X_xY_yO_z$

$\therefore$ The value of $(x+y+z)-(a+b+c) = (2+2+5)-(1+1+3) = 4$

52.(7) Let radius of hollow sphere $B = r$

$\therefore$ Edge length $(a) = 4r/\sqrt{3}$

Volume of unit cell $= a^3 = (4r/\sqrt{3})^2$

Volume of B unoccupied by A (having radius $= r/2$) in unit cell $= 2 \times \left[\dfrac{4}{3}\pi r^3 - \dfrac{4}{3}\pi\left(\dfrac{r}{2}\right)^3\right]$

Volume of B unoccupied by A

$$\therefore \quad \frac{\text{in unit cell}}{\text{volume of unit cell}} = \frac{\frac{4}{3}\pi \times \frac{7r^2}{8} \times 2}{\left(\frac{4r}{\sqrt{3}}\right)} = \frac{7\pi\sqrt{3}}{64}$$

$\therefore$ $A \times \dfrac{7\pi\sqrt{3}}{64} = \dfrac{7\pi\sqrt{3}}{64}$

$\therefore$ $A = 7$

53.(6) Statements (a), (b), and (c) are correct.
So total score $= 1 + 2 + 3 = 6$
Statement (a, b) are factual.

Statement (c): $\dfrac{r_{\oplus}}{r} = \dfrac{0.35}{0.95} = 0.368$

The radius ratio lies in the range of $0.225 - 0.414$, which corresponds to TV and the CN of TV = 4

54.(13) Single unit cell consists of three cubes

Number of Ba^{2+} ions = 2 per unit cell

Number of Y^{4-} ions = 1 per unit cell

Number of Cu^{2+} ions = 8 in each cube at corners

$= 8 \times 3$ (in three cubes) $\times \dfrac{1}{8}$ (per corner share)

= 3/unit cell

Number of o^{2-} ions = 10 (at edge center of cube 1)
+8 (at edge center of cube 2)
+10 (at edge center of cube 3)

$=28$ (edge center) $\times\frac{1}{4}$ (per edge center share) = 7/unit cell

Formula : $Y^{4+}_{(a)}Ba^{2+}_{(b)}Cu^{2-}_{(d)}$

$\Rightarrow$ $Y_1^{4+}Ba_2^{2+}Cu_3^{2-}O_7^{2-}$ [Total +ve charge (14) is equal to total –ve charge (14)]

$\therefore$ $a+b+c+d=1+2+3+7=13$

55.(8) On truncating tetrahedron, triangle is generated at each corner and hexagon on each face. Hence 4 triangular and 4 hexagonal faces.

56.(12) Next nearest neighbour of Zn_{+2} would be = no. of nearest surrounded zn_{2+} ions

Next nearest neighbour of S_2. Would be = no. of nearest S_2 ions = 12 (due to FCC)

And their number of neighbour ratio is 1 : 1 and that make Zn^{2+} neighbour are 12.

Theory of Solutions

1.(B) Consider

$$\begin{array}{lccc} & A_N \longrightarrow & \frac{N}{2}A^+ + & \frac{N}{2}A^- \\ & 1 & 0 & 0 \\ \text{After diss} & 1-\alpha & \frac{N}{2}\alpha & \frac{N}{2}\alpha \end{array}$$

Total moles after dissociation = $1-\alpha+N\alpha$

$$i=\frac{1-\alpha+N\alpha}{1} \quad \Rightarrow \quad \alpha=\frac{i-1}{N-1}$$

2.(C) Water solidifies first, and solute is left in liquid phase because, in general, solute's solubility is more in liquid phase.

3.(C) $\Delta T_f = K_f \cdot m \quad \Rightarrow \quad \frac{\Delta T_f}{m}=K_f$ Thus $\lim\limits_{m\to 0}\left(\frac{\Delta T_f}{m}\right)=K_f$

4.(C) Urea $\longrightarrow$ non-electrolyte NaCl $\longrightarrow$ Na^+Cl^- strong electrolyte

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$ strong electrolyte Since $\Delta T_f = i\,K_f \cdot m$, and $i_{Na_2SO_4}=3$,

$i_{NaCl}=2$, $i_{urea}=1$, the depression in freezing point is in ratio of $1:2:3$ for urea, NaCl and Na_2SO_4 solutions.

5.(D) Only solvent molecules can pass through the semi permeable membrane.

6.(BD) Ideal solution contains $\Delta V_{mix}=0$ and $\Delta H_{mix}=0$ Chlorobenzene + Bromobenzene $\Rightarrow$ ideal solution n-butyl chloride + n-butyl bromide $\Rightarrow$ ideal solutions.

7.(A) Osmotic pressure depends on concentration of solute.

8.(ACD) Addition of nonvolatile solute depresses the freezing point of solvent. For weak electrolyte, degree of dissociation increases on dilution or decreasing concentration of solution.

For solution formation $\Delta H_{sol}=\Delta H_{hyd}+$ lattice energy, if $|\Delta H_{hydr}|>$ lattice energy, heat is released when solution is formed. $\Delta S_{mix}>0$ for ideal and non-ideal solutions

9.(ABD) The solubility depends on temperature, nature of solute and nature of solvent. Pressure doesn't affect solubility of solid solutes.

10.(B) Going up in the atmosphere, pressure is decreased, it causes low concentration of oxygen in blood and tissues of people living at high altitude.

11.(A) $\Delta T_b = K_b \cdot m \quad \Rightarrow \quad K_b=\frac{\Delta T_b}{m}=\frac{K}{mol/kg}$ $\quad K_b = K\ mol^{-1}\ Kg$

12.(BCD) $\Delta T_f = K_f \cdot m$, the value of K_f is different for different solvent, so, depression in freeing point is not same.

Since $BaCl_2$ is strong electrolyte and CH_3COOH is weak electrolyte, $BaCl_2$ produces more concentration of particle in the solution. Thus osmotic pressure is maximum in the case of $BaCl_2$ solution and lowest for CH_3COOH solution. According to Raoult's Law : $p_A = x_A P_A^{\circ}$

13.(ACD) Both osmotic and atmospheric pressures have unit of pressure.

In reverse osmosis, solvent molecules pass through the semi-permeable membrane from higher concentration to lower concentration region. K_f depend on the nature of solvent.

Relative lowering of vapour pressure is the ratio of change in vapour pressure of solvent on addition of solute and vapour pressure of pure solvent. Thus it is unit-less.

14.(C) Since NaCl is strong electrolyte, its solution of all concentration has 100% dissociation of NaCl. So Van't Hoff factor is equal in each case.

15.(A) NaCl being nonvolatile, its addition reduces vapour pressure of water.

16.(A) When interaction between A and B stronger than any one $A - A$ or $B - B$, vapour pressure is less than the vapour pressure of anyone of pure A or pure B, so, it boils at highest temperature and called maximum boiling azeotrope.

17.(A) In acetone and methanol mixture, strong hydrogen bonds break between methanol molecules and weaker hydrogen bonds are formed. Thus it shows positive derivation and it boils at a temperature lesser than boiling point of any one of the component. It forms minimum boiling azeotrope.

18.(C) According to Henry's Law $p = K_H$ (solubility). Thus solubility decreases with increase in K_H value.

19.(AB) Solubility of gasses depends on nature of solvent, temperature and pressure.

20.(CD) For ideal solution, no azeotrope is possible and for these solutions $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$. **21.(A)**

22.(CD) Isotonic $\Rightarrow$ Same osmotic pressure
$\Rightarrow$ Same concentration
$\Rightarrow$ Same elevation and depression in boiling and freezing point.

23.(BC) Azeotrope mixtures have same composition in liquid and vapour phase.
$\Rightarrow$ Non-ideal solutions
Water + Nitric acid $\Rightarrow$ Non-ideal
Water + Ethanol $\Rightarrow$ Non-ideal

24.(AB) A solvent with non-volatile addition solute shows colligative properties.

25.(A) Osmotic pressure $\pi = i \times MRT$

Where, i = van't Hoff factor, M = Molarity ; R = constant, T = Temperature

For 0.500 M C_2H_5OH (aq), i = 1, thus $\pi_{C_2H_5OH}(aq) = 0.5RT$

For 0.100 $Mg_3(PO_4)_2(aq)$, i = 5 $[\because Mg_3(PO_4)_2 \rightleftharpoons 3Mg^{2+} + 2PO_4^{3-}]$

Thus, $\pi_{Mg_3(PO_4)_2}(aq) = 5 \times 0.1 \times RT = 0.5\ RT$ For 0.250 M KBr (aq), $i = 2\ [\because KBr \rightleftharpoons K^+ + Br^-]$

Thus, $\pi_{KBr}(aq) = 2 \times 0.250 \times RT = 0.5\ RT$ For 0.125M $Na_3PO_4(aq)$, $i = 4[\because Na_3PO_4 \rightleftharpoons 3Na^+ + PO_4^{3-}]$

Thus, $\pi_{Na_3PO_4}(aq) = 4 \times 0.125 \times RT = 0.5\ RT$

Hence, all solutions have same osmotic pressure at given temperature.

26.(B) Coolant is glycol $(C_2H_6O_2)$ and it is non-electrolyte.

$\Delta T_f = 2.8°C$

$$\Delta T_f = \frac{1000 K_f w_1}{m_1 w_2} \Rightarrow 2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$$w_1 = 93.33\,g$$

27.(C) 5.2 molal aqueous solution of CH_3OH suggests that 5.2 moles of CH_3OH are dissolved in 1000 g of water

$$n_1(CH_3OH) = 5.2\,;\; n_2(H_2O) = \frac{1000}{18} = 55.56 \qquad \therefore \qquad n_1 + n_2 = 5.20 + 55.56 = 60.76\text{ mol}$$

$$\therefore \qquad X_{CH_3OH} = \text{Mole fraction of } CH_3OH = \frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086$$

28.(A) van't Hoff factor (i) is related to degree of dissociation (α) as $\alpha = \frac{i-1}{n-1}$

Here, n the moles of an electrolyte (A – B) dissolved in a solvent

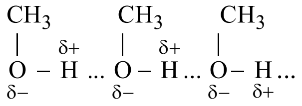
For A_xB_y $\qquad A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$ $\qquad$ Therefore, $\qquad \alpha = \frac{i-1}{(x+y-1)}$

29.(B) n-heptane and ethanol forms non-ideal solution. As a result, n-heptane - ethanol molecular interaction is very poor in comparison to ethanol-ethanol or n-heptanes, so, the resulting solution gives positive deviation from Raoult's law.

30.(B) Boiling point and freezing point depend on K_b (molal elevation constant) and K_f (molar depression constant) of the solvent respectively. Thus, equimolar solution (of the non – electrolyte), will have same boiling point and also same freezing point. $\Delta T_f = K_f \times \text{molality}$ and $\Delta T_b = K_b \times \text{molality}$

31.(B) Water and hydrochloric acid ; and water and nitric acid form miscible solution. They show negative deviation. In case of CH_3COCH_3 and $CHCl_3$. there is interaction between them, thus force of attraction between CH_3COCH_3 ……. $CHCl_3$ is larger than between $CHCl_3$ ….. $CHCl_3$ or CH_3COCH_3 … CH_3COCH_3 and thus, vapour pressure is less than expected – a negative deviation.

In case of CH_3OH, there is association by intermolecular H-bonding. When benzene is added to CH_3OH, H-bonding breaks and thus force of attraction between CH_3OH and benzene molecule is smaller than between CH_3OH or benzene molecules (in pure state). Vapour pressure of mixture is greater than expected - a positive deviation.



$$\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}} - \overset{\delta+}{H} \ldots \underset{\delta-}{\overset{\overset{CH_3}{|}}{O}} - \overset{\delta+}{H} \ldots \underset{\delta-}{\overset{\overset{CH_3}{|}}{O}} - \underset{\delta+}{H} \ldots$$

32.(D) **(A)** $p_A = X_A P_A^\circ$ True **(B)** $\pi = iMRT = MRT$ True [If van't Hoff factor, i = 1]

(C) $\pi \propto i$

Greater the value of i, larger is then value of π.

i, for $BaCl_2$ (strong electrolyte) is 3, [$BaCl_2 \rightleftharpoons Ba^{2+} + Cl^{-1}$ (2 ions)]

i for KCl is 2. [$KCl \rightleftharpoons K^+ + Cl^-$]

i for CH_3COOH lies between 1 and 2 because CH_3COOH is weak electrolyte.

i for sucrose is 1 as it is a non-electrocyte. Thus, i for $BaCl_2 > KCl > CH_3COOH >$ sucrose

(D) $\Delta T_f = K_f m$; K_f is dependent on solvent

Keeping concentration same, depression in freezing point is different for different solvent. Thus, freezing point of different solutions is different.

33.(C) $\Delta T_b = iK_bm$

For equimolal solutions, elevation of boiling point will be higher in case where solute undergoes dissociation i.e., $i > 1$.

34.(D) For an ideal solution, $\Delta S_{mix} > 0$ where ΔH_{mix}, ΔV_{mix} and $\Delta P = 0$.

35.(C) In case of dissociation, i is greater than 1 and in case of association i is less than 1.

36.(D) Addition of water to an aqueous solution of KI causes the concentration of the solution to decrease thereby increasing the vapour pressure. In the other three options the electrolytes undergo ionization, which leads to lowering of vapour pressure.

37.(D) The number of moles of ions produced by 1 mol of ionic compound $= i$

Applying, $\Delta T_f = i \times K_f \times m$

$$0.00732 = i \times 1.86 \times 0.002$$

$$\Rightarrow \quad i = \frac{0.00732}{1.86 \times 0.002} = 1.96 \approx 2$$

38.(D) Flow of water through a semipermeable membrane takes place both sides with unequal rates.

39.(C) Acetone in ethanol shows higher vapour pressure than the expected value.

40.(A) The osmotic pressure is a colligative property and it depends upon the number of moles of a solute.

Since $n_2 > n_1 > n_3$, therefore $p_2 > p_1 > p_3$.

41.(100) $80 = P°(0.8) \Rightarrow P° = 100$ torr.

42.(5) $P_s = \left(\frac{80}{100}\right)P°, w = ?$

$M_{solute} = 40, w = 114\text{ g}, M_{solvent} = 114$

$$\because \quad \frac{P° - P_s}{P_s} = \frac{w \times M_{solvent}}{M_{solute} \times W}$$

$$\text{or} \quad \frac{P° - (80/100)P°}{(80/100)P°} = \frac{w \times 114}{40 \times 57};$$

$$\therefore \quad w = 5\text{ g}$$

43.(80) Moles of $A = \frac{20}{40} \Rightarrow 0.5$;

Moles of $B = \frac{20}{80} \Rightarrow 0.25$

$$x_A = \frac{0.5}{0.5 + 0.25} = 0.67; \quad x_B = 0.33$$

$$P_{total} = P_A^o X_A + P_B^o X_B$$

$$\Rightarrow 100 \times 0.67 + 40 \times 0.33 \Rightarrow 80\text{ torr}$$

44.(125) $80.23 - 80.10 = 2.53 \times \left[\frac{0.64/x}{100} \times 10^3\right]$

$$x = 125$$

45.(8) ΔT_b (normal) $= K_bm = 2.53 \times 1 = 2.53$ K;

$$i = \frac{\Delta T_{b(obs)}}{\Delta T_{b(nor)}} = \frac{1.518}{2.53} = 0.6$$

$$i = 1 - \left(1 - \frac{1}{n}\right)\alpha; \quad \alpha = 0.8$$

$\Rightarrow \quad (.8 \times 10 = 8)$

46.(34) $\Delta H_{vap.} = \dfrac{M_{solvent} \times R \times T_{b(solvent)}^{o^2}}{1000 \times K_b}$

$\therefore \quad \Delta H_{vap.} = \dfrac{92 \times 8.314 \times (383.7)^2}{1000 \times 3.32} = 33.91 \text{ kJ / mol} = 34 \text{ kJ / mol.}$

47.(75)

$$\begin{array}{lcccccc} & XY_2 & \rightleftharpoons & X^{2+} & + & 2Y^- \\ \text{Initially} & 1 & & 0 & & 0 \\ \text{At equilibrium} & 1-\alpha & & \alpha & & 2\alpha \end{array}$$

Total no. of moles $= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}; \frac{1+2\alpha}{1} = \frac{164}{65.6}$$

$\therefore \quad \alpha = 0.75; \% \alpha = 75\%$

48.(160) Molality of solution should be same $m_1 = m_2$;

$$\frac{4}{60} \times \frac{1000}{96} = \frac{10}{M_B} \times \frac{1000}{90} \text{ or } M_B = 160$$

49.(3) $\Delta T_f = K_f \cdot m \Rightarrow 1.86 = K_f \times 1$

$\Rightarrow \quad K_f(H_2O) = 1.86$

For HCOOH; $0.02046 = 1.86 \times 0.01(1+\alpha)$; $\alpha = 0.1$; so $[H^+] = \alpha \Rightarrow 10^{-3}$; $pH = 3$

50.(4) $\Delta T_f = K_f \cdot m \cdot i$;

$$0.87 = 1.86 \times i \times \left(\frac{1}{345.5} \times \frac{1000}{25}\right); \quad i = 4$$

51.(2) $\dfrac{59.1}{760} = \left[\dfrac{0.01}{(52 \times 4 \times 17 + 96 + 35.5)}\right] \times \dfrac{1000}{25} \times 0.0821 \times 298(n)$

$\therefore \quad n = 2$

52.(8) $\dfrac{P° - P}{P} = \dfrac{n}{N} \Rightarrow \dfrac{W}{M \times N}$

$\Rightarrow \quad \dfrac{850 - 844.9}{844.9} = \dfrac{2 \times 76}{M \times 100}$

$M \approx 252; \; n = \dfrac{252}{32} \approx 8$

$\therefore$ atomicity of sulphur is 8.

53. (300) Let n_B mole of B present in 1 mole of mixture that has been vaporized. Thus, $y_B = \dfrac{n_B}{1}$

Mole fraction of B in the remaining liquid phase will be $x_B = \dfrac{1 - n_B}{1}$

$$x_B = \frac{P - P_T^o}{P_B^o - P_T^o} \qquad \ldots(1) \qquad [\because P = P_t^o + (P_B^o - P_T^o)\, x_B]$$

and $y_B = \frac{P_B}{P} \Rightarrow \frac{P_B^o x_B}{P}$ ...(2)

After substitution of values of x_B and y_B in (1) and (2)

we get $1 - n_B = \frac{P - P_T^o}{P_B^o - P_T^o}$ ...(3)

and $n_B = \frac{(1 - n_B) P_B^o}{P}$ ...(4)

or $n_B = \frac{P_B^o}{P + P_B}$

so $1 - \frac{P_B^o}{P + P_B} = \frac{P - P_T^o}{P_B^o - P_T^o} \Rightarrow P = \sqrt{P_B^o \cdot P_T^o} = \sqrt{100 \times 900} \Rightarrow 300$ torr

Electrochemistry

1.(C) $\Delta G = -nFE_{cell}$; E_{cell} is intensive property but Gibb's free energy is extensive **2.(B)**

3.(D) Inert electrode doesn't participate in the chemical reaction, they provides only surface to conduct current.

4.(C) Any spontaneous redox reaction can be reversed only if potential difference applied is more than the cell potential. Thus, for electrolytic cell $E_{cell} < E_{ext.}$

5.(C) Conductivity depends on ion and solvent interaction, if it is more solvated, its movability is decreased and its conductivity is reduced.

6.(B) The oxidation potentials of given electrodes

$$E^\circ_{Cl^-/Cl_2} = -1.36\,V; \qquad E^\circ_{Cr/Cr^{3+}} = 0.74\,V$$

$$E^\circ_{Cr^{3+}/Cr_2O_7^{2-}} = -1.33\,V; \quad E^\circ_{Mn^{2+}/MnO_4^-} = -1.51\,V$$

Oxidation potential shows the tendency of losing electrons, so, most positive value indicates strongest reducing agent.

7.(C) Reduction potential indicates the tendency of gaining electrons, so, most positive value implies strongest oxidising agent. Thus, MnO_4^- is strongest oxidising agent.

8.(B) Reducing power follows the order of oxidation potential.

$$E^\circ_{Mn^{2+}/MnO_4^-} < E^\circ_{Cl^-/Cl_2} < E^\circ_{Cr^{3+}/Cr_2O_7^{2-}} < E^\circ_{Cr/Cr^{3+}}$$

Thus order of reducing power is $Mn^{2+} < Cl^- < Cr^{3+} < Cr$

9.(D) The reduction reaction with most positive reduction potential produces most stable ions. Thus Mn^{2+} is most stable.

10.(A) The oxidation reaction with most positive oxidation potential produces most stable species. Thus, Cr^{3+} is most stable since $E^\circ_{Cr/Cr^{3+}} = +0.74$ V (most positive).

11.(C) The oxidation state of Al in Al_2O_3 is $+3$; to reduce it, $Al^{3+} + 3e^- \rightarrow Al$

Thus, 3 moles or 3F charge is required to get one mole of Al.

12.(D) Cell constant, $G^* = \frac{\ell}{A}$, depends on cell dimensions. Thus, it is constant for a given cell.

13.(A) In discharging of lead storage battery. Pb is oxidized to Pb^{2+} and PbO_2 reduced to Pb^{2+} and deposited as $PbSO_4$ on respective electrodes. On charging, reverse reaction takes place, so, $PbSO_4$ on anode is converted into Pb.

14.(B) Since NH_4OH is weak electrolyte, its limiting molar conductivity can be calculated by using Kohlrausch law.

$$\Lambda^o_{m\,(NH_4OH)} = \Lambda^o_{m\,(NH_4Cl)} + \Lambda^o_{m\,(NaOH)} - \Lambda^o_{m\,(NaCl)}$$

15.(D) At anode, oxidation takes place, so either water (H_2O) or Cl^- can oxidised at anode, but $E^\circ_{ox:(H_2O)} > E^\circ_{ox:(Cl^-)}$, so water is reduced as expected. This is valid for dilute solution of NaCl. But in slightly concentrated solution Cl^- is oxidised and Cl_2 is obtained at anode. This is so because over potential for water is very high.

16.(BD) Since reduction potential of Cu^{2+} is more than H^+/H_2, Cu^{2+} is better oxidizing agent. Cu^{2+}/Cu can accept electrons from H_2 and oxidizes it into H^+ ions. Thus, it cannot replace H_2 from acidic solution.

17.(AC) In acidic solution, H^+ ion concentration is significant, so H^+ ions reduced to H_2. At anode, water or SO_4^{2-} can be oxidized but $E^\circ_{H_2O/O_2} > E^\circ_{SO_4^{2-}/S_2O_8^{2-}}$. Thus H_2O is oxidized at anode.

18.(BC) At equilibrium, $E_{cell} = 0 = E^\circ_{cell} - \frac{2.303RT}{2F}\log K_C \quad \Rightarrow \quad \frac{2.303RT}{2F}\log K_C = 1.1$

The value of $\frac{2.303RT}{F} = 0.059$ at 25°C Thus $\log K_C = \frac{2.2}{0.059}$

19.(AB) Conductivity is defined for unit cell constant, so it doesn't depend on cell constant.

20.(AC) H_2O is very weak electrolyte, so its limiting molar conductivity can be calculated by strong acid, strong base and their salts.

21.(AC) Platinum is inert electrode, so it doesn't participate in the redox reaction. Cu^{2+} is reduced at cathode since its reduction potential is maximum. But at anode, water is oxidised to give oxygen.

22.(AB) Since $E^\circ_{Cu^{2+}/Cu} = 0.34V$, it is greater than reduction potential $(-0.83V)$ of water, so Cu^{2+} is reduced at cathode. The oxidation potential of water $(-1.23V)$ is less than oxidation potential of Cu($E^\circ_{Cu/Cu^{2+}} = -0.34V$). Thus, again Cu is oxidized at anode.

23.(AB) Conductance $G = \frac{1}{R} = \frac{1}{\rho}\times\frac{A}{\ell} = \kappa\times\frac{A}{\ell} \Rightarrow \kappa = \frac{1}{R}\times\frac{\ell}{A} = \frac{G^*}{R}$

24.(AC) Molar conductivity depends on temperature and concentration of electrolyte.

25.(BC) Cathode $\longrightarrow$ Reduction reaction ; $Cu^{2+} \xrightarrow{2e^-} Cu$

Anode $\longrightarrow$ Oxidation reaction ; $Mg \longrightarrow Mg^{2+} + 2e^-$

26.(A) For 0.2 M solution, $R = 50\,\Omega$

$\kappa = 1.4 Sm^{-1} = 1.4 \times 10^{-2} Scm^{-1}$

The resistivity of the solution is related to specific conductance by $\rho = \frac{1}{\kappa} = \frac{1}{1.4\times10^{-2}}\ \Omega\ cm$

It is known that $R = \rho\frac{\ell}{a} \Rightarrow \frac{R}{\rho} = \frac{\ell}{a} \Rightarrow \quad \frac{\ell}{a} = R\times\frac{1}{\rho} = 50\times1.4\times10^{-2} cm$

For 0.5Msolution, $R = 280\ \Omega$; $\kappa = ?$

$$\frac{\ell}{a} = 50 \times 1.4 \times 10^{-2}\,\text{cm}$$

The specific conductance of the solution is given by $\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{\ell}{a}$

$$\kappa = \frac{1}{280} \times 50 \times 1.4 \times 10^{-2} = 2.5 \times 10^{-3}\ \text{S cm}^{-1}$$

Now, the molar conductivity of the solution is given by

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{2.5 \times 10^{-3} \times 1000}{0.5} = 55\,\text{cm}^2\text{mol}^{-1} = 5 \times 10^{-4}\,\text{S}\,\text{m}^2\text{mol}^{-1}$$

Hence, the molar conductivity of 0.5 M solution of the electrolyte is $5 \times 10^{-4}\ \text{S m}^2\text{mol}^{-1}$

27.(C) Debye – Huckel Onsager equation can be written as $\lambda_c = \lambda_\infty - (B)\sqrt{C}$

Where, λ_c = Molar conductivity of the solution at centain concentration

λ_∞ = Limiting molar conductivity; C = Concentration

B = Constant that depends on temperature, charges on the ions and dielectric constant as well as viscosity of the solution

28.(B) Higher the position of element in the electrochemical series, more difficult is the reduction of its cation. Thus, among all the given elements, only calcium on electrolysis yields H_2 gas at cathode while other yields pure metals at cathode. In case of Ca^{2+} ion, water is reduced in preference to calcium.

For Cr: At cathode, $Cr^{3+} + 3e^- \longrightarrow Cr$

For Ag: At cathode, $Ag^+ + e^- \longrightarrow Ag$

For Cu: At cathode, $Cu^{2+} + 2e^- \longrightarrow Cu$

For Ca^{2+}: At cathode, $H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$

29.(A) $Mn^{2+} + 2e^- \longrightarrow Mn, E° = -1.18\ V$ **. . . .(i)**

$2(Mn^{3+} + e^- \longrightarrow Mn^{2+}),\ E° = +1.51V$ **. . . .(ii)**

Subtracting Eq. (ii) from Eq. (i), we get : $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$

$E° = -1.18 - (+1.51) = -2.69V$

Since, the value of E° is –ve, therefore the reaction is non-spontaneous.

Alternate Method :

$Mn^{2+} + 2e^- \longrightarrow Mn,\ E° = -1.18V$ **. . . .(i)**

$\Delta G° = -nFE°$ [Here, n = number of e^- involved in the reaction]

$\Delta G_1^\circ = -2F(-1.18) = 2.36\ F$

$2M^{3+} + 2e^- \longrightarrow 2Mn^{2+},\ E° = +1.151\ V$ **. . . .(ii)**

$\Delta G_2^\circ = -2F[1.51] = -3.02\,F$

Subtracting Eq. (ii) from Eq. (i), we get : $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ [n = 2]

$\Delta G_3^\circ = -2FE°$

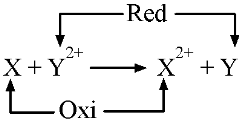
$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ = 5.38\,F \Rightarrow -2FE° = 5.38\ F \Rightarrow E° = -2.69\ V$

30.(D) Higher the SRP (Standard Reduction Potential) stronger is the oxidizing agent Among the given, electrode potential $E_{MnO_4^-/Mn^{2+}}$ is highest. Hence, MnO_4^- is the strongest oxidizing agent.

31.(D) A cell reaction is spontaneous, if $\Delta G^\circ < 0$,

Since $\Delta G^\circ = -\, nFE^\circ_{cell}$

Thus, $E^\circ_{cell} > 0,\ E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$



(a) X = Ni, Y = Fe

$Ni + Fe^{2+} \longrightarrow Ni^{2+} + Fe$

$E^\circ_{Ni/Ni^{2+}} = +\,0.23V$; $E^\circ_{Fe^{2+}/Fe} = -\,0.44V$

Thus, $E^\circ_{cell} = E^\circ_{Ni/Ni^{2+}} + E^\circ_{Fe^{2+}/Fe} = -\,0.21\ V$

$E^\circ_{cell} < 0 \Rightarrow$ Reaction is non-spontaneous.

(b) X = Ni, Y = Zn

$Ni + Zn^{2+} \longrightarrow Ni^{2+} + Zn$

$E^\circ_{Ni/Ni^{2+}} = 0.23\ V$; $E^\circ_{2n^{2+}/Zn} = -\,0.76V$ $\quad\therefore\quad$ $E^\circ_{cell} = 0.23 + (-0.76) = -\,0.53\ V$

$E^\circ_{cell} < 0 \Rightarrow$ Non – spontaneous reaction.

(c) X = Fe, Y = Zn

$Fe + Zn^{2+} \longrightarrow Fe^{2+} + Zn$

$E^\circ_{cell} = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Zn^{2+}} + Zn$; $E^\circ_{cell} = E^\circ_{Fe/Fe^{2+}} + E^\circ_{Zn^{2+}/Zn} = 0.44 - 0.76 = -\,0.32\ V$

$E^\circ_{cell} < 0 \Rightarrow$ Non – spontaneous reaction.

(d) X = Zn, Y = Ni

$Zn + Ni^{2+} \longrightarrow Zn^{2+} + Ni$

$E^\circ_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{Ni^{2+}/Ni} = 0.76 - 0.23 = 0.53\ V$

$E^\circ_{cell} > 0 \Rightarrow$ Spontaneous reaction

32.(C) For hydrogen electrode $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{(\rho_{H_2})^{1/2}}{[H^+]}$$

Here, n = number of electrons involved in the reaction $E = E^\circ - \frac{0.0591}{1}\log\frac{(\rho H_2)^{1/2}}{[H^+]}$

$$E = -\,0.0591\log\frac{(\rho_{H_2})^{1/2}}{[H^+]} \qquad [\because\ E^\circ = 0 \text{ for H – electrode}]$$

$\Rightarrow$ E will be –ve when $\frac{(\rho_{H_2})^{1/2}}{[H^+]}$ is + ve. i.e. $(\rho_{H_2})^{1/2} > [H^+]$

	p_{H_2}	$[H^+]$	$\frac{(pH_2)^{1/2}}{[H^+]}$	E_{red}
(a)	1 atm	2.0 M	0.25	+ ve
(b)	1 atm	1.0 M	1.0	0
(c)	2 atm	1.0 M	2.0	–ve
(d)	2 atm	2.0 M	0.50	+ ve

33.(D)

34.(C) $\frac{2}{3}Al_2O_2 \longrightarrow \frac{4}{3}Al + O_2$

Thus, $\frac{2}{3} \times 3(O^{2-})$ i.e., $2O^{2-} \longrightarrow O_2 + 4e^{-1}$

$\Delta G = +966 \text{ kJ mol}^{-1} = 966 \times 10^3 \text{ J mol}^{-1}$

$\Delta G = -nFE_{cell}$

$966 \times 10^3 = -4 \times 96500 \times E_{cell}$ and $E_{cell} = 2.5V$

35.(C) It is given that,

$Fe^{3+} + 3e^- \longrightarrow Fe,\ E^\circ_1 = -0.036\text{ V}$ **....(i)**

$Fe^{2+} + 2e^- \longrightarrow Fe,\ E^\circ_2 = -0.439$ **....(ii)**

We need to calculate $Fe^{3+} + e^- \longrightarrow Fe^{2+},\ E^\circ_3 = ?$ **....(iii)**

Equation (iii) can be obtained by subtracting Eq. (ii) from (i) but E_0 being an intensive property, cannot be calculated by this way. In order to calculate E°_3, concept of ΔG° is used

ΔG°_1 for Eq. (i) is given by $\Delta G^\circ_1 = -3 \times F \times (-0.036) \Rightarrow \Delta G^\circ_1 = +0.108\text{ F}$

ΔG°_2 for Eq. (ii) is given by $\Delta G^\circ_3 = -2 \times F \times (-0.439) \Rightarrow \Delta G^\circ_2 = 0.878F$

ΔG°_3 for Eq. (iii) is given by $\Delta G^\circ_3 = -1 \times F \times E^\circ_3$

$\Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2 \Rightarrow \quad -1 \times F \times E^\circ_3 = 0.108\text{ F} - 0.878F \Rightarrow E^\circ_3 = 0.770V$

36.(A) $Cr \mid Cr^{3+}\ (0.1\text{ M}) \parallel Fe^{2+}\ (0.01M) \mid Fe$

Oxidation half cell $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$ Reduction half cell $[Fe^{2+} + 2e^- \longrightarrow Fe] \times 3$

Net cell reaction : $2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe;\ n = 6$

$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red} = 0.72 - 0.42 = 0.30\text{ V}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} = 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3} = 0.30 - \frac{0.0591}{6}\log\frac{10^{-2}}{10^{-6}}$$

$$= 0.30 - \frac{0.0591}{6}\log 10^4 = 0.2606\text{ V}$$

37.(A) Molar conductivity of aqueous CH_3COOH solution can be calculated using Kohlraush's law:

$\lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COONa} + \lambda^\circ_{HCl} - \lambda^\circ_{NaCl}$

Hence, for determining the molar conductivity of CH_3COOH solution, λ°_{NaCl} is required.

38.(C) Cell is completely discharged. It means equilibrium gets established, $E_{cell} = 0$

$Zn \mid Zn^{2+}(1M) \parallel Cu^{2+}\ (1M) \mid Cu$

Cell reaction : $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

We know, $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log K_{eq}$

$$E^{\circ}_{cell} = \frac{0.0591}{n}\log K_{eq} \text{ or } 1.10 = \frac{0.0591}{2}\log K_{aq}$$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \text{antilog } \frac{2.20}{0.0591} = \text{antilog } 37.3$$

39.(D) **For 0.1 M solution** $R = 100\ \Omega$

$$\kappa = \frac{1}{R}\left(\frac{\ell}{a}\right)$$

$$\frac{\ell}{a} \text{ (cell constant)} = 1.29 \times 100 \text{ m}^{-1}$$

For 0.2 M solution

Given, $R = 520\Omega$; $C = 0.2\,M$

μ (molar conductivity) = ?

Molar conductivity, $\Lambda_m = \frac{\kappa \times 1000}{M}$ [κ can be calculated as $\kappa = \frac{1}{R}\left(\frac{\ell}{a}\right)$, now cell constant is known]

Hence, $\Lambda_m = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6} m^3 = 12.4 \times 10^{-4}\ Sm^2\ mol^{-1}$

40.(D) According to Kohlrausch's law [NaOAc = $CH_3\overset{\overset{O}{||}}{C}-O^{-}Na^{+}$]

$$\lambda^{\circ}_{CH_3COOH} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+} \quad \textbf{...(i)} \quad \text{and} \quad \lambda^{\circ}_{HCl} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} \quad \textbf{...(ii)}$$

$$\lambda^{\circ}_{CH_3COONa} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{Na^+} \quad \textbf{...(iii)}$$

Thus, on adding Eqs, (ii) and (iii), if $\lambda^{\circ}_{Na^+}$ and λ°_{HOAc}. Thus, additional value required is λ°_{NaCl}

41.(D)

$$\begin{aligned}
&AgI(s) + e^{-} \rightleftharpoons Ag(s) + I^{-}\ ;\ E^{\circ}_1 = -\ 0.152\\
&\underline{Ag(s) \longrightarrow Ag^{+} + e^{-}\ ;\ E^{\circ}_2 = -\ 0.8}\\
&AgI(s) \longrightarrow Ag^{+} + I^{-}\ ;\ E^{\circ} = -0.952\\
&\qquad\qquad\qquad [E^{\circ} = E^{\circ}_1 + E^{\circ}_2]
\end{aligned}$$

$$E^{\circ}_{cell} = \frac{0.059}{n}\log K_{sp}$$

$$-\ 0.952 = \frac{0.059}{1}\log K_{sp} \text{ and } \log K_{sp} = \frac{-0952}{0.059} = -\ 16.135$$

42.(C) CN^{-} is better complexing agent (C) as well as a reducing agent (A)

Thus, properties (A) and (C) are shown by it.

Property (C) : $Ni^{2+} + 4CN^{-} \longrightarrow [Ni(CN)_4]^{2-}$

Property (A) : $\underset{II}{CuCl_2} + 5KCN \longrightarrow K_3[\underset{I}{Cu}(CN)_4] + \frac{1}{2}(CN)_2 + 2KCl$

[CN reduces Cu^{2+} to Cu^{+}]

43.(B) Any cell (like fuel cell), works when potential difference is developed

44.(C) $Zn(s) + 2H^{+} \longrightarrow Zn^{2+}(aq) + H_2(g)$

Reaction quotient, $Q = \dfrac{[Zn^{2+}]}{[H^+]^2}$ Corresponding cell is $\underset{\text{Anode}}{\overset{}{Zn}} \mid \underset{-}{Zn^{2+}}(C_1) \parallel H^+(aq) \mid \underset{\text{Cathode}}{\overset{+}{Pt(H_2)}}$

And $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{2}\log K = E^\circ_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Zn^{2+}]}{[H^+]^2} = E^\circ_{cell} + \dfrac{0.0591}{2}\log\dfrac{[H^+]^2}{[Zn^{2+}]}$

If H_2SO_4 is added to cathodic compartment, then Q decreases (due to increase in H^+).
Hence, equilibrium is displaced towards right and E_{cell} increases.

45.(B) LHS half cell : $\underset{p_1}{H_2(g)} \longrightarrow 2H^+\ (1M) + 2e^-$

RHS half cell :

$$\begin{array}{l} 2H^+(1M) + 2e^- \longrightarrow H_2(g) \\ \hline \underset{p_1}{H_2(g)} \longrightarrow \underset{p_2}{H_2(g)} \\ \hline \end{array}$$

$E^\circ_{cell} = 0.00\,V,\ K = \dfrac{p_1}{p_2},\ n = 2$

$E_{cell} = E^\circ_{cell} - \dfrac{RT}{nF}\log_e K = 0 - \dfrac{RT}{2F}\log_e\dfrac{p_2}{p_1} \Rightarrow E_{cell} = \dfrac{RT}{2F}\log_e\dfrac{p_1}{p_2}$

46.(C) The oxidation reaction is $\underset{0.1\,mol}{\overset{+6}{Mn}O_4^{2-}} \longrightarrow \overset{+7}{Mn}O_4^- + \underset{0.1\,mol}{e^-}$

$Q = 0.1 \times F = 0.1 \times 96500\,C = 9650\,C$

47.(D) According to Faraday's second law, $\dfrac{W_{Ag}}{E_{Ag}} = \dfrac{W_{O_2}}{E_{O_2}}$ or $\dfrac{W_{Ag}}{108} = \dfrac{\frac{5600}{22400}\times 32}{8}$ or $\dfrac{W_{Ag}}{108} = \dfrac{8}{8}$

$\Rightarrow \quad W_{Ag} = 108\,g$

48.(A) Degree of dissociation $(\alpha) = \dfrac{\text{Molar conductivity at conc. c}\left(\Lambda^c_m\right)}{\text{Molar conductivity at infinite dilution}\left(\Lambda^\infty_m\right)}$

$\alpha = \dfrac{9.54\,\Omega^{-1}\,cm^2\,mol^{-1}}{238\,\Omega^{-1}\,cm^2\,mol^{-1}} = 0.04008 = 4.008\%$

49.(D) $\underset{1\,atm}{H_2} \longrightarrow \underset{10^{-10}}{2H^+} + 2e^- \quad \Rightarrow \quad E_{H_2/H^+} = 0 - \dfrac{0.059}{2}\log\dfrac{\left(10^{-10}\right)^2}{1} \quad \Rightarrow \quad E_{H_2/H^+} = +0.59\,V$

50.(D) $Mn^{2+} + 2e^- \rightarrow Mn;$ $E^\circ = -1.18\,V$

$2Mn^{2+} \rightarrow 2Mn^{3+} + 2e^-;$ $E^\circ = -1.51\,V$

For the cell :

$3Mn^{2+} \rightarrow Mn + 2Mn^{3+};$ $E^\circ = -2.69\,V$

Since the E° value is negative, so the process is non-spontaneous.

51.(A) More negative the value of reduction potential, stronger will be the reducing agent. More positive value of reduction potential shows good oxidising properties thus strongest oxidising agent is F_2.

52.(C) As the electrode potential drops, reducing power increases. So, $Z(-3.0\,V) > X(-1.2\,V) > Y(+0.5\,V)$

53.(C) Since the reduction potential of Fe^{3+}/Fe^{2+} is greater than that of I_2/I^-, Fe^{3+} will be reduced and I^- will be oxidised.

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

54.(A) Strong electrolytes are completely ionised at all concentrations. On increasing dilution the number of ions remains the same but the distance between ions increases hence ionic mobility increases and the equivalent conduction increases.

55.(B) At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated.

Hence $\Lambda^{\circ}_{Al_2(SO_4)_3} = \Lambda^{\circ}_{Al^{3+}} + \Lambda^{\circ}_{SO_4^{2-}}$

56.(A) $\left[Fe(CN)_6\right]^{3-} \rightarrow \left[Fe(CN)_6\right]^{4-}$, $E^{\circ} = +0.35\,V$

$Fe^{3+} \rightarrow Fe^{2+}$; $E^{\circ} = +0.77\,V$

Higher the $+ve$ reduction potential, stronger will be the oxidising agent. Oxidising agent oxidises other compounds and get itself reduced easily.

57.(B) If mercury is used as cathode H^+ ions are not discharged at mercury cathode because mercury has a high hydrogen overvoltage. Na^+ ions are discharged at the cathode in preference to H^+ ions, yielding sodium, which dissolves in mercury to form sodium amalgam.

At cathode : $Na^+ + e = Na$

58.(A) Conductivity of heat in metals is due to the presence of free electrons, which move due to increase in temperature.

59.(B) A cation with maximum value of standard reduction potential, has the strongest oxidising power.

60.(B) $\left(Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)\right)$

2 Faraday gives 1 mole of Cu.

Weight of deposited Cu = 63.5 g

61.(20) 1 mole Mn_3O_4 lose $\left(6 - \frac{3}{8}\right) \times 3 = 10\,\text{mole}$

e^-; so total charge required $= 2 \times 10 \Rightarrow 20\,F$

62.(75) Initial moles of $Cr^{3+} = 0.25 \times 0.2 \Rightarrow 0.05$;

Final moles of $Cr^{3+} = 0.25 \times 0.1 \Rightarrow 0.025$

Moles of Cr^{3+} reduced, $0.05 - 0.025 \Rightarrow 0.025$;

$\therefore$ eq. of Cr^{3+} reduced, $0.025 \times 3 = \frac{t \times 96.5}{96500}$;

$\Rightarrow t = 75\,\text{sec}$

63.(3) $3.05 = \frac{114.8}{n} \times \frac{3.2 \times 40 \times 60}{96500} \quad \therefore \quad n = 3$

64.(6) $\frac{W}{M} \times n = \frac{I \times t}{96500}$; $\frac{0.838}{184} \times n = \frac{40 \times 60 \times 0.1}{96500} \Rightarrow n = 6$

65.(3) The cell reaction is

$$H_2(g) + I_2(s) \rightleftharpoons 2H^+(aq) + 2I^-(aq)$$

$$0.7714 = 0.535 - \frac{0.0591}{2} \log \frac{[H^+]^2[I^-]^2}{P_{H_2}} \Rightarrow pH = 3$$

66.(39) Conductance $(G) = \frac{1}{2} \Rightarrow \frac{1}{300}$

$\because \quad \kappa = G\left(\frac{\ell}{A}\right)$

Cell constant $\left(\frac{\ell}{A}\right) = \frac{0.013}{1} \times 300 = 3.9\,\text{cm}^{-1}$

$\Rightarrow \quad (3.9 \times 10 = 39)$

67.(50) $\wedge_{eq} = \frac{150}{3} = 50\,\text{scm}^2\text{eq}^{-1}$

68.(50) $\Lambda_m^{\infty}(\text{NaBr}) = \Lambda_m^{\infty}(\text{NaCl}) + \Lambda_m^{\infty}(\text{KBr}) - \Lambda_m^{\infty}(\text{KCl})$

$\lambda_m^{\infty}(\text{Na}^+) + \lambda_m^{\infty}(\text{Br}^-) = 126.5 + 151.5 - 150$

$\lambda_m^{\infty}(\text{Na}^+) = 50$

69.(100) $\kappa = G \cdot G^* \quad \Rightarrow \quad \frac{1}{200}2 \quad \Rightarrow \quad 0.01$

$\Lambda_{aq} = \frac{\kappa}{N} \times 1000 \quad \Rightarrow \quad \frac{0.01}{0.1} \times 1000 \quad \Rightarrow \quad 100$

70.(203) $\Rightarrow 127 + 76 = 203$

71.(1) $G^* = \frac{1}{a} = \frac{10}{100} = 0.1;\ G = 0.0001\text{S}$

$V = 100 \times 10 = 100\,\text{cm}^3 = 1\,\text{litre}$

$\kappa = GG^* = 0.1 \times 0.0001 = 10^{-5}$

$\Lambda_m = \frac{\kappa \times 100}{M} = \frac{(0.1 \times 0.0001) \times 1000}{0.1} = 0.1\text{Scm}^2\text{mol}^{-1}$

$\Rightarrow \quad (.1 \times 10 = 1)$

72.(964) At anode : $2H_2O(\ell) \longrightarrow 4H^+(aq) + O_2(g) + 4e^-$

At cathode : $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Eq. of O_2 evolved = Eq. of Ag formed $\Rightarrow$ 0.1

Total loss in mass $= \frac{0.1 \times 0.32}{4} + 0.1 \times 108$

$\Rightarrow \quad 0.8 + 10.8 \quad \Rightarrow \quad 11.6$

Mass of final solution $= 108 - 11.6 \quad \Rightarrow \quad 96.4\,\text{g}$

$\Rightarrow \quad (96.4 \times 10 = 964)$

73.(55) For normal calomel electrode $E_{RP} = E^{\circ}_{RP}$

$\therefore \quad E_{cell} = (0.28 - 0) - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2}}$

$0.5755 = 0.28 + 0.0591\,\text{pH} + \frac{0.0591}{2}\log(0.1) \quad \Rightarrow \quad \text{pH} = 5.5$

$\Rightarrow \quad (5.5 \times 10 = 55)$

74.(1) E° for normal calomel electron = E° for saturated calomel electrode

$0.33 = 0.27 - \frac{0.06}{2}\log[Cl^-]^2;\ [Cl^-] = 0.1\,\text{M}$

$\Rightarrow \quad (.1 \times 10 = 1)$

Chemical Kinetics

1.(C) Reaction is of zero order as the unit of rate constant is $\text{mol L}^{-1}\text{s}^{-1}$.

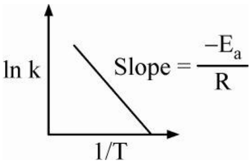
$\therefore \quad$ Concentration of $B = k \times t = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72\,\text{M}$

2.(A) According to Arrhenius equation.

$k = Ae^{-Ea/RT}$

$\ln k = \ln A - \frac{E_a}{RT}$

Here, If lnk is plotted against of 1/T, slope of the line will be $-\frac{E_a}{R}$.



3.(C) $\text{Rate}_1 = k[A]^2[B]^3$ $\quad \text{Rate}_2 = k[2A]^2[2B]^3$ $\quad \text{Rate}_2 = 32k[A]^2[B]^3$ $\quad \therefore \quad \text{Rate}_2 = 32(\text{Rate}_1)$

4.(B) At 10°C rise, rate increases by 2 $\quad \frac{r_{100°C}}{r_{10°C}} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512\,\text{times}$

5.(A) Rate constant is independent of the initial concentration of the reactants. It has a constant value at fixed temperature. Hence the value of rate constant can be increasing the temperature.

6.(D) For the given reaction, $\quad BrO^-_{3(aq)} + 5Br^-_{(aq)} + 6H^+ \rightarrow 3Br_{2(\ell)} + 3H_2O_{(\ell)}$

Rate of reaction in terms of Br_2 and Br^- is, rate $= \frac{1}{3}\frac{d[Br_2]}{dt} = \frac{-1}{5}\frac{d[Br^-]}{dt}$ $\quad \therefore \quad \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

7.(A) $A \rightarrow$ products

If $-\frac{dx}{dt} = k$, it means $-\frac{dx}{dt} = k[A]^0 = k$. Hence order of reaction must be zero.

8.(B) $2A \rightarrow B + C$

The rate equation of this equation may be expressed as $r = k[A]^0$. $\quad$ [Order $= 0$]. $\quad r = k$.

$\therefore$ The rate is independent of concentration.

9.(C) For a given chemical reaction, $k = Ae^{-E_a/RT}$ (Arrhenius equation)

10.(A) Enzymes act like catalyst in biochemical reactions. Presence of an enzyme increases the rate of reaction by lowering the activation energy of the reactant.

11.(ABCD) **(A)** Extent of reaction (α) is given by : $\alpha = 1 - e^{kt}$ $\quad \left[\text{Use} : kt = \ell n\frac{1}{1-\alpha}\right]$

(B) $C_1 = C_0 e^{-kt}$ [For reactants] **(C)** $C_1 = C_2\left(1 - e^{-kt}\right)$ [For Products]

(D) $\log C_t = \log C_0 - kt$

12.(D) Rate law equation is given by $\frac{dc}{dt} = k[A]^x[B]^y$ $\quad \therefore \quad \frac{dc}{dt}$ for C at various concentrations are

$1.2 \times 10^{-3} = k(0.1)^x(0.1)^y$ **.....(i)** and $1.2 \times 10^{-3} = k(0.1)^x(0.2)^y$ **.....(ii)**

$2.4 \times 10^{-3} = k(0.2)^x(0.1)^y$ **....(iii)**

Solving for *x* [divide Eq. (iii) by Eq. (i)] $\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.2)^x(0.1)^y}{k(0.1)^x(0.1)^y} \Rightarrow 2 = (2)^x \Rightarrow x = 1$

Solving for *y* [divide Eq. (iii) by Eq. (i)] $\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.2)^x(0.1)^y}{k(0.1)^x(0.2)^y}$ or $2 = (2)^x\left(\frac{0.1}{0.2}\right)^y$

Put x = 1 in above Eq., we get : $2=(2)^1\left(\frac{0.1}{0.2}\right)^y$ or $1 = (0.5)^y \Rightarrow y = 0$

Thus, $\frac{dc}{dt}=k[A]^1[B]^0 \Rightarrow \frac{dc}{dt}=k[A]^1$

13.(A) Form Arrhenius equation, $\log\frac{k_2}{k_1}=\frac{-E}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

Given, $\frac{k_2}{k_1}=2$; $T_2 = 310$ K

$T_1 = 300$ K

On putting values, $\Rightarrow \log 2=\frac{-E_a}{2.303\times 8.314}\left(\frac{1}{310}-\frac{1}{300}\right) \Rightarrow E_a = 53603.93$ J/mol = 53.6 kJ/mol

14.(B) Rate constant for the first order reaction is given by $k=\frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

a = 0.1 M and $(a-x)=0.025$ M ; t = 40 min $\therefore$ $k=\frac{2.303}{40}\log\frac{0.1}{0.025}M = 0.0347\ \text{min}^{-1}$

$\text{Rate}=\left(\frac{dx}{dt}\right)=k[A]^1=0.0347\times 0.1=3.47\times 10^{-4}\ \text{M min}^{-1}$

15.(C) For every 10°C rise of temperature, rate is doubled. Thus, temperature coefficient of the reaction = 2

When temperature is increased by 50°, rate becomes $= 2^{(50/10)} = 2^5$ times = 32 times

16.(B) $A\xrightarrow{k_1}B$, $A\xrightarrow{k_2}C$,

By Arrhenius equation,

$k_1 = A'e^{-E_{a_1}/RT}$ and $k_2 = A'e^{-E_{a_2}/RT}$ [A′ is Arrhenius constant]

$\because$ $E_{a_2}=2E_{a_1}$ $\therefore$ $k_2 = A'e^{-2E_{a_1}/RT}$

$\frac{k_1}{k_2}=\frac{A'e^{-E_{a_1}/RT}}{A'e^{-2E_{a_1}/RT}}=e^{E_{a_1}/RT}$ $\therefore$ $k_1 = k_2e^{E_{a_1}/RT}$

17.(C) Half-life for a zero order reaction is given by $t_{1/2}=\frac{[A_0]}{2k}$ [where $[A_0]$ = initial concentration of reactant]

$\Rightarrow k_0=\frac{[A_0]}{2t_{1/2}}=\frac{2.0\ \text{mol L}^{-1}}{2\times 1\text{h}}=1.0\ \text{mol L}^{-1}\ \text{h}^{-1}$

Rate constant for a zero order reaction is given by $k=\frac{1}{t}[(A_0)-(A)]$

$\Rightarrow t=\frac{1}{k}[(A_0)-(A)]$ or $t=\frac{(0.50)-(0.25)\ \text{mol L}^{-1}}{1\ \text{mol L}^{-1}\ \text{h}^{-1}}$ =0.25 hr

18.(B) According to Arrhenius equation $k = Ae^{-E/RT}$ where, E is the activation energy below which the colliding molecules will not react.

19.(C) Catalyst doesn’t affect enthalpy of reaction.

20.(B) $\frac{k_2}{k_1}=\exp\left[\frac{-Ea}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$ If k_2 at T_2 and k_1 at T_1 is known, above equation gives value of Ea **21.(A)**

22.(A) $\ln k=\ln A-\frac{Ea}{RT}$ Above equation implies straight line with negative slope if ln k is plotted vs 1/T **23.(D)**

24.(C) The time interval taken is (0-40 minute). The H_2 produced till 40 minute = V_3. Thus average rate $= \frac{V_3}{40}$

25.(C) Order of reaction can be integer or fractional. It can be determined experimentally.

26.(B) Instantaneous rate can be calculated by measuring slope of tangent of concentration-time graph at that particular instant. Thus slope which is calculated by the points on tangent line gives its slope. (V_4, 50) is not lie on the tangent line, so, it cannot give its slope.

27.(A) The reaction which produces more stable product.

28.(C) With threshold energy, proper orientation also required **29.(B)** ΔG remains same for the reaction

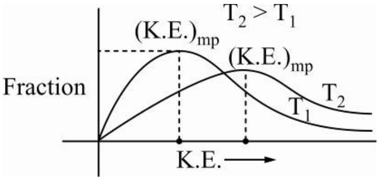
30.(B) **31.(B)** In case (B), [A] decreases exponentially and [B] increases exponentially.

32.(ACD) Only elementary reaction gives rate law without experimental data.

33.(AD) Molecularity is always equal to order and it is defined for elementary reaction, it can have positive integer values only.

34.(AB) **35.(D)** **36.(ACD)** **37.(AD)**

38.(AC) Fraction of most probable K.E. decreases but most probable K.E. increases with increasing temperature.



39.(AD)

40.(AB) k changes exponentially with E_a and T but for increase in k, Ea should decrease and T should increase.

41.(BD) Catalyst provide different path way for the reaction in which activation energy is decreased.

42.(AD) Rate is constant during reaction in zero order kinetics.

43.(AD) For first order reaction, $\log\frac{[R]_0}{[R]} = \frac{k}{2.303}\cdot t$ and $t_{1/2} = \frac{0.693}{k}$ **44.(A)** **45.(C)**

46.(8)

47.(4) Rate of reaction $= k[A]^2$

Rate of disappearance of $A = -\frac{d[A]}{dt}$

Rate of appearance of $B = +\frac{d[B]}{dt}$

Rate of reaction $= -\frac{d[A]}{dt} = +\frac{d[B]}{dt} = k[A]^2$

Rate of appearance of B after double the conc. of A.

$$\frac{d[B]}{dt} = k[2A]^2$$

48.(33) Elementary reaction,

$$x(g) \longrightarrow y(g) + z(g)$$

Rate $= k[x]$, first order

$$k = \frac{1}{t}\ln\frac{[A_0]}{[A_t]}$$

$$\frac{\ln 2}{10\,\text{min}} = \frac{1}{t}\ln\frac{100}{10}$$

$$\frac{0.3}{10}=\frac{1}{t} \quad \Rightarrow \quad t = 33\,\text{min}$$

49.(150) $K=\frac{1}{100}\ln\frac{100}{25}=\frac{1}{t}\ln\frac{100}{12.5}$

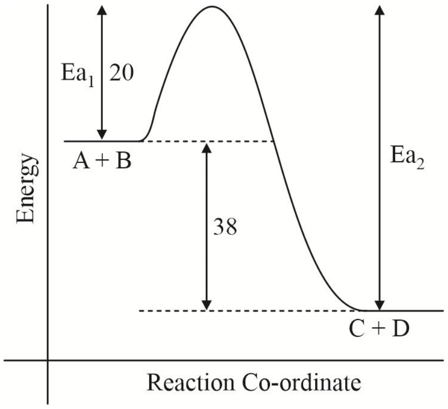
50.(48) $k=\frac{2.303}{32}\log\left(\frac{a}{a-x}\right)$

$$k=\frac{2.303}{32}\log\left(\frac{100}{1}\right) \quad \Rightarrow \quad \frac{2.303}{16}$$

$$t=\frac{2.303\times16}{2.303}\log\left(\frac{100}{0.1}\right)=48\,\text{min}$$

51.(0) For zero order $t_{1/2}\propto[\text{conc.}]^0$

52.(58) $Ea_2 = 58$



53.(100) $\lambda=\frac{0.693}{69.3}=10^{-2}\,\text{min}^{-1};\ N=\frac{-\frac{dN}{dt}}{\lambda}=\frac{100}{10^{-2}}=10000$

$\Rightarrow (10000\div100=100)$

54.(43) t for 20% left

$$\Rightarrow \quad t_1=\frac{2.303}{\lambda}\log\frac{1}{1-0.8}=\frac{\ln5}{\lambda}$$

t for 50% left

$$\Rightarrow \quad t_2=\frac{1}{\lambda}\ln2$$

$$\frac{t_2}{t_1}=\frac{\frac{1}{\lambda}\ln2}{\frac{1}{\lambda}\ln5}=0.43 \quad \Rightarrow \quad t_2=0.43\,t_1$$

$\Rightarrow (0.43\times100=43)$

55.(200) $\Delta t=\left|t_1-3t_{1/2}\right|=200$

56.(100) $\lambda t=\ln\left(\frac{A_0}{A}\right)=\frac{0.693}{t_{1/2}}=\ln\left(\frac{2140}{535}\right)=t_{1/2}=100\,\text{min}$

57.(100)

$$\begin{array}{lccccccc} & A & + & B & \longrightarrow & C & + & D \\ t=0 & 1 & & 1 & & & & \\ t & 1-x & & 1-x & & x & & x \end{array}$$

$r=k[A]^{1/2}[B]^{1/2} \quad \Rightarrow \quad \frac{dx}{dt}=k(1-x)^{1/2}(1-x)^{1/2}$

or $\frac{dx}{dt} = k(1-x)$

$\Rightarrow \quad t = \frac{1}{k}\ln\left(\frac{1}{1-x}\right) \quad \Rightarrow \quad t = \frac{2.303}{2.303\times10^{-2}}\log\left(\frac{1}{0.1}\right) = 100$

58.(35) 1 mole of A will form 2 moles B and C.

After completion of reaction when 75% A converted into B and C then total number of moles

$= 0.5 + 2\times1.5 = 3.5\,\text{moles}$

$\Rightarrow \; 3.5\times10 = 35$

59.(100) $e^{-\frac{E_a}{RT}}\times100 = 3.8\times10^{-16}; \; e^{-\frac{E_a}{RT}} = 3.8\times10^{-18}$

$-\frac{E_a}{RT} = \ln(3.8\times10^{-18}); \; R = 8.314 \text{ and } T = 300$

$E_a = 100\,\text{kJ/mol}$

60.(30) $\frac{A_0(X)}{A_0(Y)} = \frac{4}{1}; \; \frac{A_x}{A_y} = 1, \; \lambda_y - \lambda_x = \frac{1}{t}\ln\left(\frac{(A_0)_y}{(A_0)_x}\times\frac{A_x}{A_y}\right)$

$(\lambda_y - \lambda_x)t = \ln\left(\frac{1}{4}\right); \; (t_{1/2})_y = 30\,\text{min}$

Surface Chemistry

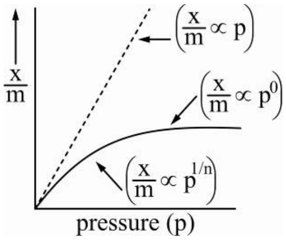
1.(B) According to Hardy Schulze rule greater the charge on oppositely charged ion, greater is its coagulating power. Since arsenic sulphide is a negatively charged sol, thus, the order of coagulating power is $Na^+ < Ba^{2+} < Al^{3+}$.

2.(D) By Freundlich adsorpotion isotherm $\frac{x}{m} = kp^{1/n}$ [In between low and high pressure range]

When $n = 1, \; \frac{x}{m} \propto p^1$ [In low pressure range]

When n is large, $\frac{x}{m} = k$ [Independent of pressure]

Thus, $\frac{x}{m} \propto p^0$ [At high pressure range when saturation point is reached]



3.(C) Higher the gold number, lesser will be the protective power of colloid.

4.(C) The adsorption of a gas is directly proportional to the pressure of the gas.

5.(B) Mixing the sols together can cause coagulation, since the charges are neutralised.

6.(A) Size of colloidal particles = 1 to 100 nm (Say 10 nm)

$V_C = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(10)^3$

Size of true solution particles $\approx 1\,\text{nm}$

$V_S = \frac{4}{3}\pi(1)^3 \qquad \text{Thus,} \quad \frac{V_C}{V_S} = 10^3$

7.(C) Adsorption of H_2 gas over tungsten follows zero order because it doesn't depend on hydrogen's amount.

8.(BC) The formation of micelles takes place only above a particular temperature called Kraft temperature (T_k) and above a particular concentration called critical micelle concentration (CMC).

9.(AB) Catalyst provides different route for the reaction, so, no change in enthalpy for a given reaction. Also for a given reaction there can exist a particular catalyst, so, changing catalyst may change outcome of reaction.

10.(AC) $\lim\limits_{1/n\to 0}\left(\frac{x}{m}\right) = \lim\limits_{1/n\to 0}\left(kp^{1/n}\right) = k$

$\lim\limits_{n\to 0}\left(\frac{x}{m}\right) = \lim\limits_{n\to 0}\left(kp^{1/n}\right) = \text{not determined}$

11.(BC) In the case of H_2, van der Waals forces are very small and also its critical temperature is very low

12.(BD) **13.(BD)**

14.(AD) Positively charged ions or electrolyte can precipitate negatively charged emulsions.

15.(CD) Reversible colloids are very stable. **16.(AC)** **17.(BC)**

18.(AB) Catalyst remains unchanged chemically during the reaction

19.(AD) On Chalk stick, different colours are adsorbed at different rate but solvent of ink is also absorbed.

20.(B) Al^{3+} can coagulate negatively charged colloids particles.

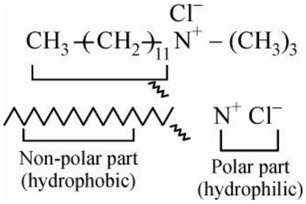
21.(D) Tyndall effect is due to the scattering of light by colloidal particles and not due to the charge.

22.(D) The enzyme activity rises rapidly with temperature and becomes maximum at definite temperature, called optimum temperature.

23.(D) $\frac{x}{m} = p \times T$

24.(A) Langmuir adsorption isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether nearby sites are occupied or not occupied.

25.(A)



26.(D) Adsorption causes decrease in surface energy which appears as heat. Thus adsorption is an exothermic process and hence lowers the activation energy of the reaction.

27.(A) Micelles are the clusters or aggregates formed in solution by association of colloids. Usually such molecules have a lyophobic group and a lyophobic group. The long hydrocarbon is the lyophobic portion which tries to recede away from the solvent water and the ionisable lyophilic group which tends to go into water resulting into ions. As the concentration is increased the lyophobic parts receding away from the solvent approach each other and form a cluster, the lyophobic ends are in the interior lyophilic groups projection outward in contact with the solvent.

28.(A) Adsorption in the ability of a substance to concentrate or hold gases, liquids or dissolved substances upon its surface. Solids adsorb greater amounts of at lower temperature. In general, adsorption decreases with increase in temperature.

29.(A) The soap conc. at which micelles (spherical colloids molecules) first appear is called as critical micellar concentration (CMC). At this condition the surfactant molecules associate with each other.

30.(B) Both magnitude of charge and nature of charge effect coagulation of a given colloid. Greater the magnitude of the charge, quicker with be the coagulation.

31.(4) Haemoglobin is positively charged sol. Hence the sol with negative charge can coagulate haemoglobin, i.e., starch, clay, As_2S_3, CdS

32.(3) Silicic acid is negatively charged sol. Hence the sol with positive charge can coagulate silicic acid, i.e., $Fe(OH)_3$, $Ca(OH)_2$, $Al(OH)_3$,

33.(4) 2 mL of 1 M NaCl contains $\text{NaCl} = \frac{2}{1000} = 2\,\text{mmol}$

Thus 500 mL of As_2S_3 sol require NaCl for complete coagulation = 2 mmol

Hence 1 L, i.e., 1000 mL of the sol require NaCl for complete coagulation = 4 mmol

Therefore, flocculation value of $\text{NaCl} = 4$.

34.(3) Haemoglobin added to 100 mL of gold sol to prevent coagulation by 1 mL of 10% NaCl so = 0.03 g = 30 mg. Haemolobin required to be added to 10 mL of gold sol to prevent coagulation by 1 mL of 10% NaCl sol = 3 mg. Therefore, gold number of haemoglobin = 3.

35.(1) Gold number of gelatin = 0.01 or 0.01 mg glatin required to be added to 10 mL of gold sol to completely prevent coagulation of 1 mL of 10% NaCl solution.

Therefore gelatine added to 1000 mL of gold sol to prevent coagulation $= \frac{0.01 \times 1000}{10} = 1\,\text{mg}$.

36.(4) Mass of HCl acid adsorbed by 10 g charcoal $= 526.3 \times 10^{-3}(0.5 - 0.4) \times 38 = 2$ (Mw of HCl = 38 g mol^{-1})

The amount of adsorption $\frac{x}{m} = \frac{2}{0.5} = 4$

37.(2) As_2S_3 sol is negatively charged owing to preferential adsorption of S^{2-} ions. Cation would be effective ion in coagulation.

Flocculating value = millimole of the effective ion per litre of sol

$$-\frac{5 \times 0.006 \times 10^3}{5 + 10} = 2$$

38.(6) $\log\frac{x}{m} = \log K + \frac{1}{n}\log P$

$\therefore$ plot of $\log\frac{x}{m}$ versus $\log P$ is linear with slope $= \frac{1}{n}$ and intercept $= \log K$

Thus $\frac{1}{n} = \tan\theta = \tan 45° = 1$ or $n = 1$

$\log K = 0.301$ or $K = \text{anti}\log 0.301 = 2$

At $P = 3\,\text{atm}$

$\frac{x}{m} = KP^{1/n} = 2 \times (3)^1 = 6$

39.(3) Gold number $= \frac{6.0 \times 10^{-5} \times 10^3(\text{mg}) \times 10}{20} = 0.03$

40.(1) As_2S_3 sol is negatively charged owing to preferential adsorption of S^{2-} ions. Cation would be the effective ion in coagulation.

Flocculating value = minimum milli mol of the effective ion per liter of sol $= \frac{4 \times 0.005 \times 10^3}{4 + 16} = 1.0$

41.(3) The diameter of colloidal particles range from 1 nm to $1\mu\text{m}$.

General Principles & Processes of Isolation of Elements

1.(C) For purification, impurities like Se, Te, Ag, Au gets oxidised (de-electronation) falling into solution near anode and settle as anode mud.

2.(AD)

3.(AB) CaF_2 is mixed to decrease melting point and increasing electric conductivity.

4.(AC) In froth floatation process, collector is added to decrease wettability of particles. This process is used to separate sulphide ores.

5.(BC) To separate two sulphide ores, depressant is used and proper ratio of oil & water is required.

6.(CD) Bauxite is the ore of aluminum which is found with Fe_2O_3 and SiO_2 impurities.

7.(AC) Calcination is the process to remove volatile impurities from oxygen containing ores in absence of air.

8.(AB) $Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$ $\quad ZnCO_3 \xrightarrow{\Delta} ZnO \xrightarrow{C} Zn + CO$ **9.(AD)**

10.(AB) $Ni + CO \longrightarrow Ni(CO)_4 \xrightarrow{\text{Heating}} Ni + CO$ (Mond's process)

$Ti + I_2 \longrightarrow TiI_4 \xrightarrow{\text{Heating}} Ti + I_2$ (Van-Arkel process)

11.(AC) **12.(BC)**

13.(D) van-Arkel method is used for refining Titanium and Zirconium. This method is useful for removing volatile impurities lime O_2, N_2, I_2 present in the metals of Zr and Ti. In this method, metal iodine is formed by direct combination of metal and iodine. The metal iodide undergo decomposition on a tungsten filament and thus, pure metal is deposited on the filament.

14.(B) During electrolysis, noble metals (inert metals) like Ag, Au and Pt are not affected and separate as anode mud from the impure anode.

15.(C) Froth-floatation is used to concentrate sulphide ores [Galena (PbS)].

16.(D) Aluminium is extracted by electrolysis of fused mixture of alumina (2-8%), synthetic cryolite Na_3AlF_6 (80-85%), AlF_3 and fluorspar. This makes alumina good conductor and lowers the fusion temperature also.

17.(B) Cyanide process or Mac Arthur-Forest cyanide process

$$2Ag_2S + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH + 2S$$

Soluble silver complex is filtered and treated with zinc dust and silver gets precipitated.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

18.(B) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$ **19.(D)**

20.(D) Magnetic is Fe_3O_4 and contains upto 70% of the metal.

21.(B) Pig iron contains about 4% carbon and many other impurities such as Mn, P, Si etc. in minor amount

22.(D) Leaching process involves the treatment of the ore with suitable reagent as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical method. Argentite or silver glance, Ag_2S is an ore of silver. Silver is extracted from argentite by the Mac-Arthur and Forest process (leaching process).

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

23.(D) The standard free energies of formation $\left(\Delta G_f^\circ\right)$ of most of the sulphides are greater than those of CS_2 and H_2S. Hence, neither carbon nor hydrogen can reduce metal sulphides to metal. The standard free energies of formation of oxides are much lower than those of SO_2. Therefore, oxidation of metal sulphides to metal oxides is thermodynamically favourable. Hence sulphide ore is roasted to the oxide before reduction.

24.(B) Calcium is obtained by the electrolysis of a fused mixture of anhydrous $CaCl_2$ and CaF_2 in a graphite linked tank which serves as anode. The cathode is a hollow movable iron rod which is kept cool. During electrolysis, calcium is deposited at cathode while Cl_2 is librated at anode.

25.(D) Equation at cathode

$$Al^{+3}(melt) + 3e^- \rightarrow Al(l)$$

At Anode

$$C(s) + O^{2-}(melt) \rightarrow CO(g) + 2e^-$$

$$C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e^-$$

In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity.

The fused matrix is electrolyzed. Na_3AlF_6 alone is not the electrolyte.

26.(2) Azurite – $Cu_3(CO_3)_2(OH)_2$

Chalcocite – Cu_2S

Iron pyrites – FeS_2

Limonite – $Fe_2O_3 \cdot 3H_2O$

27.(3) Ti, B and Zr

28.(2) Na & Al

29.(4) Roasting process involves heating of enriched ore in the presence of oxygen.

30.(3) Calcination process involves heating of ore in the absence of oxygen.

31.(4) MgO, CaO, FeO and $MgCO_3 \cdot CaCO_3$ are basic flux.

32.(2) Ag_2O and HgO

33.(4) Cassiterite (SnO_2), Pyrolusite (MnO_2), Rutile (TiO_2) and magnetite (Fe_3O_4) are concentrated by magnetic separation.

34.(3) Si, Ge and Ga

35.(3) Cu, Fe and Sn

36.(2) Borax $(Na_2B_4O_7)$ and P_2O_5

37.(2) Mn & Cr

38.(3) Pb, Hg & Cu

39.(3) Sn, Zn & Fe

40.(2) Ag & Au

41.(4) Al, Mg, K & Na

42.(4) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ is alumino-thermite process. Rest are slag formation processes.

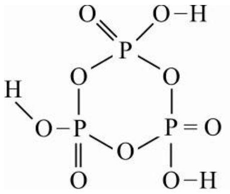
The p-Block Elements

1.(C) Violet colour is due to I_2. Since it is obtained from I^- reacting with conc. H_2SO_4, HI is oxidised to I_2.

2.(B) Copper is precipitated as copper sulphide when in its acidified solution, H_2S is passed.

$$Cu^{2+} \xrightarrow{H_2S} \underset{(black)}{CuS\downarrow} \xrightarrow{\text{dil. } HNO_3} Cu^{2+} \xrightarrow{NH_3} \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}}$$

3.(C) Cyclotrimetaphosphoric acid



Single Bonds = 12
Double Bonds = 3

4.(C) Phosphorous belongs to 3rd period, so, it contains d orbitals. It can participate in $p\pi - d\pi$ bonding.

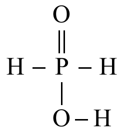
5.(A) CO_3^{2-} and NO_3^-, both contain 32 electrons and both trigonal planar.

6.(A) $H-F$ is strongest bond, because formed by $1s-2p$ overlapping.

7.(D) SbH_3 is strongest reducing agent because its bond dissociation energy is lowest. It gives H^- ion easily.

8.(C) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3\uparrow$

9.(C) H_3PO_4 can donate three protons, so, it can form three series of salts.

10.(C)  $H - \overset{\overset{O}{||}}{\underset{\underset{O-H}{|}}{P}} - H$ one $O-H$ and two $P-H$ bonds are exist.

11.(B) $2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$ **12.(A)** Only one form of nitrogen exist (N_2)

13.(C) No of valence electrons are five, so, maximum of five electron can participate in bond formation, three covalent and one co-ordinate.

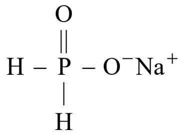
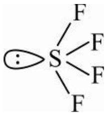
14.(A) Single $N-N$ bond is weaker than $P-P$ bond because of electron repulsion.

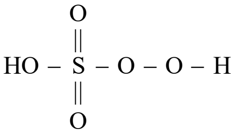
15.(A) Brown ring is formed because of $\left[Fe(H_2O)_5 NO\right]^{2+}$.

16.(B) Flourine is most electronegative due to which all valence electron of Bi participates in bond formation.

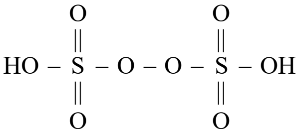
17.(A) $(NH_4)_2 Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$Ba(N_3)_2 \xrightarrow{\Delta} 3N_2 + Ba$

18.(C)  $H - \overset{\overset{O}{||}}{\underset{\underset{H}{|}}{P}} - O^-Na^+$ Thus oxidation state $= +3-2 = +1$ **19.(C)**  Sea Saw

20.(A)  $HO - \overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}} - O - O - H$

H_2SO_5

 $HO - \overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}} - O - O - \overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}} - OH$

$H_2S_2O_8$

Both contains peroxy bond.

21.(C) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

22.(A) $\underset{-3}{NH_3} \longrightarrow \underset{+3}{NX_3}$ MnO₂ reacts with HCl and Cl₂ gas is evolved $\underset{-3}{NH_3} + 3Cl_2 \longrightarrow \underset{+3}{NCl_3} + 3HCl$ **23.(C)**

24.(D) $[PCl_4]^+[PCl_6]^-$ packing of cation and anion exist in solid state.

$[PCl_4]^+ \longrightarrow$ tetrahedral

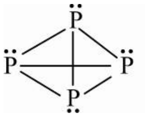
$[PCl_6]^+ \longrightarrow$ Octahedral

25.(C) More is the reduction potential, more easily it can accept electrons, i.e. it can oxidise other element easily.

Thus oxidising order : $BrO_4^- > IO_4^- > ClO_4^-$

26.(B) **27.(AC)** $Cl_2 \xrightarrow{NaOH} Cl^- + ClO_3^-$

28.(BC) $B.E_{F_2} < B.E_{Cl_2} > B.E_{Br_2} > B.E_{I_2}$ Ionic character decreases down the group in metal halides.

29.(BD)  six P – P bonds four lone pairs

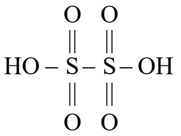
30.(ACD) **31.(AC)** SO_2 is Bent.

32.(CD) $2PCl_5 \longrightarrow \underset{\text{tetrahedral}}{\underset{\downarrow}{[PCl_4]^+}}\ \underset{\text{Octahedral}}{\underset{\downarrow}{[PCl_6]^-}}$ solidstate In P_4, angle strain makes it reactive

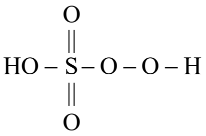
33.(AD) Enthalpy of vapourisation : $PH_3 < AsH_3 < NH_3$

Electron gain Enthalpy : $I < Br < F < Cl$

34.(AB) $H_2S_2O_6$:



$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$; H_2SO_5 :



$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-H$; $2SO_2+O_2 \overset{Pt}{\rightleftharpoons} 2SO_3 \quad \Delta H=(-)ve$

35.(BC) $HI \xrightarrow{H_2SO_4} I_2$ (oxidised) $Cu \xrightarrow{H_2SO_4} Cu^{2+}$ (oxidised)

36.(AB) $XeF_6+3H_2O \longrightarrow XeO_3+3H_2F_2$

37.(C) OF_2 (oxygen difluoride) is a fluoride of oxygen because fluorine is more electronegative than oxygen.

38.(B) NO_2 is not used as a food preservative.

39.(A) As the atomic size increases down the group, the bond length increases and the bond strength decreases and the cleavage of $E-H$ bond becomes easier thus, more will be the acidity. Thus, the correct order is : $H_2S<H_2Se<H_2Te$.

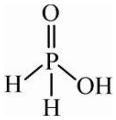
40.(B) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2+Cr_2O_3+4H_2O$

$Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2+3O_2$

$KClO_3 \xrightarrow{\Delta} KCl+3/2O_2$

$2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4+Cr_2O_3+3/2O_2$

41.(B) Hypophosphorous acid is a monoprotic acid.



42.(B) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3+3SO_3$

43.(B) Acidic strength of hydrides increase with increase in molecular mass.
Thus order of acidic strength is

$HF<HCl<HBr<HI$

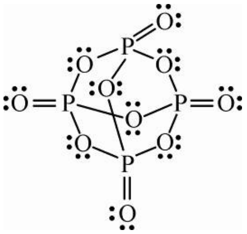
$H_2O<H_2S<H_2Se<H_2Te$

$NH_3<PH_3<AsH_3<SbH_3$

And as acidic strength increases, pK_a decreases. Thus order of pK_a

$H_2O>H_2S>H_2Se>H_2Te$

44.(A)



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 bond is weaker in comparison to Cl – Cl and Br – Br bonds.

46.(B) Fluorine is more reactive than chlorine. So bond energy of chlorine is greater than fluorine. Silicon exhibits 6 coordination number.

47.(B) White phosphorus has low ignition temperature so it is most reactive among all the allotropes.

48.(D) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2\uparrow$

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$

49.(A) Ammonium sulphate is a salt of strong acid (H_2SO_4) and weak base (NH_4OH). Therefore repeated use of ammonium sulphate would increase the concentration of sulphate would increase the concentration of sulphuric acid, while ammonium from NH_4OH is used up by the plant. Hence the acidity of soil will increase.

50.(A)

	$O-O$	$S-S$	$Se-Se$	$Te-Te$
$kJ\,mol^{-1}$	142	226	172	126

51.(C) Cl_2 is better oxidizing agent than Br_2

$Cl_2 + Br^- \longrightarrow Br_2 + Cl^-$

52.(C) N, O and F are highly electronegative non metals and will have the strongest tendency to form anions by gaining electrons from metal atoms.

53.(A) Caustic soda is manufactured by the electrolysis of NaCl solution where Cl_2 is evolved at the anode and H_2 at the cathode.

At anode : $Cl^- \rightarrow Cl + e^-,\ Cl + Cl \rightarrow Cl_2\uparrow$

At cathode : $H^+ + e^- \rightarrow H_2$

54.(B) $\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{From } HNO_3}{18[O]} \longrightarrow \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O$

55.(C) $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$

56.(B) Bromide in the mother liquor (containing $MgBr_2$) is reducing agent.

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

57.(A) $PH_4I + NaOH \rightarrow NaI + PH_3 + H_2O$

58.(D) $NH_4Cl + NaNO_2 \xrightarrow{\text{Heat}} NH_4NO_2 + NaCl \xrightarrow{\Delta} N_2 + 2H_2O$

59.(D) Bleaching action of chlorine is due to oxidation in pressure of moisture. It is permanent.

$$H_2O + Cl_2 \rightarrow 2HCl + [O]$$

Coloured matter + $[O] \rightarrow$ colorless matter

60.(A) Red phosphorus is insoluble in CS_2 and only white P is soluble in CS_2.

61.(D) On heating, it gives pyrophosphoric acid at 525 K and metaphosphoric acid at 875 K.

$$2H_3PO_4 \xrightarrow[-H_2O]{525\,K} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[-H_2O]{875\,K} \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

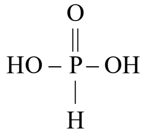
62.(B) Chlorine does not react directly with oxygen.

63.(B) Alkaline pyrogallol absorbs O_2 and oil or cinnamon absorbs O_3.

64.(D) For inter-halogen compounds $(X-X')$ bond energy is lesser than general $X-X$ bond {except for F - F}, and also inter-halogen bond is polar. So they are more reactive.

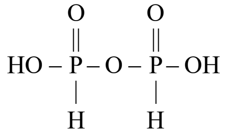
65.(D) Down the group in inert gases inter-particle forces increase, so boiling point increases.

66.(D) H_3PO_3 is orthophosphorous acid :



$\mathrm{HO}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{OH}$

$H_4P_2O_5$ is pyrophosphorous acid :



$\mathrm{HO}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{O}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{OH}$

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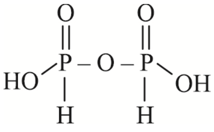
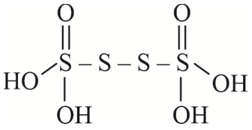
67.(D) $Zn + \underset{\text{conc.}}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

$4Zn + \underset{\text{dil}}{10\,HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5\,H_2O$

68.(2) $H_4P_2O_5$



69.(3) $H_2S_4O_6$

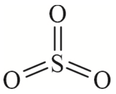


70.(1.5) $AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + \frac{10}{2}2$

(NO_2 and O_2 are paramagnetic gases)

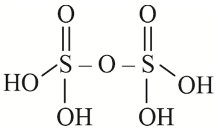
71.(2)

72.(2) SO_3

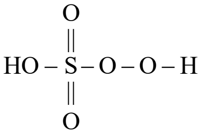


Number of $d\pi - p\pi$ bond in SO_3 are 2

73.(0)



74.(6)



$\mathrm{HO}-\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}-\mathrm{O}-\mathrm{O}-\mathrm{H}$

75.(3) Brown ring complex is $[Fe(H_2O)_5(NO)]$

Here Fe is in +1 oxidation state

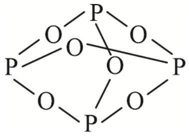
No. of unpaired electrons are 3

76.(2) $(NH_4)_2CO_3, (NH_4)_2SO_4$

77.(5) $I_2 + \text{conc.}HNO_3 \longrightarrow HIO_3$ **78.(2)**

Oxidation state of $I = +5$

79.(12)



The d & f-Block Elements

1.(A) $Cu^{2+} : 3d^9$ unstable electronic configuration.

$Cu^{+} : 3d^{10}$ stable E.C

But hydration energy is more for Cu^{2+} so, +2 oxidation state is more stable in aqueous solutions.

2.(B) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ **3.(B)** CuF_2 becomes blue in most air

4.(A) $2KMnO_4 + 2H_2SO_4 \xrightarrow{\text{cold}} Mn_2O_7 + 2KHSO_4 + H_2O$; $2Mn_2O_7 \xrightarrow{\text{warm}} 4MnO_2 + 3O_2$

5.(B) $3d^5$ contains maximum ($5\ e^-s$) unpaired electrons

6.(A) Only $Cu^+ \longrightarrow Cu^{2+} + Cu$ is disproportionation.

7.(D) After formation of some Mn^{2+}, it auto-catalyses the reaction.

8.(A) $KMnO_4$ oxidises S^{2-} ions into S and itself converts into Mn^{2+} in acidic medium.

$$Mn^{7+} \xrightarrow{H^+} Mn^{2+}$$

Thus $5e^-$ reduces $= 1\text{mol } KMnO_4$

$$2e^- \text{ reduces} = \frac{1}{5} \times 2 = \frac{2}{5}\text{mol of } KMnO_4$$

9.(A) E.C. of Gd : $[Xe]4f^7 5d^1 6s^2$ **10.(D)** Interstitial compounds are chemically un reactive.

11.(C) $2KMnO_4 + KI + H_2O \longrightarrow 2KOH + 2MnO_2 + KIO_3$

12.(A) Copper cannot liberate hydrogen from acids.

13.(C) $Cr^{6+} \longrightarrow Cr^{3+}$ reduction ; $Sn^{2+} \longrightarrow Sn^{4+}$ oxidation (Stable oxidation state of Sn)

14.(D) Oxygen can form double bond while fluorine forms only single bond.

15.(C) Zr and Hf have same atomic radii due to lanthanide contraction **16.(B)** $KMnO_4$ oxidises Cl^- to Cl_2

17.(AB) **18.(AD)** $Co^{2+} : [Ar]3d^7$; 3unpaired e^-s $Cr^{3+} : [Ar]3d^3$; 3unpaired e^-s

19.(C) **20.(BD)** Pu and Np shows +7 oxidation state.

21.(AB) ${}_{92}U : [Rn]5f^3 7s^2 6d^1$; ${}_{93}Np : [Rn]5f^4 7s^2 6d^1$

22.(BC) Eu and Yb also shows +2 oxidation state **23.(B)** $Mn^{2+} : [Ar]3d^5$

24.(AB) **25.(BC)** Mo and W both contains only +6 oxidation stable as stable one **26.(BC)**

27.(B) **(A)** $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$

The above equation is incorrect because K_2O, a stronger base cannot be generated by a weaker base, Li_2O.

(B) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$

The above equation is correct because amine complexes decompose under acidic medium. Thus, the complex $[CoCl(NH_3)_5]^+$ decomposes in acidic conditions to give ammonium ions.

(C) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$

The above equation is incorrect because the product formed would be $[Mg(EDTA)]^{2-}$.

(D) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$

The above equation is incorrect. Thus, the correct equation is :

$$2CuSO_4 + 10KCN \longrightarrow 2K_3[Fe(CN)_6] + 2K_2SO_4 + \underset{\text{(Cyanogen)}}{(CN)_2}$$

28.(A) **(A)** V^{2+} = 3 unpaired electrons ; Cr^{2+} = 4 unpaired electrons

Mn^{2+} = 5 unpaired electrons ; Fe^{2+} = 4 unpaired electrons

Hence, the order of paramagnetic behaviour should be $V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(B) Ionic size decreases from left to right in the same period

(C) **(As per data from NCERT)**

$Co^{3+}/Co^{2+} = 1.97;\ Fe^{3+}/Fe^{2+} = 0.77;\ Cr^{3+}/Cr^{2+} = -0.41$

Sc^{3+} is highly stable (It does not show $+2$).

(D) The oxidation states increases as we go from group 3 to group 7 in the same period.

29.(D) SRP value normally increases from the left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. e.g., $E^{\circ}_{Mn^{3+}/Mn^{2+}} = +1.57$ V;

Thus, $E^{\circ}_{M^{3+}/M^{2+}} = +1.97$ is highest for Co.

30.(D) **(A)** $FeO > Fe_2O_3$ (basic). Thus, it is correct statement.

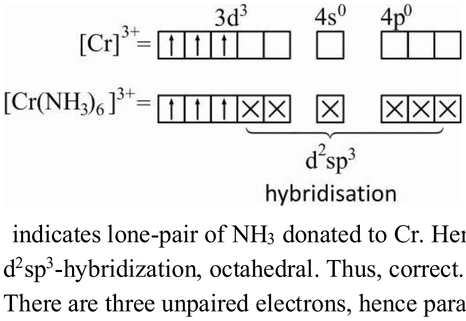
(B) $FeCl_2 > FeCl_3$ (ionic), larger the charge greater the polarizing power. Thus, greater the covalent nature. Thus, the given statement is correct.

(C) Fe^{2+} salts are more ionic thus less volatile than Fe^{3+} salts. Thus, given statement is correct

(D) Greater the covalent nature, more easily they are hydrolyzed. Thus, $FeCl_3$ is more hydrolyzed than $FeCl_2$. Thus, statement (D) is incorrect.

31.(C) $$\underbrace{[Cr(NH_3)_6]}_{\text{Coordinate sphere}}\ \underbrace{Cl_3}_{\text{Ionisable}} \rightleftharpoons [Cr(NH_3)_6]^{3+} + 3Cl^- \xrightarrow{AgNO_3} \underset{\text{White Precipitate}}{AgCl\downarrow}$$

In $[Cr(NH_3)_6]^{3+}$ Cr exists as Cr^{3+} ion. The outer orbital electronic configuration of Cr is $3d^3\ 4s^0$. The orbital diagram is represented by



Here, ☒ indicates lone-pair of NH_3 donated to Cr. Hence,

(A) d^2sp^3-hybridization, octahedral. Thus, correct.

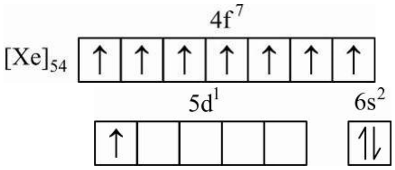
(B) There are three unpaired electrons, hence paramagnetic. Thus, correct.

(C) d^2sp^3-inner orbital complex, thus incorrect

(D) Due to ionisable Cl^- ions, white precipitate with $AgNO_3$, thus correct

Therefore, **(C)** is wrong.

32.(D) Gd (64)



All the electrons 4f-orbital are unpaired, hence stable. Thus, Gd (64) has EC as $[Xe]_{54}$ $4f^7$, $5d^1$, $6s^2$. Instead of $[Xe]_{54}$ $4f^8$, $6s^2$

33.(A) Usually across the first transition series, the negative values for standard electrode potential decrease except for Mn due to stable d^5 – configuration. So, correct order : $Mn > Cr > Fe > Co$

34.(C) The most common oxidation state of lanthanoid is $+3$. Lanthanoids in $+3$ oxidation state usually have unpaired electron in f-subshell and impart characteristic colour insolid as well as in solution state due to f-f trasition. (Except lanthanum and lutetium).

35.(B) As oxidation state increase, electronegativity increases thus acidic characteristic increase not basic.

36.(B) Lanthanoids : $[Xe]4f^{1-14}5d^{0-1}6s^2$ Actinoides : $[[Rn]5f^{1-14}6d^{0-1}7s^2$

Lanthanoids and actinoids use d and f orbitals also to show higher oxidation state. As actionoids have comparatively low energy difference between f and d orbitals, thus they show more number of oxidation states.

37.(D) 4f orbital is nearer to nucleus as compared to 5f orbital. Therefore, shielding of 4f is more than 5f orbital.

38.(A) Cerium $Ce_{58} = [Xe]\ 4f^1\ 5d^1\ 6s^2$. Its most stable oxidation state is +3 but +4 is also existing.

39.(D) Imperfect shielding on outer electrons by 4f electrons from the nuclear charge is due to the diffused large shape of 4f-orbitals. This imperfect shielding is unable to counterbalance the effect of the increasing nuclear charge. Hence, the net result shows contraction in size.

40.(D) Following reaction takes place during bessemerisation.

$$2Cu_2O + Cu_2S \longrightarrow Cu + SO_2$$

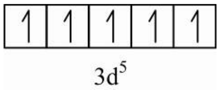
41.(D) $$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg(NH_2)Cl + \underset{\text{black}}{Hg\downarrow} + NH_4Cl + 2H_2O$$

42.(A) Larger the number of unpaired electrons, greater the magnetic moment, $u = \sqrt{n(n+2)}$

where, n = Number of unpaired electrons

$Mn_{25} = [Ar]\ 4s^2,\ 3d^5$

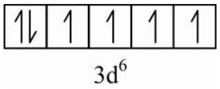
$Mn^{2+} = [Ar]\ 3d^5\ 4s^0$



Number of unpaired electrons = 5

$Fe_{26} = [Ar]\ 4s^2,\ 3d^6$

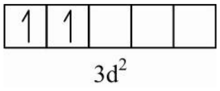
$Fe^{2+} = [Ar]\,3d^6,\ 4s^0$



Number of unpaired electrons = 4

$Ti_{22} = [Ar]\ 4s^2\ 3d^2$

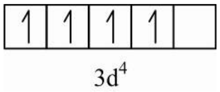
$Ti^{2+} = [Ar]\ 3d^2\ 4s^0$



Number of unpaired electrons = 2

$Cr_{24} = [Ar\ 3d^5,\ 4s^1$

$Cr^{2+} = [Ar]\,3d^4,\ 4s^0$



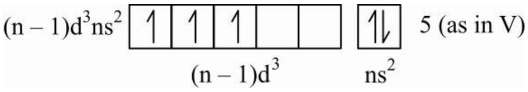
Number of unpaired electrons = 4

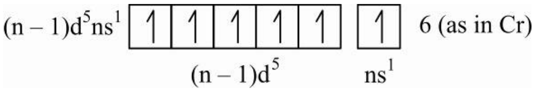
Hence, Mn^{2+} : $[Ar]\ 3d^5$ with five unpaired electrons have maximum magnetic moment.

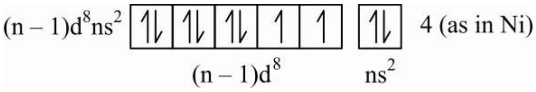
43.(B) Due to lanthanoid contraction, the atomic radii of the elements belonging to the same group of the 2nd and 3rd transition series becomes same. Thus, ${}_{40}$Zr[160 pm] and ${}_{72}$Hf[159 pm] have almost same radii.

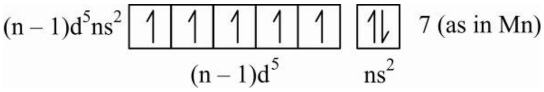
44.(C) +3 and +4 states are shown by Ce in aqueous solution. Thus, statement (C) is incorrect.

45.(D)









46.(A) Cu, Ag, Au are called coined metals because in the early times, they were used in making coins.

47.(D) Metal oxides lying below Hg in electrochemical series decompose to form metal.

$$\text{ZnO, MgO, CuO} \xrightarrow{\Delta} \text{no effect}$$

$$Ag_2O \xrightarrow{\Delta} Ag + O_2$$

$$AgNO_3 \xrightarrow{\Delta} Ag_2O \longrightarrow Ag + O_2$$

48.(A) Mercury (Hg) solidifies after glass, so used mercury for making good quality mirrors.

49.(B) Ammoina can dissolve precipitate of AgCl due to the formation of complex as given below

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2Cl]$$

50.(B) Hgl_2 becomes soluble in water, when Kl is added to it due to the formation of K_2Hgl_4 complex which is soluble in water.

$$Hgl_2 + 2Kl \longrightarrow \underset{\text{(Soluble)}}{K_2Hgl_4}$$

But when Hgl_2 is heated, Hgl_2 decomposes to give violet coloured fumes of l_2 that deposits on the cooler parts of the test tube.

$$Hgl_2 \xrightarrow{\Delta} Hg + l_2 \uparrow$$

51.(B) In acidic solution, N atoms of NH_3 donates their lone pair electrons to protons forming NH_4^+ ions. Therefore, lone pair electrons of NH_3 are not available for forming the complex with cooper ions.

52.(B) **53.(A)** Zr and Hf have nearly same radii due to lanthanoid contraction.

54.(B) Hydrogen peroxide is oxidised to O_2.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

or, $$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

55.(A) Due to poor shielding effect of 4f-orbitals, nucleus will exert a strong attraction and size of atom or ion goes on decreasing as move in the series with increase in atomic number.

56.(D) Interstitial compounds are generally chemically inert.

57.(B) $Sm^{2+}(Z = 62)$: $[Xe]4f^6$

$Eu^{2+}(Z = 63)$: $[Xe]4f^7$

$Yb^{2+}(Z = 70)$: $[Xe]4f^{14}$

$Ce^{2+}(Z = 58)$: $[Xe]4f^1 5d^1$

Only Yb^{2+} is diamagnetic.

58.(B) Invar $\Rightarrow$ $\mathrm{Ni(metal)+Fe(metal)}$ Steel $\Rightarrow$ $\mathrm{C(non\text{-}metal)+Fe(metal)}$

Bell metal $\Rightarrow$ $\mathrm{Cu(metal)+Sn(metal)+Fe(metal)}$ Bronze $\Rightarrow$ $\mathrm{Cu(metal)+Sn(metal)}$

59.(B)

60.(C) U exhibits $+3, +4, +5, +6$

Th exhibits $+3, +4$; Ac exhibits $+3$ only

Pa exhibits $+3, +4, +5$

61.(C)

Element	Ti < V < Cr < Mn
Number of oxidation state	3 4 5 6

Given order is correct

Magnetic moment $(\mu) = \sqrt{n(n+2)}$ B.M.

For Ti^{3+} $n = 1$, $\mu = \sqrt{1(1+2)} = \sqrt{3}$ B.M. For V^{3+} $n = 2$, $\mu = \sqrt{2(2+2)} = \sqrt{8}$ B.M.

For Cr^{3+} $n = 3$, $\mu = \sqrt{3(3+2)} = \sqrt{15}$ B.M. For Mn^{3+} $n = 4$, $\mu = \sqrt{4(4+2)} = \sqrt{24}$ B.M.

Thus magnetic moment : $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$

Melting point order : $\underset{1245^\circ C}{Ti} < \underset{1668^\circ C}{V} < \underset{1875^\circ C}{Mn} < \underset{1900^\circ C}{Cr}$

2nd ionization enthalpy order	Ti	<	V	<	Mn	<	Cr
kJ/Mol	1320		1376		1513		1635

62.(C)

Element	Co	Ni	Cu	Fe
$E^\circ_{M^{2+}/M}(V)$	-0.28	-0.25	$+0.34$	-0.44

63.(A) The order can be explained using the idea of spin correlation. Spin correlation refers to lowering of energy for like (parallel) spins. Spin correlation leading to decrease in repulsion for electrons of like spins than for electrons of different spins is called exchange energy.

Spin correlation and its exchange energy gives an electronic configuration a special stability which is greatest for half-filled electronic configurations.

$Mn^{2+}(d^5)$ gets stabilisation due to half-filled configuration.

In $Fe^{2+}(d^6)$ the placing of one extra electron in a subshell destabilises. Placing of 2 electrons on $Co^{2+}(d^7)$ destabilises it more. $Cr^{2+}(d^4)$ has one vacant subshell Fe^{2+} gets more stabilisation compared to Cr^{2+} through exchange energy. So the order is as follows :

64.(B) $Ti^{3+}(Z = 22)$

Ions which have unpaired electrons exhibits colour in solution. Ti^{3+} has an outer electronic configuration of $4s^0 3d^1$, i.e., 1 unpaired electron. Thus its solution will be coloured.

$Sc^{3+} \rightarrow d^0$

In case of La^{3+}, $4f^0$ configuration is present and in Lu^{3+}, $4f^{14}$ is present. So, there is no f-f transition, hence these ions do not appear coloured.

65.(D)

66.(C) The 5f-orbitals extend into space beyond the 6s and 6p-orbitals and participate in bonding. This is in direct contract to the lanthanides where the 4f-orbitals are buried deep inside in the atom, totally shielded by outer orbitals and thus unable to take part in bonding.

67.(D) Oxides of transition metals in low oxidation states $+2$ and $+3$ $(\mathrm{MO}, \mathrm{M_3O_4}$ and $\mathrm{M_2O_3})$ are generally basic except $\mathrm{Cr_2O_3}$ which is amphoteric in character.

Basic character generally decreases with increase in atomic number.

68.(C) **69.(C)** $\mathrm{K_2Cr_2O_7 + 2\,NaOH \rightarrow 2\,Na_2CrO_4 + H_2O}$ or $\mathrm{Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2CrO_4^{2-} + H_2O}$

70.(C) When calomel reacts with $\mathrm{NH_4OH}$, it turns black due to the formation of a mixture of mercury and ammonium basic mercury (II) chloride.

$$\underset{\text{(calomel)}}{\mathrm{Hg_2Cl_2}} + 2\,\mathrm{NH_4OH} \rightarrow \mathrm{NH_4Cl + 2\,H_2O + Hg + HgNH_2Cl}$$

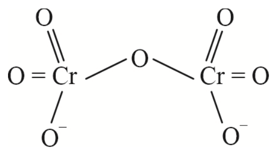
71.(B) AgBr is highly photosensitive and is used as an ingredient for photographic films and plates.

72.(B) $$2\,\mathrm{CuSO_4} + \mathrm{K_4\left[Fe(CN)_6\right]} \rightarrow \underset{\text{chocolate ppt.}}{\mathrm{Cu_2\left[Fe(CN)_6\right]}} + 2\,\mathrm{K_2SO_4}$$

73.(4) In $\mathrm{CuSO_4 \cdot 5H_2O}$, 4 water molecules are co-ordinately bonded with Cu and 1 water molecule is attached by Hydrogen bonding.

74.(3) $\mathrm{Cu^{2+} + \underset{excess}{KCN} \longrightarrow K_3[Cu(CN)_4]}$

75.(6)



76.(5) $\mathrm{I^- + MnO_4^- \xrightarrow{OH^-} IO_3^-}$

77.(3.87) $\mathrm{Cr^{3+}}: 3d^3$

$\mu = \sqrt{n(n+2)}$ $\quad n = 3$

$\mu = \sqrt{3(3+2)}$

78.(3) Most common oxidation state of Lanthanide is +3

79.(2) $\mathrm{KMnO_4 + KI \xrightarrow{H_2O} 2MnO_2 + 2KOH + KIO_3}$

80.(26)

81.(3) $\mathrm{Cr_2O_3, V_2O_3, ZnO}$

82.(5) $\mathrm{KMnO_4}$, $\mathrm{ToCl_2}$, $\mathrm{K_2Cr_2O_7}$, $\mathrm{Ce(SO_4)_2}$, $\mathrm{K_4[Fe(CN)_6]}$

83.(8)

84.(4) $\mathrm{MnF_4}$

Coordination Compounds

1.(AC) $\mathrm{Co^{3+} \longrightarrow [Ar]3d^6}$

$\mathrm{NH_3}$ is strong field ligand due to which all six electrons shifts into t_{2g} orbitals leaving e_g orbitals empty. In this way, $\mathrm{Co^{3+}}$ contains no unpaired electron and d^2sp^3 are used to form complex (diamagnetic). Similarly,

$\mathrm{Mn^{3+} \longrightarrow [Ar]3d^4 \longrightarrow}$ Paramagnetic

$\mathrm{Fe^{2+} \longrightarrow [Ar]3d^6 \longrightarrow}$ Diamagnetic

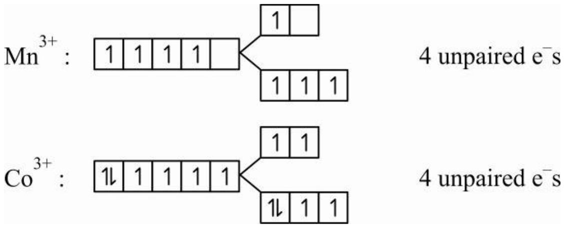
$\mathrm{Fe^{3+} \longrightarrow [Ar]3d^5 \longrightarrow}$ Paramagnetic

2.(AC) $\mathrm{Cl^-}$ and $\mathrm{F^-}$ are weak field ligand, so, these form outer orbital octahedral complexes.

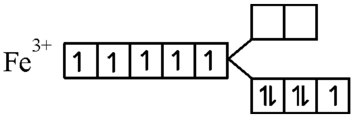
$\mathrm{[MnCl_6]^{3-} \longrightarrow Mn^{3+} \longrightarrow [Ar]d^4}$

$[FeF_6]^{3-} \longrightarrow Fe^{3+} \longrightarrow [Ar]d^5$

$[CoF_6]^{3-} \longrightarrow Co^{3+} \longrightarrow [Ar]d^6$



3.(AC) E.C of Fe = $[Ar]3d^6 4s^2$ and E.C of Fe^{3+} = $[Ar]3d^5$



Due to strong filed ligand CN^- octahedral splitting is high and the coupling of electrons takes place in t_{2g}. Out of five electrons one electron left unpaired. Thus it is d^2sp^3 hybridized and paramagnetic

4.(BC) $[Co(H_2O)_6]^{2+} \longrightarrow$ pink solution

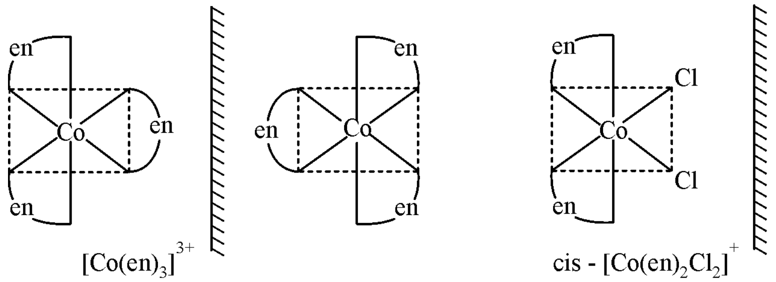
$[CoCl_4]^{2-} \longrightarrow$ deep blue solution In general, tetrahedral crystal field splitting is lower than octahedral.

5.(AC) When only one type ligand present in complex, it is called homoleptic.

6.(BD) Different type of ligand present in the complex called heteroleptic.

7.(AC)

non superimposable mirror images



$[Co(en)_3]^{3+}$ cis - $[Co(en)_2Cl_2]^+$

8.(ABC) $H_2N - CH_2 - CH_2 - NH_2$ Thus it is neutral, didentate and chelating ligand

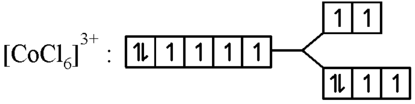
9.(AC) NO_2^- and SCN^- are ambidentate ligands, so, complexes containing these ligand will show linkage isomerism.

10.(C) Energy α 1/λ .

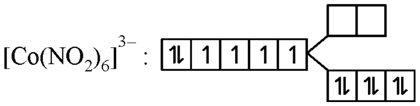
11.(A) CN^- is much more strong field ligand than H_2O. Thus, complex containing CN^- ligand has more splitting.

12.(B) In $[CoCl_6]^{3-}$ and $[Co(NO_2)_6]^{3-}$, Co is in + 3 oxidation state. E.C. of Co^{3+} = $[Ar]3d^6$.

Cl^- is weak field legend, thus

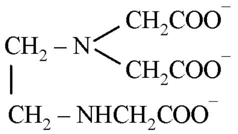


NO_2^- is strong field ligand, thus



It means $[CoCl_6]^{3-}$ contain more unpaired electrons due to which it is paramagnetic and called high spin complex.

13.(C) Ethylenediamine triacetate ion contain two N-atoms and three O-atoms as donor atoms. Thus, it contains five donor atoms



14.(D) **15.(A)** All structures contain plane of symmetry due to which no optical isomerism is possible.

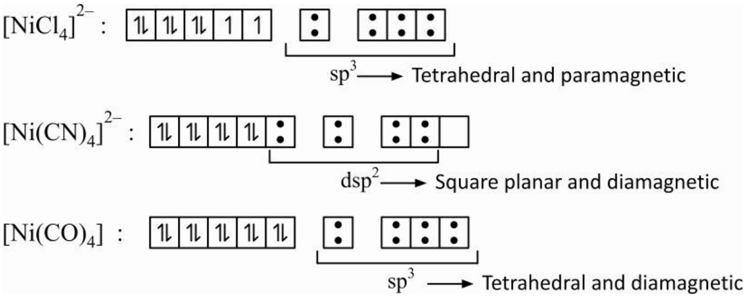
16.(A) **17.(D)** All statement are correct

18.(D) The E.C. of Cu^{2+} is $[Ar]3d^9$, in the presence of NH_3 unpaired electron jumps to higher energy level due to which it is hybridized as dsp^2 and forms square planar complex. Thus $[Cu(NH_3)_4]^{2+}$ is square planar and paramagnetic.

19.(D) **20.(C)** Alphabetical order of ligand is considered. **21.(B)**

22.(B) Ionization isomers given different ions in solution.

23.(C)

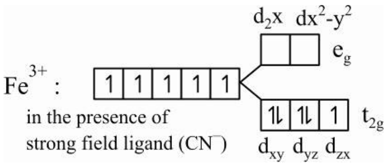


24.(A) EC of Mn:[Ar] $3d^5\ 4s^2$, the oxidation state of Mn in $[MnO_4]^-$ is Mn^{7+}, thus all the d electrons are removed from manganese. $[MnO_4]^- \longrightarrow$ no d electrons . In other cases, few d electrons left there after oxidization of metal atom.

25.(C) Fe^{2+} and Fe^{3+} contains different no of unpaired electrons, so, can be identify by measuring magnetic moment.

26.(B) In octahedral complexes, splitting of d orbital is according as given :

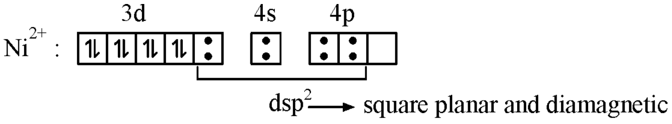
Thus d-electrons exist in d_{xy}, d_{yz}, and d_{zx}



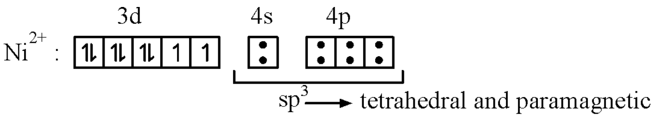
27.(ACD) In case of A, C & D, ligands are chelating

28.(A) $K_2[Ni(CN)_4]$ → Potassium tetracyanonickelate (II) $K_2[NiCl_4]$ → Potassium tetrachloronickelate (II)

29.(C) $[Ni(CN)_4]^{2-} \longrightarrow$ square planar



$[NiCl_4]^{2-} \longrightarrow$ tetrahedral



30.(A) A $\longrightarrow dsp^2$ B $\longrightarrow sp^3$

31.(B)

Ligand	L_1	L_2	L_3	L_4
Coloured region of absorbed wavelength	Red	Green	Yellow	Blue

Coloured regions of visible light (VIBGYOR) are arranged in the increasing order of wavelength or decreasing order of energy [$\because E \propto 1/\lambda$]. Therefore, $\underset{(L_1)}{E_{Red}} < \underset{(L_3)}{E_{yellow}} < \underset{(L_2)}{E_{green}} < \underset{(L_4)}{E_{blue}}$

This suggests that L_4 will absorbs higher energy wavelength followed by L_2, L_3 and L_1. Since, higher absorbed energy corresponds to greater extent of crystal field splitting and thus, higher field strength of the ligand. Hence, the increasing order of ligand strength of the four ligands is : $L_1 < L_3 < L_2 < L_4$

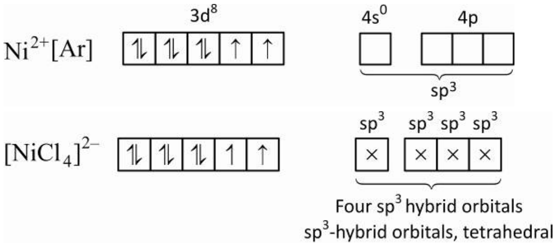
32.(C) Optical isomerism is exhibited by only those complexes which lacks elements of symmetry $[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, both the form contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

33.(B) Two Br, two (en) and one Cr are parts of complex. Charge on the complex is : $\left.\begin{array}{l} 2(Br) = -2 \\ 2(en) = 0 \\ 1(Cr) = +3 \end{array}\right\} = +1$

Thus, complex ion is $[Cr(en)_2Br_2]^+$. Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]Br$. **34.(B)**

35.(C) $[NiCl_4]^{2-}$; oxidation number of Ni, $x - 4 = -2$

$\therefore \quad x = +2, Ni_{(28)}\ [Ar]\, 3d^8, 4s^2$



Since, Cl^- is a weak ligand, thus unpaired electrons are not paired. Lone pairs from $4\ Cl^-$ are accommodated in four sp^3 hybrid orbitals.

n = unpaired electron = 2, paramagnetic

Magnetic moment (spin only) $= \sqrt{n(n+2)}$ BM $= \sqrt{8} = 2.828$ BM

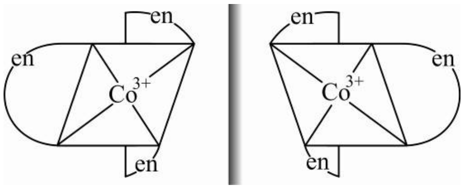
36.(B) Based on spectrochemical series, ligands arranged in increasing order of crystal field strength area as

$NH_3 < en < CN^- < CO$

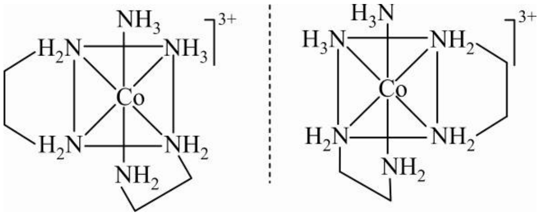
37.(C)

Complex		**Isomerism shown**
(A)	$\lvert Co(en)_3\rvert^{3+}$	Optical only
(B)	$\lvert Ni(NH_3)_5Br\rvert^{+}$	No geometrical isomer
(C)	$\lvert Co(NH_3)_2(en)_2\rvert^{3+}$	Cis and trans
(D)	$\lvert Cr(NH_3)_4(en)\rvert^{3+}$	No geometrical isomer

38.(B) Complex $[Co(en)_3]^{3+}$ has no plane of symmetry and centre of symmetry. That's why, it is optically active.



39.(D)



40.(B) Linkage isomers are caused due to the presence of ambidenate ligands $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers due to SCN, an ambidenate ligand. Thus, SCN can linked to Pd by both N as well as S through their lone pairs.

41.(D) en, $\begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array}$ is bidentate ligand

Hence, coordination number of the element E in the given complex comes out to be 6. The complex can be ionised as $[E(en)_2(C_2O_4)]\,NO_2 \longrightarrow [E(en)_2(C_2O_4)]^+\,NO_2^-$

Oxidation number $x + 0 + (-2) = +1$ $\Rightarrow$ Oxidation number, $x = 3$

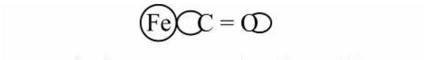
42.(A) CFSE (crystal field splitting energy) for octahedral complex, Δ_0 depends on the strength of negative ligand. Spectrochemically, it has been found that the strength of splitting is as follows

$CO > \underline{CN^-} > NO_2^- > en > \underline{NH_3} > py > NCS^- > H_2O > O^{2-} > OX^{2-} > OH^- > F^- >$

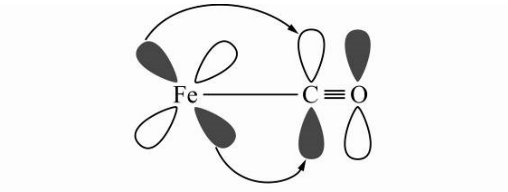
$Cl^- > SCN^- > S^{2-} > Br^- > I^-$

43.(D) Cl^- is a weak ligand but Cl^- cause the pairing of electrons with large Pt^{2+} and consequently give dsp^2 hybridisation and square planar geometry.

44.(B) $Fe(CO)_5$ is an organometallic coordinated compound in which electrons from d-orbitals of Fe are partially transferred to anti-bonding molecular orbitals $(\overset{*}{\pi})$ of CO. This type of bonding is called π - backbonding.



σ-Bond Electron Donation from CO to Fe



Electron Donation through symbol π-backbonding

Thus, $Fe(CO)_5$ possesess both σ and π - character.

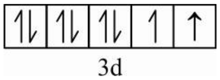
45.(D) The IUPAC name for the complex

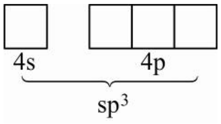
$[Co(NO_2)(NH_3)_5]Cl_2$

Pentammine nitrito-N-cobalt (III) chloride

46.(B) $_{28}\text{Ni} = [\text{Ar}]4s^2, 3d^8$

$\text{Ni}^{2+} = [\text{Ar}]3d^8$



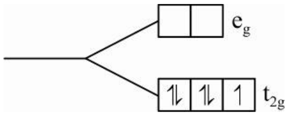


Nickel has two unpaired electrons and geometry is tetrahedral due to sp^3 hybridisation.

47.(D) **(A)** d^5 in strong field

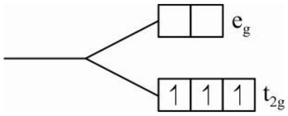
n = unpaired electron = 1

Magnetic moment = $\sqrt{n(n+2)}$ BM $= \sqrt{3}$ BM $= 1.73$ BM



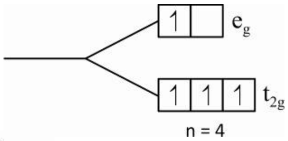
(B) d^3 in strong/weak field

Magnetic moment = $\sqrt{15} = 3.87$ BM

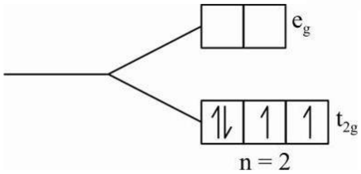


(C) d^4 in weak field

Magnetic moment = $\sqrt{24} = 4.90$ BM



(D) d^4 in strong field



Magnetic moment = $\sqrt{8} = 2.83$ BM

48.(C) $K_3[Fe(CN)_6]$

Cation Anion

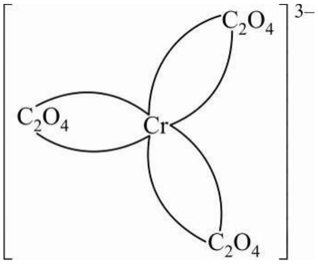
Oxidation state of Fe in anion = +3. Thus, it is potassium hexacyanoferrate (III).

49.(A)

Hybridisation		**Unpaired electrons**	**Magnetic moment**
(A)	$[Co(CN)_6]^{3-}$	d^2Sp^3 (0)	0
(B)	$[Fe(CN)_6]^{3-}$	$d^2sp^3(1)$	$\sqrt{3}$ BM
(C)	$[Mn(CN)_6]^{3-}$	d^2sp^3 (2)	$\sqrt{8}$ BM
(D)	$[Cr(CN)_6]^{3-}$	$d^2sp^3(3)$	$\sqrt{15}$ BM

Thus, least paramagnetism is (A).

50.(B)



Mirror image is not superimposable, hence optical isomerism is possible.

51.(A) Coordination number is the maximum covalency shown by a metal or metal ion. It is the maximum number of ligands attached to metal by sigma bonds or coordinate bonds.

52.(D) All the given compounds, exhibits geometrical (cis and trans isomers) but only cis isomer of $[Co(en)_2Cl_2]^+$ posses optical isomer (d and l) due to the presence of symmetrical didentate, en [ethylediamine].

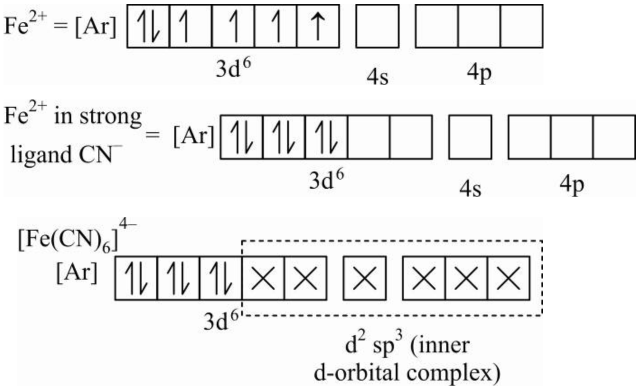
53.(A) Number of unpaired electrons in $[Fe(CN)_6]^{4-}$ is zero.

Thus, magnetic moment = $\sqrt{n(n+2)}$ = BM (n = unpaired electrons)

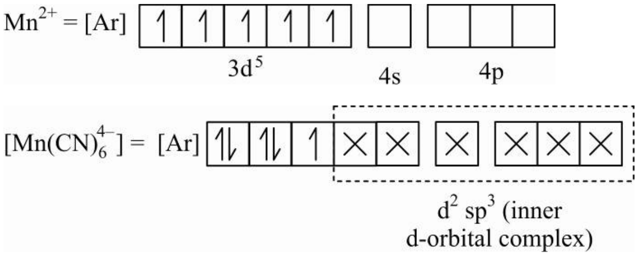
n in $[MnCl_4]^{2-} = 5, \sqrt{35}$ BM

n in $[CoCl_4]^{2-} = 3, \sqrt{15}$ BM

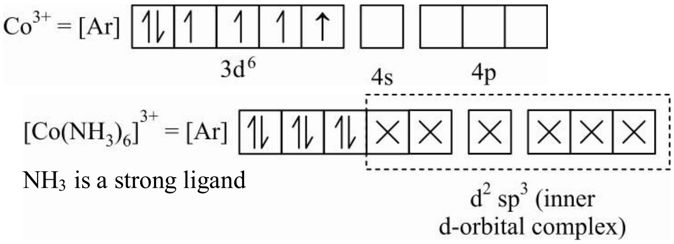
54.(D) **(A)**



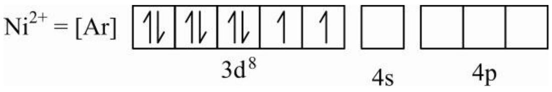
(B)



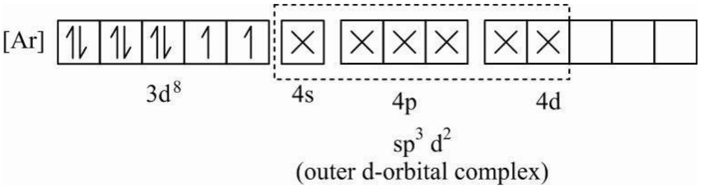
(C)



(D)



In this case also, NH_3 is a strong ligand but electrons remain unpaired, since only one orbital is left vacant in 3d. Thus, $[Ni(NH_3)_6]^{2+}$



55.(A) The oxidation state of nickel is $[Co(NH_3)_5Cl]\,Cl_2 \rightleftharpoons \underbrace{[Co(NH_3)_5Cl]^{2+} + 2Cl^-}_{\text{three ions}}$

56.(B) The oxidation state of nickel is

$$K_4[Ni(CN)_4] \longrightarrow 4K^+ + [Ni(CN)_4]^{4-}$$
$$[Ni(CN)_4]^{4-} \longrightarrow x + 4(4x-1) = -4$$
$$x - 4 = -4 \text{ or } x = 0$$

57.(B) $[Cr(NH_3)_5NO_2]\ Cl_2$ (Pentamminenitrito chromium (III) chloride) exhibits linkage isomerism as $-NO_2$ is ambidentate ligand. Isomer is $[Cr(NH_3)_5ONO]\ Cl_2$. This complex can exhibit ionization isomerism also.

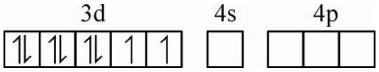
58.(C) A square planar geometry is the result of dsp^2 hybridisation where inner d sub-shell ($d_{x^2-y^2}$ orbital) participates.

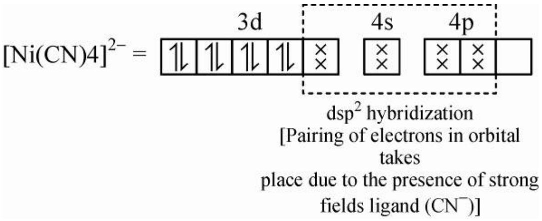
59.(C) Stability of complex increases with increase in charge on the central metal ion and with increase in basic strength of ligand. In $[Fe(CN)_6]^{3-}$, oxidation state of Fe is +3 and basicity of CN^- is higher than OH^-, Cl^- and H_2O.

60.(D) $\left[Ni(CN)_4\right]^{2-}$:

Oxidation number of $Ni = +2$

Electronic configuration of Ni^{2+} : $3d^8 4s^0$





61.(D) $\left[M(en)_2(C_2O_4)\right]Cl$:

Oxidation number of metal $= +3$; Coordinate number of metal $= 6$

$\therefore$ Sum of oxidation number and coordination number $= 3 + 6 = 9$

62.(C) For octahedral complexes, coordination number is 6.

Hence, $CoCl_3 \cdot 3NH_3$ i.e., $\left[Co(NH_3)_3Cl_3\right]$ will not ionize and will not give test for Cl^- ion with silver nitrate.

63.(C) $\left[Co(CN)_6\right]^{3-}$, oxidation number of $Co = +3$

$Co^{3+} = 3d^6$

As CN^- is a strong field ligand, so all electrons will be paired up and complex will be low spin complex.

64.(B) H_2O is a weak field ligand, hence $\Delta_o <$ pairing energy.

$CFSE = (-0.4x + 0.6y)\Delta_o$

Where, x and y are number of electrons occupying t_{2g} and e_g orbitals respectively.

For $\left[Fe(H_2O)_6\right]^{3+}$ complex ion,

$Fe^{3+}(3d^5) = t_{2g}^3\, e_g^2 = -0.4\times3+0.6\times2 = 0.0$ or 0 Dq

65.(B)

66.(B) $CFSE = (-0.4x+0.6y)\Delta_o$

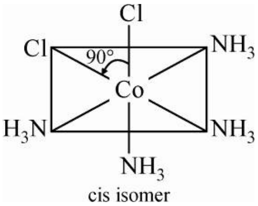
where x = Number of electrons occupying t_{2g} orbitals

y = Number of electrons occupying e_g orbitals

$= (-0.4\times3+0.6\times1)\Delta_o$ $\quad [\because \text{High spin } d^4 = t_{2g}^3\, e_g^1]$

$= (-1.2+0.6)\Delta_o = -0.6\,\Delta_o$

67.(B)



cis isomer

68.(C) Chelating ligands having conjugated double bonds form more stable six membered rings **69.(B)**

70.(C) $Co^{2+} = 3d^7$

Bromine is a weak ligand but it is known that all tetrahedral complexes are high spin regardless of the splitting power of the ligand. Therefore it has 3 unpaired electrons. So it is paramagnetic in nature.

71.(C) $Ni(dmg)_2$ is square planar in structure not tetrahedral.

72.(A) The presence of positive charge on the metal carbonyl would resists the flow of the metal electron charge to π^* orbitals of CO. This would increase the CO bond order and hence CO in a metal carbonyl cation would absorb at a higher frequency compared to its adsorption in a neutral metal carbonyl.

73.(D) O.S of Ti in the complex $\left[Ti(NH_3)_6\right]^{3+}$

$Ti^{3+} = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^1$

Number of unpaired electron in d-orbital is one.

$= x+2\times0+2\times(-1)+2\times0 = +1$

$\therefore \quad x = +3$

$V^{3+} = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^2$

Number of unpaired electron in d-orbitals is two

O.S of Fe in the given complex is $+2$ $\quad\therefore\quad Fe^{2+} = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^6$

Number of unpaired electron in d-orbitals is four

O.S of Co in the given complex $\left[Co(ox)_2(OH)_2\right]^- = x+2\times(-2)+2\times(-1) = -1 = x-4-2 = -1$

$\therefore \quad x = +5$

(not possible, common ox. number of $Co = +2, +3, +4$)

$Co^{5+} = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^4$

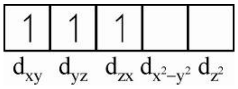
It should be an inner orbital complex (d^2sp^3 hybridization) containing only one unpaired electron. So the complex having highest paramagnetism would be the complex of iron containing four unpaired electrons.

74.(D) Magnetic moment $= \sqrt{n(n+2)}$

$3.83 = \sqrt{n(n+2)}$ or $(3.83)^2 = n(n+2)$ or $14.6689 = n^2 + 2n$

On solving the equation, $n = 3$

$Cr^{3+} \to [Ar]3d^3$



75.(A) $Al(OC_2H_5)_3$ contains bonding through O and thus it does not have metal-carbon bond.

76.(D) π-bonded organometallilc compound includes organometallic compounds of alkenes, alkynes and some other carbon containing compounds having electrons in their p orbitals.

77.(D) Copper being more electropositive readily precipitate silver from their salt (Ag^+) solution.

$Cu + 2AgNO_3 = Cu(NO_3)_2 + Ag$

In $K[Ag(CN)_2]$ solution a complex anion $[Ag(CN)_2]^-$ is formed so Ag^+ ions are less available in the solution and Cu cannot displace Ag from this complex ion.

78.(D) $[Cr(SCN)_2(NH_3)_4]^+$ shows linkage, geometrical and ionisation isomerisms.

79.(D) The isomers of the complex compound $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ are :

(i) $[Cu(NH_3)_3Cl][Pt(NH_3)Cl_3]$ **(ii)** $[Pt(NH_3)_3Cl][Cu(NH_3)Cl_3]$

(iii) $[Pt(NH_3)_4][CuCl_4]$

80.(2) $Na_4[Fe(CN)_5(NOS)]$

$4 + x - 5 - 1 = 0$

$x = 2$

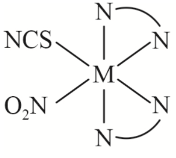
81.(5) $26 + 2x = 36$

$x = 5$

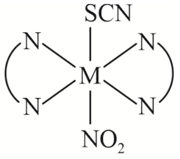
82.(5) 0.01 mole $MBr_4 \cdot xNH_3$ gives 0.03 mole yellow precipitate. It indicates 3 Br are present outside co-ordination sphere. Complex is $[M(NH_3)_5Br] \cdot Br_3$

83.(6) Secondary valency means co-ordination number.

84.(3)



Cis
(Optically active)



Trans

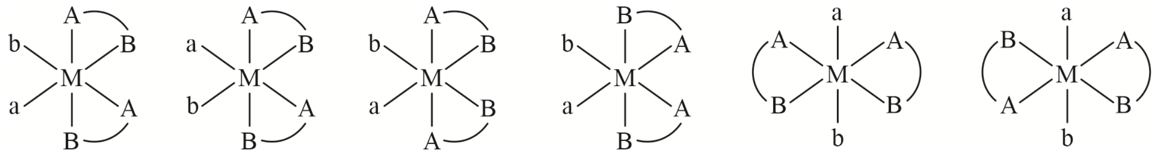
85.(2) $[Fe(CN)_6]^{3-}$: Fe^{3+}

: $3d^5$

$CFSE = (-0.4 \times 5)\Delta_o$

$= -2\Delta_o$

86.(6)



87.(0) $[Co(H_2O)_6]^{3+}$

Co^{3+} : $3d^6$

It is low spin complex No. of unpaired electron = 0

88.(0) - $Ni(CO)_4$

- sp^3 hybridized

No. of ‘d’ orbitals used in hybridization = 0

89.(4) Fe^{2+} : $3d^4$

No. of unpaired electron in high spin complex = 4

No. of unpaired electron in low spin complex = 0

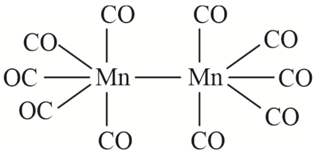
Difference = 4

90.(3) $CoCl_4^{2-}, [Fe(H_2O)_6]^{3+}, [Mn(H_2O)_6]^{2+}$

91.(1) Total number of EDTA required to form 1 Octahedral complex is 1

92.(3) dien forms 2 Ring and en form 1 ring

93.(0)



94.(6) Number of m M – M bonds in $Ir_4(CO)_{12}$ is 6

Total electron count $= (77 \times 4) + (12 \times 2) = 332$

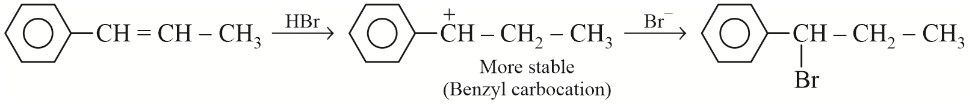
Expected electron cound $= 86 \times 4 = 344$

Number of M–M bonds $= \dfrac{344 - 332}{2} = 6$

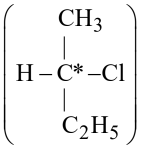
Organic Halides & Organic Concepts

1.(A) In case of optically active alkyl halides, S_N1 reaction is accompanied by racemisation. The carbocation formed in the slow step being sp^2 hybridised is planar and attack of nucleophile may take place from either side resulting in a mixture of products, one having the same configuration and other having inverted configuration. Though isomer corresponding to inversion is present in slight excess.

2.(C)



3.(D) Due to chirality



$$\left(\begin{array}{c} CH_3 \\ | \\ H-C^*-Cl \\ | \\ C_2H_5 \end{array}\right)$$

, only compound (D) will undergo racemisation.

4.(B) I and II are staggered and eclipsed conformers, respectively of 2, 3-Dibromobutane.

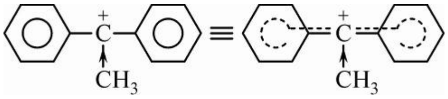
5.(C) More nucleophilic fluoride will form transition state easily with R-I. For more nucleophilic fluoride there should be poor ion pairing between M^+ and F^- hence metal ion should be Rb^+. i.e., larger size cation.

6.(C) Observing the product given, if reaction were S_N1, there would have been the formation of carbocation resulting in rearrangement. Since, in these reactions there is no rearrangement hence both should follow S_N2 mechanism.

7.(C) S_N1 reactions proceed via the formation of a carbocation intermediate.

More stable is the carbocation more reactive is the halide towards S_N1.

In $C_6H_5C^+(CH_3)(C_6H_5)$ carbocation, the two phenyl rings by their $+R$ effect and $-CH_3$ by its $+I$ effect stabilises the positive charge and make it stable.



8.(A) I < II < IV < III

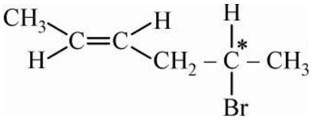
The order of reactivity is dependent on the stability of the intermediate carbocation formed by cleavage of $C-X$ bond. The 3° carbocation (formed from III) will be more stable than its 2° counter part (formed from IV). The aryl halide has a double bond character in the $C-X$ bond which makes the cleavage more difficult. But II will be more reactive than I (*will not give S_N reaction*) due to the presence of the electron withdrawing $-NO_2$ group (at *o* and *p* positions). $C-X$ bond becomes weak and undergoes Nucleophilic substitution reaction (*activated S_N2 reaction*).

9.(C)

$$C_6H_5CH_2Br \xrightarrow{Mg/ether} C_6H_5CH_2MgBr \xrightarrow{H_3O^+} C_6H_5CH_3 + Mg\begin{array}{l} Br \\ OH \end{array}$$

10.(D) $\overset{\ominus}{O}H$ acts as $Na^{\ominus}$ and $X^{\ominus}$ acts as leaving group

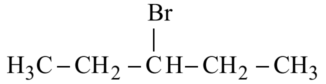
11.(C) The given compound may be written as :



Both geometrical isomerism (cis-trans form) and optical isomerism is possible in the given compound.

12.(A) Meso compound does not rotate plane polarised light. Compound which contains tetrahedral atoms with four different groups but the whole molecule is achiral known as *meso compound.* It possesses a plane of symmetry and is optically inactive. One of the symmetric carbon atoms turns the plane of polarised light to the right and other to the left to the same extent so that the rotation due to upper half is compensated by the lower half, i.e., internally compensated, and finally there is no rotation of plane polarised light.

13.(ABC)



$$H_3C-CH_2-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_2-CH_3$$

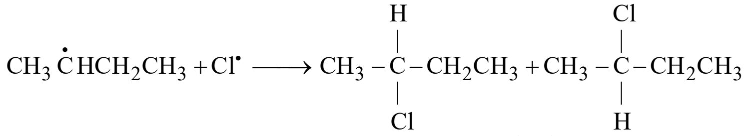
Due to absence of asymmetric carbon atom, (D) is achiral while others are clearly chiral.

14.(A) These two are non-superimposable mirror images of each other, so they are enantiomers, while others are not.

15.(B) Chlorination of n-butane takes place via free radical formation. i.e. $Cl_2 \rightarrow Cl^\bullet + Cl^\bullet$

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl^\bullet} CH_3\dot{C}HCH_2CH_3 + HCl$$

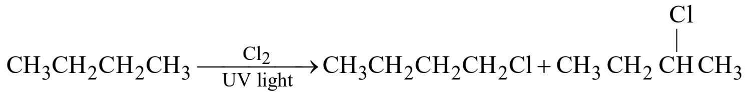
sp^2-hybrid planar shape intermediate and $Cl^\bullet$ may attack from either side to give



$$CH_3\dot{C}HCH_2CH_3 + Cl^\bullet \longrightarrow CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_2CH_3 + CH_3-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2CH_3$$

Racemic mixture
(Mixture of 50% d-form and 50% ℓ-form)

16.(A) Cl_2 reacts with saturated hydrocarbons in the presence of light.



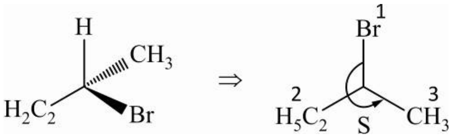
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{UV light}]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3$$

17.(A) Density $\propto$ Molecular wt. Thus order of density is $I < II < III < IV$

18.(C) Branching reduces surface area of molecule, it causes decrease in dispersion forces and reduces its boiling point.

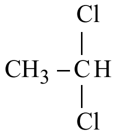
19.(B) Four different groups attached to a carbon is asymmetric carbon. Thus I, II and III contain asymmetric carbon atom.

20.(A) The configuration of given compound is 'S'. Interchange of $-CH_3$ and $-C_2H_5$ in given compound produces its enantiomer and it matches with compound given in option (A).



21.(C) Br^1 is connected with sp^2 carbon atom, so, it is vinylic. Br^2 is connected with sp^3 carbon atom which is at alpha position of sp^2 carbon atom, so, it is allylic.

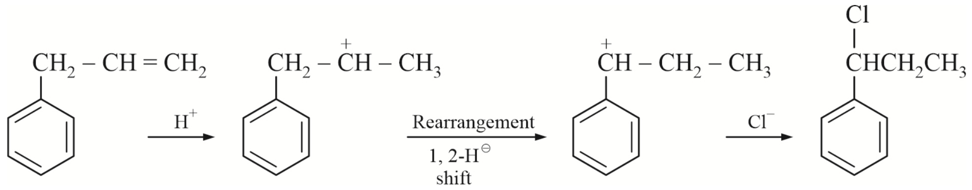
22.(B) Ethylidine is

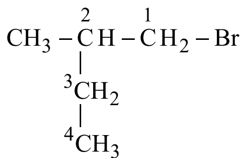


$$CH_3-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}H$$

23.(D) $C-I$ bond is weakest which breaks in rate determining step in S_N1, so, iodoalkane reacts fastest.

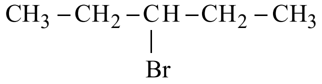
24.(D) 2°- benzylic carbocation is much more stable than 2° -carbocation, it rearranges very fast to give benzylic carbocation.



25.(C) 

$$CH_3-\underset{\underset{\underset{\underset{{}^4CH_3}{|}}{{}^3CH_2}}{|}}{\overset{2}{C}H}-\overset{1}{C}H_2-Br$$

1-Bromo-2-methylbutane

26.(B) 

$$CH_3-CH_2-\underset{\underset{Br}{|}}{C}H-CH_2-CH_3$$

3-bromopentane

27.(C) Excess of ammonia prohibit the formation of more substituted amine, so, primary amine is the major product.

28.(A) $C_6H_5CH_2Br$ produces benzylic carbocation, so, reaction occurs through S_N1.

29.(B) b and c are asymmetric carbon since they are sp^3 hybridised and contain four different groups.

30.(A) If S_N1 takes place at chiral carbon, it produces racemic mixture.

31.(C) $-NO_2$ groups helps to reduce electron density in benzene ring, so, the ring becomes prone to attack by nucleophilic. If $-NO_2$ is attached at o- or p-position in haloarenes, nucleophile substitute halogen group from benzene ring. Thus, order is $I < III < II$.

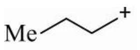
32.(D) $I < II < III$

33.(C) $-CH_3$ group suppress nucleophilic substitution on benzene ring, but increases its activity towards electrophilic substitution. Thus, order is $III < II < I$

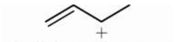
34.(A) Boiling point $\propto$ Molecular weight

35.(D) Boiling point $\propto$ Molecular weight so, Boiling point order is: Bromobenzene > 1-bromobutane > 1-bromopropane > 1- bromoethane

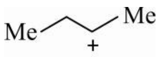
36.(A) In S_N1, carbocation are produced as



1° Carbocation



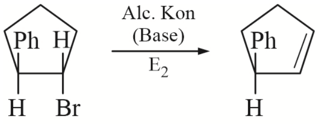
2° Allylic Carbocation



2° Carbocation

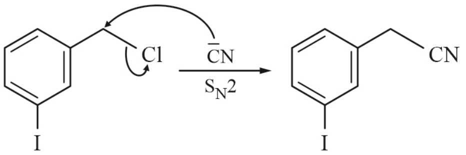
Since allylic carbocation are more stable, the order of S_N1 reaction is $II > III > I$

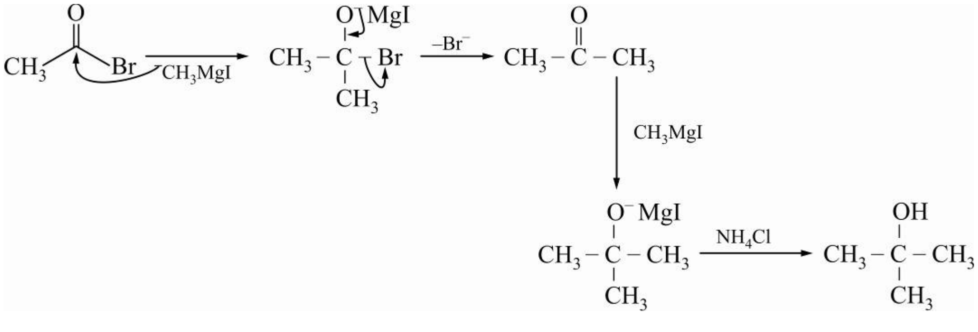
37.(D) CH_3Cl reacts only through S_N2 mechanism.

38.(D) 

3-Phenyl Cyclopentane

39.(A) Nucleophilicity order is $IV > III > I > II$

40.(D) 

41.(C) 

42.(B) Chlorobenzene + $CCl_3CHO \xrightarrow{H_2SO_4} DDT$

43.(D) Carbylamine reaction takes place which converted $-NH_2$ group into $-NC$ (isocyanide)

44.(A) Wurtz reaction : It involved the reaction of alkyl halides with Na in ethanol solution to form higher alkenes.

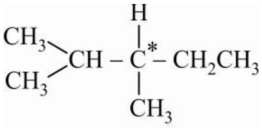
$$2R-X+2Na \rightarrow R-R+2NaX$$

In the given problem, $C_4H_9Cl+Na \xrightarrow{\text{ethanol}} C_4H_9 \cdot C_4H_9+2\,NaCl$

Compound A has to be *tert*-butyl chloride as in this all $-CH_3$ group have primary hydrogen only and able to give only one monochloro derivative.

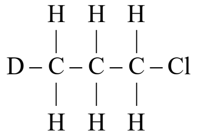
$$(CH_3)_3CC(CH_3)_3 \xrightarrow[hv]{Cl_2} CH_2Cl(CH_3)_2C-C(CH_3)_3.$$

45.(A) Organic compound exhibits the property of enentiomerism (optical isomerism) only when molecules are chiral. Most chiral compounds have a chiral centre, which is an atom bonded to four different atoms or groups.



2, 3-Dimethyl pentane

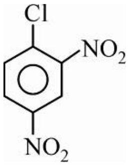
46.(ABD)



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

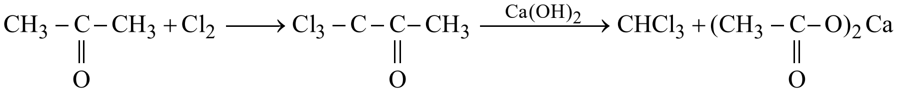
The above compound has no chiral 'C'-atom. All the 'C' atoms are attached to two identical 'H' atoms, so they are not asymmetrical.

47.(B) Withdrawal of electrons by $-NO_2$ groups from ortho/para positions causes easier removal of $-Cl$ atom due to the development of positive charge on o- and p- positions (*activated S_N2 reaction*).



48.(B) $CaOCl_2+H_2O \rightarrow Ca(OH)_2+Cl_2$

Cl_2, so obtained acts as a mild oxidising as well as chlorinating agent.



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3+Cl_2 \longrightarrow Cl_3-C-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{Ca(OH)_2} CHCl_3+(CH_3-\underset{\underset{O}{\|}}{C}-O)_2Ca$$

49.(B) $C_6H_5Cl \xrightarrow{Mg} C_6H_5MgCl \xrightarrow{CH_3CH_2OH} C_6H_6+CH_3CH_2OMgCl$

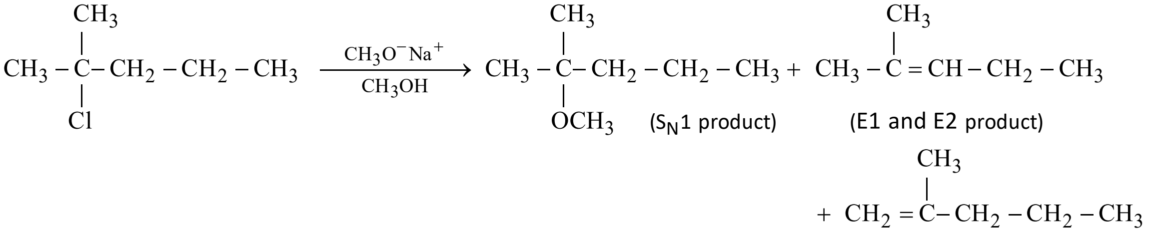
50.(A) In 2, 4, 6-trinitrochlorobenzene, three NO_2 groups (being deactivating) at *o* and *p*-positions make it most easy to get hydrolysed.

51.(D) Carbonyl chloride ($COCl_2$).

52.(A) Phenetole is formed when sodium phenoxide is heated with ethyl iodide. (S_N2 : Williamson's synthesis)

$$C_6H_5ONa+C_2H_5I \xrightarrow{\Delta} \underset{\text{Phenetole}}{C_6H_5OC_2H_5}$$

53.(D)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2-CH_2-CH_3 \xrightarrow[CH_3OH]{CH_3O^-Na^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}-CH_2-CH_2-CH_3 \ (S_N1\text{ product}) + CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3 \ (\text{E1 and E2 product})$$

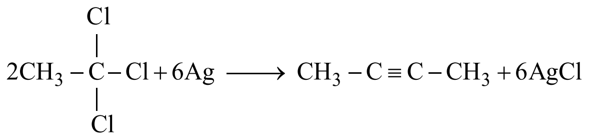
$$+\ CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-CH_3$$

54.(D) Alkyl fluorides are generally formed by swartz Reaction.

$$R-X \xrightarrow{AgF/Hg_2F_2/CoF_2} R-F+\text{ppt.}$$

$$X=Cl/Br$$

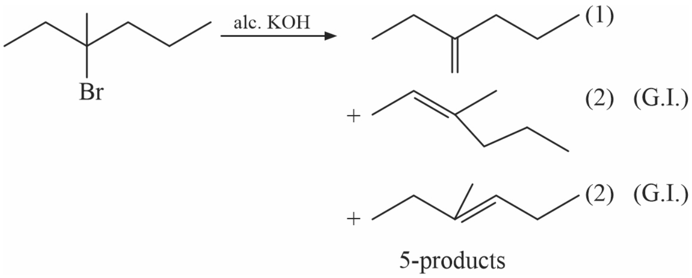
55.(D)



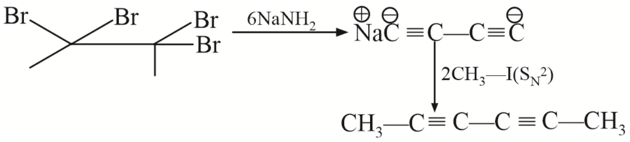
$$2CH_3-\underset{Cl}{\overset{Cl}{C}}-Cl+6Ag \longrightarrow CH_3-C\equiv C-CH_3+6AgCl$$

56.(9) Rate of S_{N^2} = K [Substrate] [Nu]

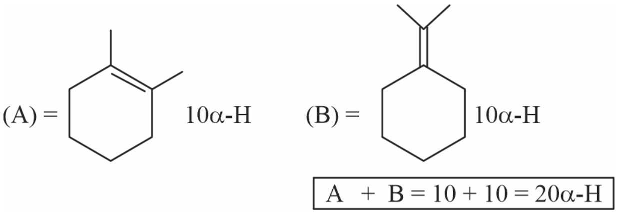
57.(5)



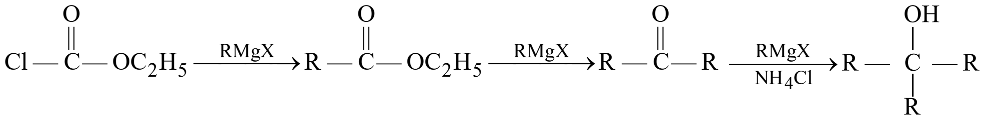
58.(8)



59.(20)

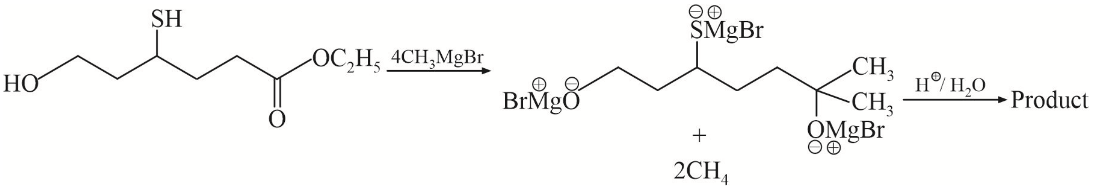


60.(3)

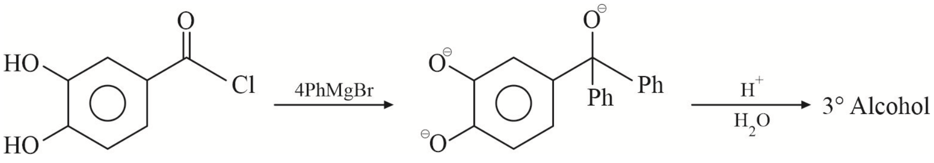


$$Cl-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{RMgX} R-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{RMgX} R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[NH_4Cl]{RMgX} R-\underset{R}{\overset{OH}{C}}-R$$

61.(4)

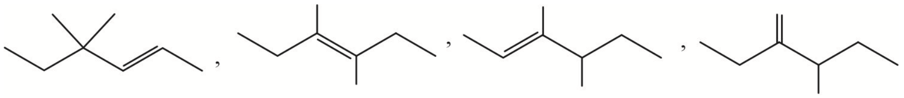


62.(4)



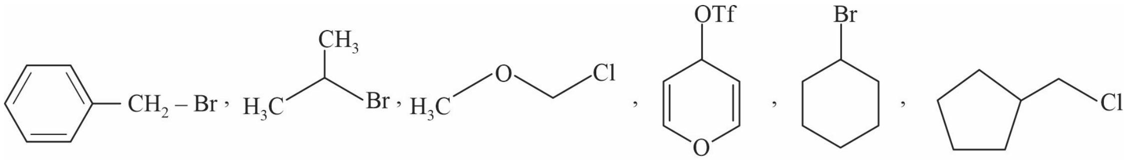
63.(4) a, c, e, g

64.(7)



Both cis-trans form   Both cis-trans form   Both cis-trans form

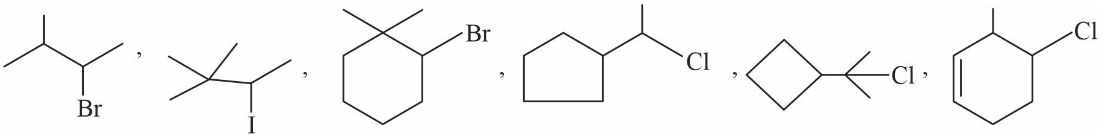
65.(6)



66. **(i)** (5) c, d, e, f, h
(ii) (3) b, c, f
(iii) (4) a, g, i, j

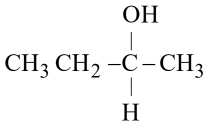
67. **(i)** (5) a, b, c, h, i
(ii) (2) g, j

68.(6)



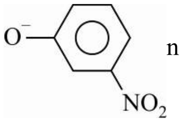
Alcohols, Phenols & Ethers

1.(A) Only secondary alcohol can be chiral



$$CH_3CH_2-\underset{H}{\overset{OH}{C}}-CH_3$$

2.(B) In general, ROH is weaker acid than H_2O, so RO^- is the stronger base than HO^-. In $C_6H_5O^-$ &



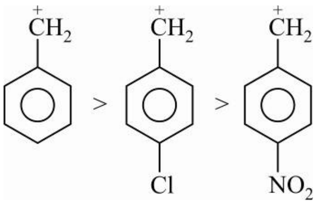
negative charge is delocalised, so these are weaker bases.

3.(B) Nitrophenol is more acidic than alcohol because $-NO_2$ group withdraws electrons through –I effect and –R effect. In case of o-methyl phenol and o-methoxy phenol, $-CH_3$ and $-OCH_3$ group donates electrons through +H and +R respectively, so acidic strength of phenol is decreased.

4.(D) $-Cl$ inductively withdraws electron at meta position, so makes m-chlorophenol more acidic.

5.(B) $-NO_2$ at ortho and para position is most effective to withdraw electrons from $-OH$ group, so, it is most acidic. $-OCH_3$ group denotes electron most effectively at ortho and para position, so, it decreases acidic strength most when $-OCH_3$ is attached at para position. So order is b > d > a > c > e.

6.(C) Since S_N1 passes through formation of carbocation (which is rate determining step), reaction is fastest in which most stable carbocation is formed.



Thus reactivity order is $C_6H_5CH_2OH > Cl-C_6H_5CH_2OH > O_2N-C_6H_5CH_2OH$

7.(A) Boiling point $\propto$ molecular wt $\propto \dfrac{1}{\text{branching}}$

Thus order is $\text{propan}-1-\text{ol} < \text{butan}-2-\text{ol} < \text{butan}-1-\text{ol} < \text{pentan}-1-\text{ol}$

8.(ABC) Reduction of RCHO can be done by H_2/Pd, $LiAlH_4$ and $NaBH_4$ **9.(ABC)**

10. (ACD) CrO_3/ An hydrous medium,  or Heat in presence of Cu at 573K

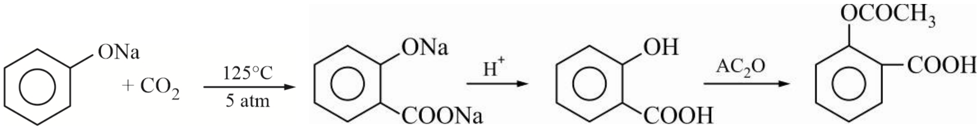
Oxidises primary alcohol into aldehyde

11.(AC) phenol $\xrightarrow[\text{water}]{Br_2}$ decolourises Br_2 water ethanol $\xrightarrow[\text{water}]{Br_2}$ no reaction

phenol $\xrightarrow{FeCl_3}$ voilet colour $C_2H_5OH \xrightarrow{FeCl_3}$ reaction

12.(D) **13.(A)** **14.(D)** **15.(D)** **16.(C)** **17.(C)** **18.(C)**

19.(A)



20.(D) PCC is most suitable to convert primary alcohol into aldehydes

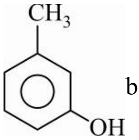
21.(C) $-NO_2$ is strong electron withdrawing group $-OCH_3$ is strong electron donating group.
Thus order is III > I > II > IV

22.(B) Tertiary alcohol reacts fastest with Lucas reagent by S_N1 mechanism **23.(A)** **24.(B)**

25.(A) In basic conditions C = C is not reduced.

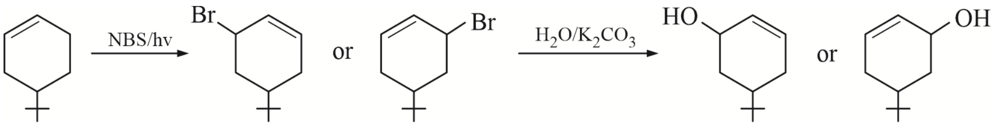
26.(D) KBr and $KBrO_3$ produces Br_2 in acidic medium which convert phenol into 2, 4, 6 tribromophenol.

27.(B) p – nirtophenol > m – nitrophenol > phenol > cresol

28.(A)  both ortho and para positions relative to –OH group are free for bromination.

29.(B) $CHCl_3 + NaOH$ produces carbene $(:CCl_2)$ which reacts with phenol.

30.(A)



NBS is used for allylic bromination.

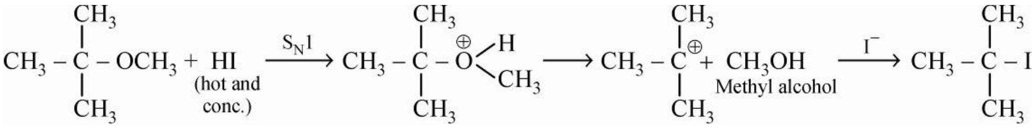
31.(D) 1° and 2° alcohols react with HCl in presence of anhydrous $ZnCl_2$ as catalyst while in case of 3° alcohols $ZnCl_2$ is not required.

32.(ABD) The reaction is as follows :

$$\text{Acid} + NaHCO_3 \longrightarrow \underset{\text{(soluble)}}{\text{Sodium salt of acid}} + H_2CO_3$$

Among all the given compounds, o-nitrophenol is weaker acid than HCO_3^-. Hence, it does not react with $NaHCO_3$.

33.(AC)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3 + \underset{\text{(hot and conc.)}}{HI} \xrightarrow{S_N1} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{O}\genfrac{}{}{0pt}{}{H}{CH_3} \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{I^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

Option (C) is obviously correct.

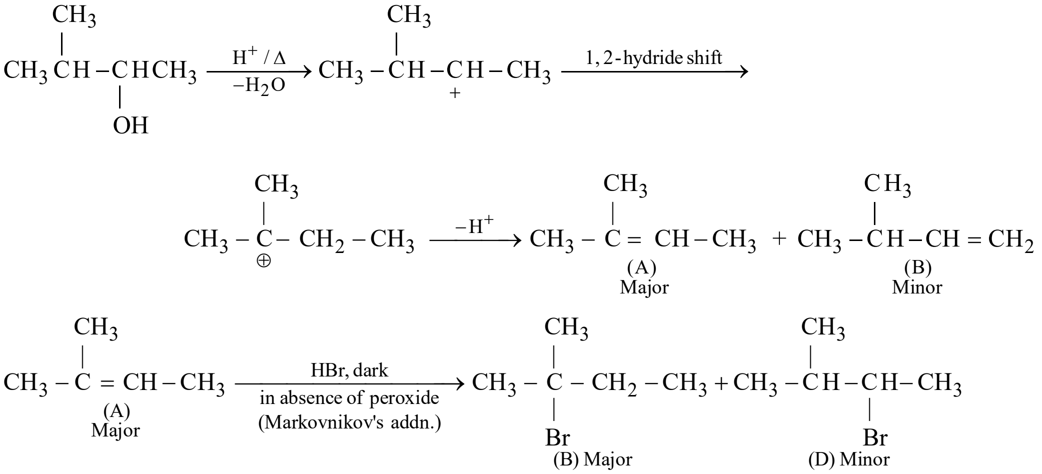
34.(B) The iodoform test is positive for alcohols with formula $R-CHOH-CH_3$ (apart from ethyl alcohol). Among $C_6H_{14}O$ isomers, the ones with positive iodoform test are :

I. $\underset{\text{2-Hexanol}}{CH_3-CH_2-CH_2-CH_2-CHOH-CH_3}$ **II.** $\underset{\text{3-Methyl-2-Pentanol}}{CH_3-CH_2-CH(CH_3)-CHOH-CH_3}$

III. $\underset{\text{4-Methyl-2-Pentanol}}{(CH_3)_2CH-CH_2-CHOH-CH_3}$ **IV.** $\underset{\text{3,3-Dimethyl-2-butanol}}{(CH_3)_3C-CHOH-CH_3}$

35.(B)

36.(B)



$$CH_3\overset{CH_3}{CH}-\underset{OH}{CH}CH_3 \xrightarrow[-H_2O]{H^+/\Delta} CH_3-\overset{CH_3}{CH}-\underset{+}{C}H-CH_3 \xrightarrow{1,2\text{-hydride shift}}$$

$$CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{-H^+} \underset{\text{(A) Major}}{CH_3-\overset{CH_3}{C}=CH-CH_3} + \underset{\text{(B) Minor}}{CH_3-\overset{CH_3}{CH}-CH=CH_2}$$

$$\underset{\text{(A) Major}}{CH_3-\overset{CH_3}{C}=CH-CH_3} \xrightarrow[\text{in absence of peroxide (Markovnikov's addn.)}]{\text{HBr, dark}} \underset{\text{(B) Major}}{CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2-CH_3} + \underset{\text{(D) Minor}}{CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3}$$

37.(A) III > II > IV > I

Since phenols and carboxylic acids are more acidic than aliphatic alcohols, we find that cyclohexanol (I) is least acidic. Out of the two given phenols, III (picric acid) is more acidic than IV. This is because of the presence of three highly electron withdrawing $-NO_2$ groups on the benzene ring which makes the $O-H$ bond extremely polarized. This facilities the release of H as H^+. Thus, III > IV. Picric acid has a pK_a value of nearly 1 so it is most acidic (*even more acidic than all aliphatic acids*).

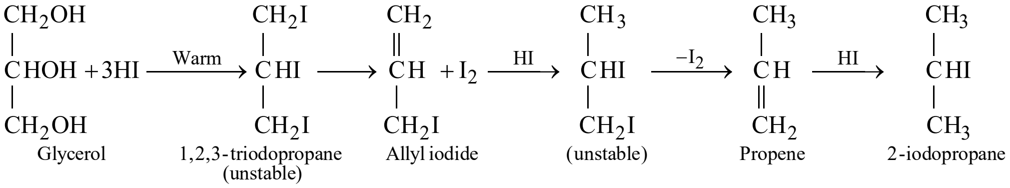
In acetic acid the electron withdrawing $-\overset{\overset{\displaystyle O}{||}}{C}-$ in the $-COOH$ group polarises the $O-H$ bond and increases the acidic strength. Acetic acid is therefore more acidic than phenol or cyclohexanol.

∴ The order is III > II > IV > I.

38.(A) In phenols, the presence of electron releasing groups decrease the acidity, whereas presence of electron withdrawing groups increase the acidity, compared to phenol. Among the meta and para-nitrophenols, the letter is more acidic as the presence of $-NO_2$ group at para position stabilises the phenoxide ion to a greater extent than when it is present at meta position. Thus, correct order of acidity is :

$$\underset{(iv)}{\text{Para - nitrophenol}} > \underset{(iii)}{\text{meta - nitro}} > \underset{(i)}{\text{phenol}} > \underset{(ii)}{\text{methyl phenol}}$$

39.(A)

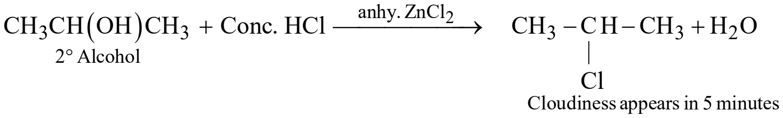


$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}} + 3HI \xrightarrow{\text{Warm}} \underset{\substack{\text{1,2,3-triodopropane}\\\text{(unstable)}}}{\begin{matrix}CH_2I\\|\\CHI\\|\\CH_2I\end{matrix}} \longrightarrow \underset{\text{Allyl iodide}}{\begin{matrix}CH_2\\\|\\CH\\|\\CH_2I\end{matrix}} + I_2 \xrightarrow{HI} \underset{\text{(unstable)}}{\begin{matrix}CH_3\\|\\CHI\\|\\CH_2I\end{matrix}} \xrightarrow{-I_2} \underset{\text{Propene}}{\begin{matrix}CH_3\\|\\CH\\\|\\CH_2\end{matrix}} \xrightarrow{HI} \underset{\text{2-iodopropane}}{\begin{matrix}CH_3\\|\\CHI\\|\\CH_3\end{matrix}}$$

40.(C) $\underset{1^\circ \text{ Amine}}{CH_3CH_2CH_2CH_2NH_2} \xrightarrow[CHCl_3]{\text{KOH (alc.)}} \underset{\text{Disagreeable smell}}{CH_3CH_2CH_2CH_2NC} + 3KCl + 3H_2O$

$CH_3C \equiv CH + \text{Amm.}AgNO_3 \longrightarrow \underset{\text{While ppt.}}{CH_3C \equiv \bar{C}Ag^+} \downarrow + HNO_3$

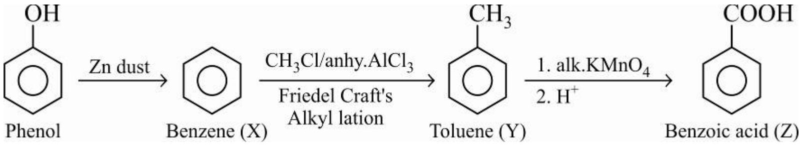
$CH_3CH_2COOCH_3 + NaOH \xrightarrow{\text{Heat}} CH_3CH_2COONa + CH_3OH$



$$\underset{2^\circ \text{ Alcohol}}{CH_3CH(OH)CH_3} + \text{Conc. HCl} \xrightarrow{\text{anhy. }ZnCl_2} \underset{\text{Cloudiness appears in 5 minutes}}{CH_3-\underset{\substack{|\\Cl}}{C}H-CH_3} + H_2O$$

(Lucas test for 2° alcohols)

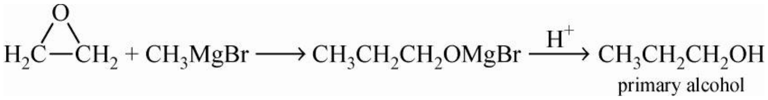
41.(B)



42.(C) The alkyl iodide produced depends on the nature of the alkyl groups. If one group is Me and the other a primary or secondary alkyl group, it is methyl iodide which is produced. This can be explained on the assumption that the mechanism is S_N2, and because of the steric effect of the larger group, I^- attacks the smaller methyl group.

When the substrate is a methyl *tert*-alkyl ether, the products are *tert*-R-I and MeOH. This can be explained by an S_N1 mechanism, the carbocation produced being 3° and since tertiary carbocation is more stable than a primary or secondary carbocation.

43.(A)

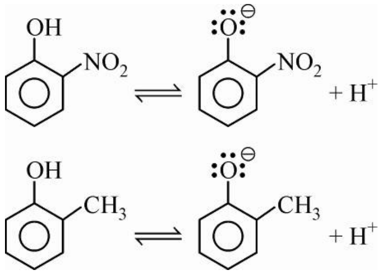


44.(A) With HI, a mixture of alkyl iodide and alcohol is formed. In the case of mixed ethers, the halogen atom attaches to a smaller via S_N2 path as none of alkyl groups is 3°

$$CH_3OCH(CH_3)_2 + HI \rightarrow CH_3I + (CH_3)_2CHOH$$

45.(C) Phenols are much more acidic than alcohols, due to the stabilisation of phenoxide ion by resonance.

(C) $-NO_2$ is the electron withdrawing group (via –I and –R effect) and helps in stabilizing the negative charge on the oxygen hence equilibrium shifts in forward direction. Hence it is most acidic.



(D) $-CH_3$ is the electron donating group (via +I and hyperconjugation effect), hence electron density increases on the oxygen and destabilizes the conjugate base making it less acidic.

46.(A) Diethyl ether is a saturated compound, so it is resistant to nucleophilic attack by a hydroxyl ion (OH^-).

47.(A) Hydrogen bonding in ethanol.

48.(D) $-OCH_3, -CH_3$ are electron donating groups (via +R and +H effect respectively) decreases the acidic character of phenols.

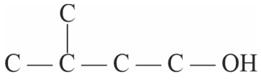
$-NO_2, -CN$ are electron withdrawing groups (via $-R$ effect), tend to increase the acidic character. Thus, the order is p-methoxyphenol < p-methylphenol < p-nitrophenol.

49.(A) Primary alcohol undergoes catalytic dehydrogenation to give aldehyde. $RCH_2OH \xrightarrow[\Delta]{Cu} RCHO$

50.(D) $CO + 2H_2 \xrightarrow{ZnO-Cr_2O_3} CH_3OH$

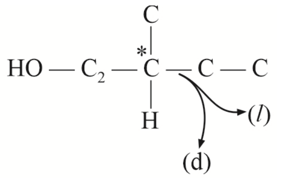
51.(5) (1) C — C — C — C — C — OH

(2)



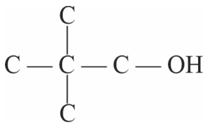
$C-\overset{\displaystyle C}{\overset{|}{C}}-C-C-OH$

(3)



Five 1° alcohol are possible
(Including Stereo isomers)

(4)



$C-\underset{\underset{\displaystyle C}{|}}{\overset{\overset{\displaystyle C}{|}}{C}}-C-OH$

52.(3) 92g of a compound react with excess of CH_3MgI to give $x \times 22400$ mL of CH_4 STP.

1 g of a compound react with excess of CH_3MgI to give $\dfrac{x \times 22400}{92}$

0.092 of a compound react with excess of CH_3MgI to give $\dfrac{x \times 22400}{92} \times 0.092$

$$\frac{x \times 22400 \times 0.092}{92} = 67.2 \text{ mL of } CH_4 \text{ at STP}$$

$$x = \frac{67.2 \times 92}{22400 \times 0.092} = \frac{67.2 \times 92 \times 1000}{22400 \times 92} = \frac{672}{224} = 3$$

$x \Rightarrow$ number of active hydrogen in compound.

Active $H \Rightarrow 3$

53.(5) Number of Hydroxyl group $n = \dfrac{m' - m}{42}$

Where m' = mass of product

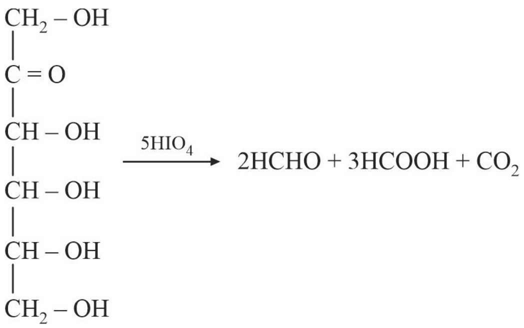
m = mass of unknown compound

$$n = \frac{390-180}{42} = 5$$

54.(3) A, B, F

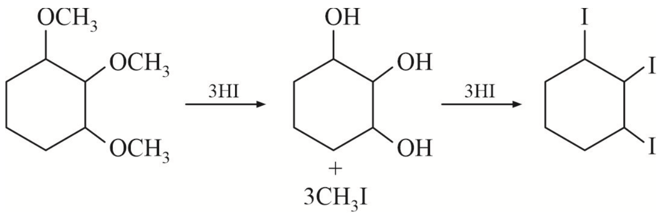
55.(3) B, C, F

56.(5)

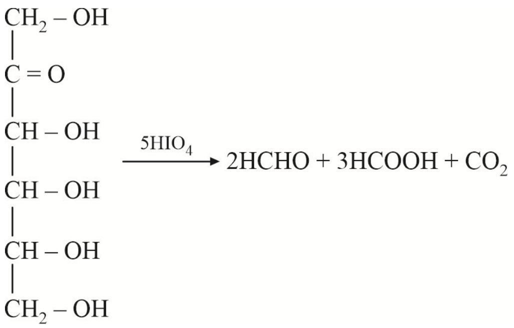


$$\begin{array}{l} CH_2-OH \\ | \\ C=O \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{5HIO_4} 2HCHO + 3HCOOH + CO_2$$

57.(6)



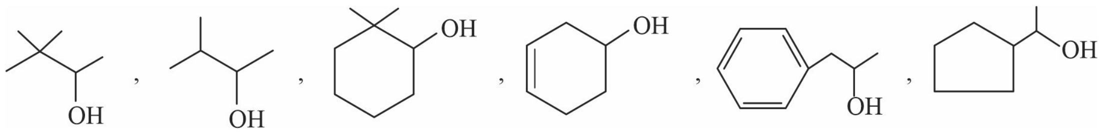
58.(3)



$$\begin{array}{l} CH_2-OH \\ | \\ C=O \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{5HIO_4} 2HCHO + 3HCOOH + CO_2$$

59.(4) $HCl/ZnCl_2, PCl_3, PCl_5, SOCl_2$

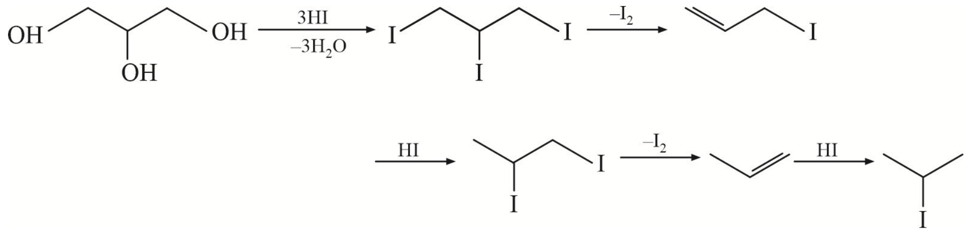
60.(6)



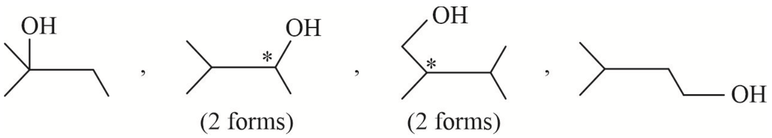
61.(4) C, D, E, F

62.(4) b, c, e, h

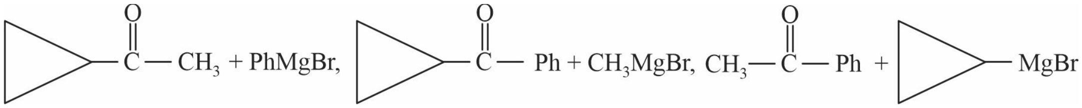
63.(5)



64.(6)



65.(3)

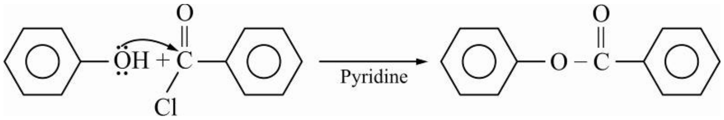


Aldehyde, Ketones & Carboxylic Acids

1.(A) The most positive carbonyl carbon gives fastest nucleophilic addition reaction. Aldehydes are relatively more reactive than ketones and aromatic aldehydes are less reactive than aliphatic aldehydes in this reaction.

2.(C) In general, carboxylic acids and phenols are more acidic than alcohols and carboxylic acids are more acidic than phenols. Chloroacetic acid is more acidic than acetic acid because –I effect is applied by –Cl in chloroacetic acid to stabilize its conjugate base. Thus order is Chloroacetic acid > Acetic acid > phenol > ethanol

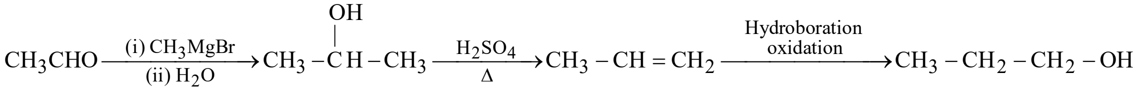
3.(B)



4.(C) Fehling solution responds to aliphatic aldehydes

5.(D) CH_3CHO gives aldol condensation in alkali solutions.

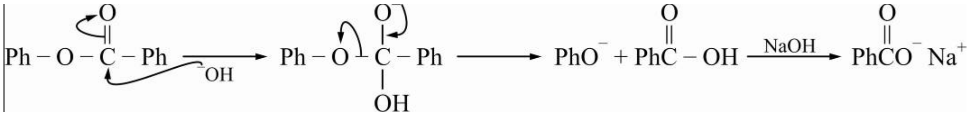
6.(B)



$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3-CH=CH_2 \xrightarrow{\text{Hydroboration oxidation}} CH_3-CH_2-CH_2-OH$$

7.(BD) For adol consdensation, aldehyde should contain α - hydrogen. Benezaldehyde and $(CH_3)_3-C-CHO$ lack in α -hydrogen, so no aldol reaction is possible in these cases.

8.(BC)

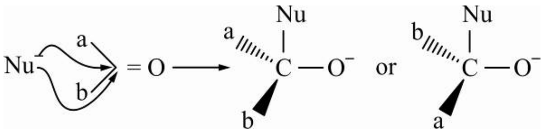


9.(BD) Clemmenson reduction converts carbonyl group into hydrocarbons.

10.(AC) Grignard reaction, and aldol reaction are used to form $C-C$ bond, so, these reactions can increase number of carbon atoms.

11.(AB)

12.(AB)



Nucleophiles can attack carbonyl carbon atom from either side which results into production of recemic mixture.

13.(A) **14.(A)**

15.(C) Aromatic aldehyde and formaldehyde contains no α- hydrogen, so undergo Cannizaro reaction. And aromatic aldehydes are less reactive than formaldehyde.

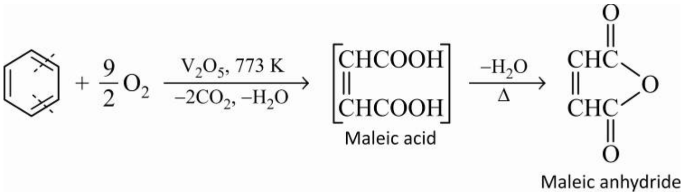
16.(B) Fehling solution oxidises only aldehydes, not ketones **17.(C)** **18.(D)**

19.(AD) It can give chloroform as well.

20.(B) Hydride transfer is the slowest step in Cannizaro-reaction when PhCHO reacts with base.

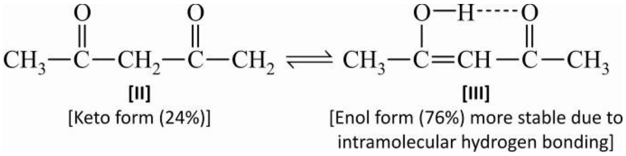
21.(B) $LiAlH_4$ reduces $-COOH$ group, $C=C$ is nonpolar due to which $LiAlH_4$ is unable to reduce it.

22.(A)



23.(D) Electron withdrawing groups increase the reactivity towards Nucleophilic substitution reaction by increasing polarity of $-C=O$ bond and $-NO_2$ is a strong electron withdrawing group.

24.(D)



25.(ACD) Zn-Hg and conc. HCl is unable to reduce carboxylic acid group.

26.(A) As $-I$ effect increases, COOH group becomes more electron deficient and tendency to loose H^+ ions increases i.e., acid strength increases. As $+I$ effect increases, acid strength decreases.
Thus correct order of acid strength is :

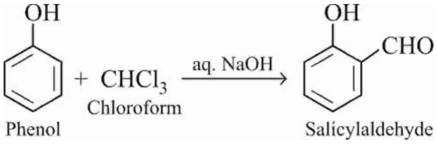
$$CF_3COOH > CCl_3COOH > HCOOH > CH_3COOH$$
$$(B) > (A) > (D) > (C)$$

27.(D) Here hydrazine is added to protonated carbonyl group and then H_2O is lost finally so it is a nucleophilic addition-elimination reaction.

28.(D)

(A)	Benzaldehyde	**(ii)**	Benzoin condensation
(B)	Phthalic anhydride	**(i)**	Phenolphthalein
(C)	Phenyl benzoate	**(iv)**	Fries rearrangement
(D)	Methyl salicylate	**(iii)**	Oil of wintergreen

29.(ACD) **(A)** Reimer-Tiemann reaction :



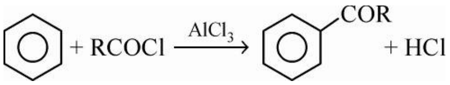
(B) Cannizzaro reaction :

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{50\%\ NaOH} \underset{\text{Sodium formate}}{HCOO^- Na^+} + \underset{\text{Methanol}}{CH_3OH} \text{ (NO new } -C-C- \text{ bond is formed)}$$

(C) Wurtz reaction :

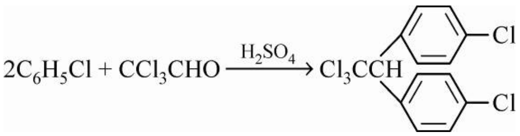
$$\underset{\text{Methyl iodide}}{H_3C-I} + 2Na + I-CH_3 \rightarrow \underset{\text{Ethane}}{CH_3-CH_3} + 2NaI$$

(D) Friedel-Crafts reaction :

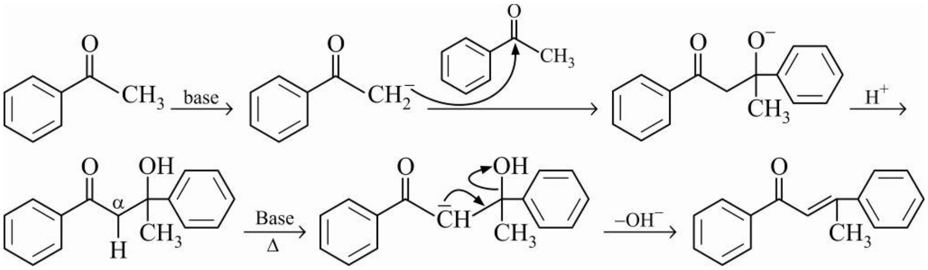


30.(D) CH_3COCl is most susceptible to Nucleophilic attack. The susceptibility of a substrate towards Nucleophilic attack depends on how good a leaving group is attached to it. Cl^- is a weak base and therefore a good leaving group.

31.(C) It gives D.D.T (p, p′-dichlorodiphenyltrichloro ethane)

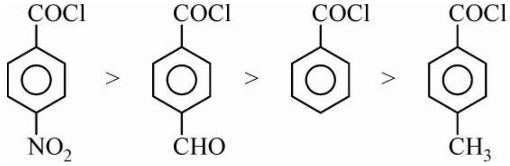


32.(C) The first step is carbanian (enolate) formation followed by typical Nu^- addition. The last step is an example of El cB mechanism and the leaving group is hydroxide. Due to the stability of the product, which is a conjugate carbonyl compound, $-OH$ is leaving group.



33.(A) The base (OH^-) ion removes one of the α-hydrogen atom (which is some what acidic) from aldehyde and ketone to form a carbanion (the enolate ion). The acidity of α-hydrogen is due to resonance stabilization of enolate anion.

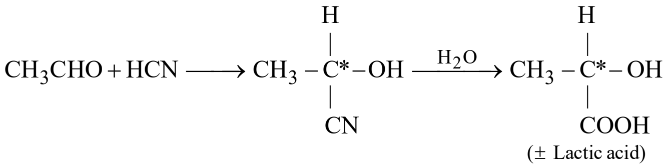
34.(C) The ease of hydrolysis depends depends upon the magnitude of the +ve charge on the carbonyl group. Electron-withdrawing groups increase the magnitude of positive charge and electron donating groups decreases the magnitude of positive charge. Hence the decreasing order of reactivity towards hydrolysis is :



35.(C) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

Acidity decreases as the strength of $-I$ effect of the group decreases, F is the most electronegative atom and hence it has highest $-I$ effect among the halogens.

36.(BD)



$$CH_3CHO + HCN \longrightarrow CH_3-\underset{CN}{\overset{H}{\underset{|}{\overset{|}{C^*}}}}-OH \xrightarrow{H_2O} CH_3-\underset{\substack{COOH\\(\pm\text{ Lactic acid})}}{\overset{H}{\underset{|}{\overset{|}{C^*}}}}-OH$$

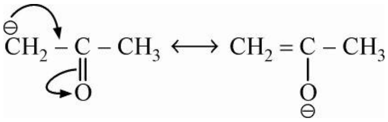
(* : Chiral centre)

Similarly for benzaldehyde.

37.(C) Ethyl acetate undergoes Claisen condensation in presence of sodium ethoxide involving α-hydrogen atom in which two molecules of ethyl acetate combine together to form aceto-acetic ester.

$$CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[2.\ H^+]{1.\ C_2H_5\bar{O}Na} \underset{\text{Acetoacetic ester}}{CH_3COCH_2COOC_2H_5} + C_2H_5OH$$

38.(A) They are resonating forms as shown :



$$\overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-CH_3 \longleftrightarrow CH_2=\underset{\underset{\underset{\ominus}{O}}{|}}{C}-CH_3$$

39.(B) Glucose reduces Fehling solution because glucose has an aldehyde $(-CHO)$ group which is readily oxidised.

40.(D) O-atom is more electronegative than C-atom, therefore O-atom bears partial $-ve$ charge and C-atom to which it is attached bear particle $+ve$ charge.

41.(A) $CH_3-C\equiv N + 2[H] \xrightarrow[\text{ether}]{HCl} \underset{(X)}{CH_3-CH=NH}$ (aldimine)

$CH_3-CH=NH \xrightarrow[\Delta]{H^+/H_2O} \underset{(Y)}{CH_3-CHO} + NH_4^+$

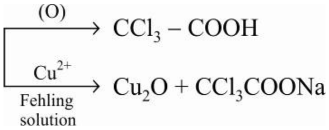
42.(BD) The esters having α-hydrogen show Claisen Condensation reaction. As $C_6H_5-COOC_2H_5$ and $HCOOC_2H_5$ have no α-hydrogen atom or active methylene group, so it cannot undergo Claisen-Condensation reaction.

43.(C)

44.(A) A tertiary alcohol is difficult to oxidise. But when it is treated with a strong oxidising agent ($K_2Cr_2O_7/H^+/\Delta$) some conditions, it is oxdised to ketone and then to acids. Both the ketone and acid contain the lesser number of atoms than the starting alcohol.

45.(D) $\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{LiAlH_4} \underset{\substack{\text{Phenylmethanol}\\\text{(Benzyl alcohol)}}}{C_6H_5CH_2OH}$

46.(C) $\underset{\text{(Ethylalcohol)}}{CH_3CH_2OH} \xrightarrow[-2\,HCl]{Cl_2} \underset{\text{(Acetaldehyde)}}{CH_3CHO} \xrightarrow[-3\,HCl]{3\,Cl_2} \underset{\text{Chloral}}{CCl_3CHO}$



$CCl_3CHO \xrightarrow{(O)} CCl_3-COOH$

$CCl_3CHO \xrightarrow[\substack{\text{Fehling}\\\text{solution}}]{Cu^{2+}} Cu_2O + CCl_3COONa$

47.(AD) Since CH_3CH_2CHO and $C_6H_5CH_2CHO$ have α-hydrogen atom, therefore it will undergo aldol condensation in the presence of dilute alkali.

48.(B) $2\,HCOONa \xrightarrow{\Delta} \underset{\text{Sodium oxalate}}{\begin{array}{c}COONa\\|\\COONa\end{array}} + H_2$

49.(B) $(CH_3)_2C=CHCOCH_3 \xrightarrow[2.\ H^+]{1.\ NaOI} (CH_3)_2C=CHCOOH + CHI_3$

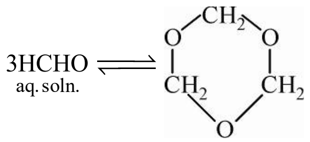
$(NaOH + I_2) \equiv NaOI$ is the best suitable reagent for the above reaction.

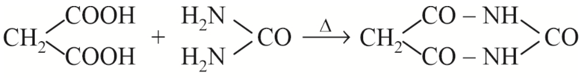
50.(AD) Ketones on oxidation give carboxylic acids with lesser number of carbon atoms i.e.,

$CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$

Also, $C_6H_5CH_2CHO \xrightarrow{(O)} C_6H_5COOH$

When an alpha $-H$ is attached to benzene ring, it forms benzoic acid.

51.(A)  Trioxane.

52.(C) 

$$CH_2\begin{matrix}COOH\\COOH\end{matrix} + \begin{matrix}H_2N\\H_2N\end{matrix}CO \xrightarrow{\Delta} CH_2\begin{matrix}CO-NH\\CO-NH\end{matrix}CO$$

Malonic acid Barbituric acid

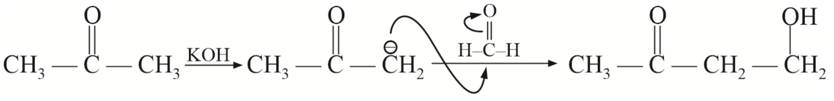
53.(B) $HCHO + KOH \xrightarrow{50\%\ KOH} HCOOK + CH_3OH$

The above reaction is called as Cannizzaro's reaction.

54.(D) $C_6H_5-CH_3 \xrightarrow{KMnO_4} C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[BaSO_4]{H_2\ /\ Pd} C_6H_5CHO$

55.(ACD) Reagents in (A), (C) and (D), being mild oxidising agents oxidises only aldehydes not ketones.

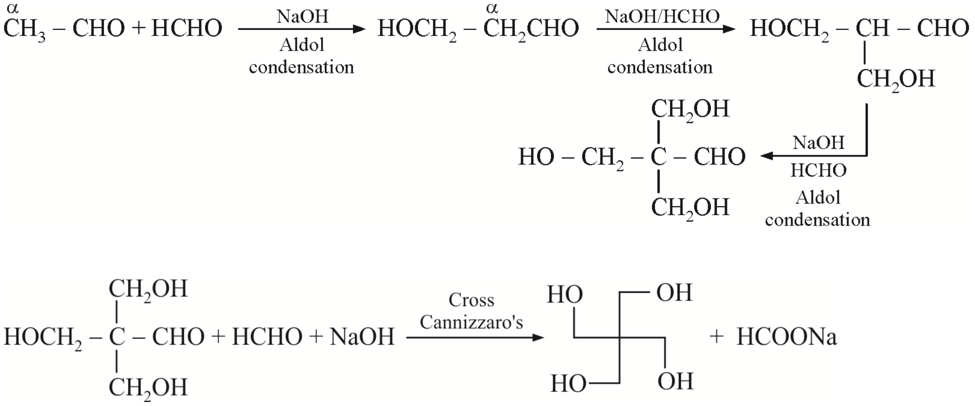
56.(21) $\dfrac{50\times60\times70}{100\times100\times100}\times100 = 21$

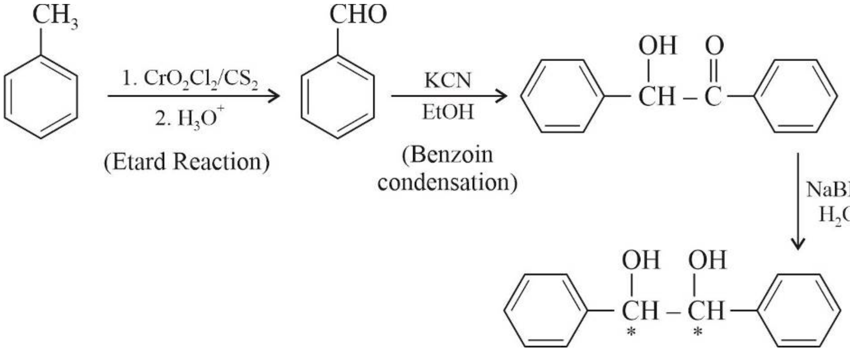
57.(6) 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{KOH} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2 \xrightarrow{H-\overset{O}{\overset{\|}{C}}-H} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}H_2}$$

One mole of HCHO gives $1-CH_2-OH$ group. Total $-CH_2-OH$ groups added in product = 6. Hence moles of HCHO consumed = 6.

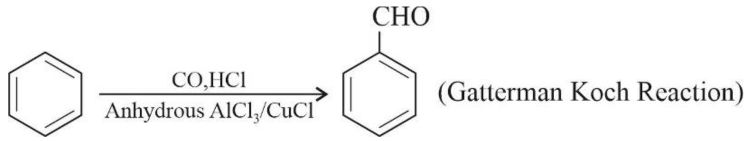
58.(4) At $(n = 4)$

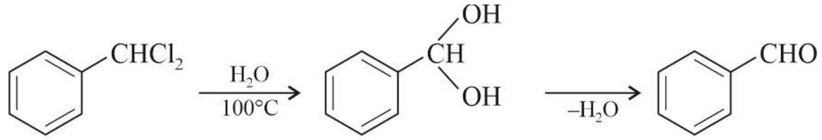
59.(4) 

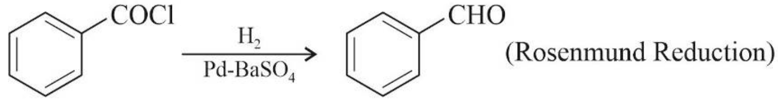
60.(3) 

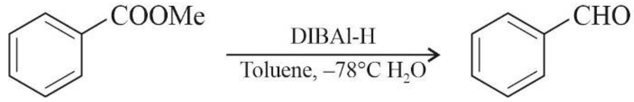
- 2 chiral centre
- Due to plane of symmetry, a total of '3' stereoisomers are formed.

61.(4)









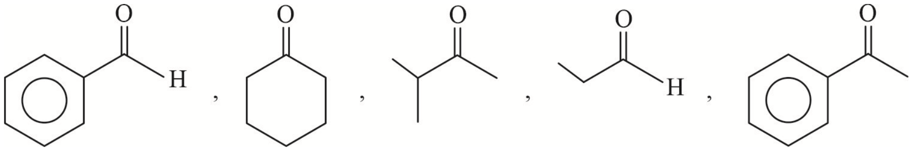
62.(72) Aldehydes or ketone $\xrightarrow{OH^-}$ aldol (ketol)

mol. wt. = x   mol. wt. = 2x

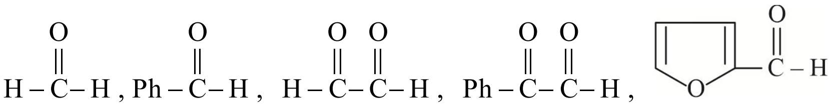
$\therefore$ $\beta-$hydroxy ketone: $2x = 144 \Rightarrow x = 72$

63.(6) Aldehyde, formic acid, Hemiacetal and $\alpha-$Hydroxyketone can give silver mirror test (Tollen's reagent)

64.(5)

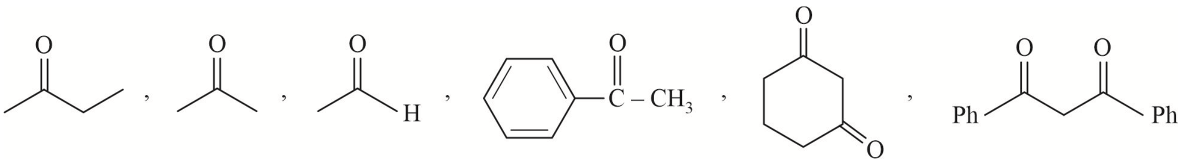


65.(5)

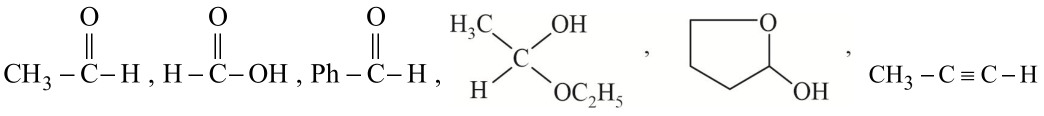


$H-\overset{O}{\overset{\|}{C}}-H$, $Ph-\overset{O}{\overset{\|}{C}}-H$, $H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$, $Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$,

66.(6)

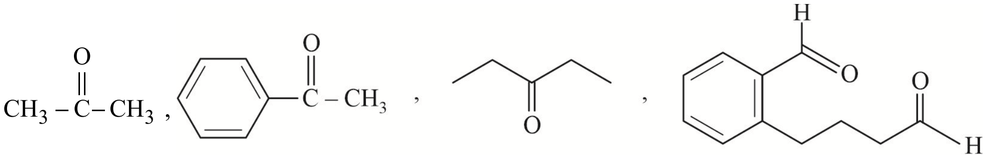


67.(6)



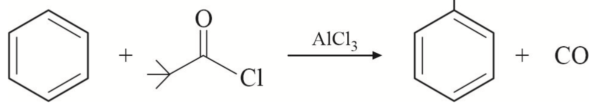
$CH_3-\overset{O}{\overset{\|}{C}}-H$, $H-\overset{O}{\overset{\|}{C}}-OH$, $Ph-\overset{O}{\overset{\|}{C}}-H$, , , $CH_3-C\equiv C-H$

68.(4)

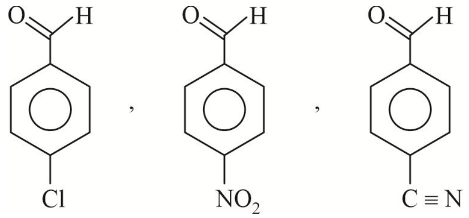


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$,

69.(5)

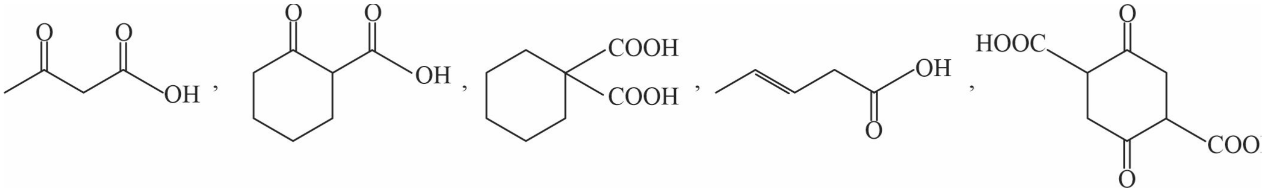


70.(3)

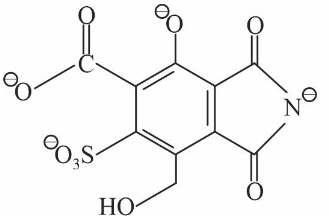


71.(3) **(a, d, e)**

72.(5)

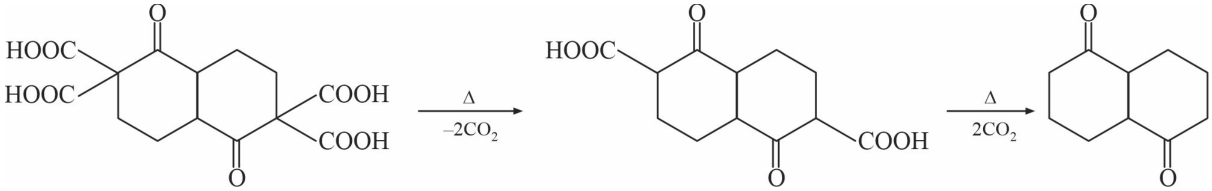


73.(4)

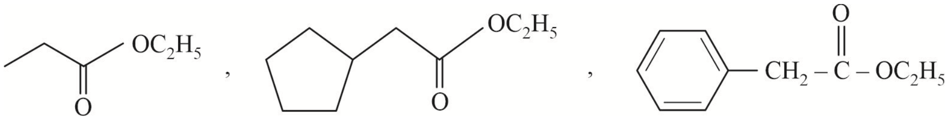


; Alcohols do not react with NaOH

74.(4)

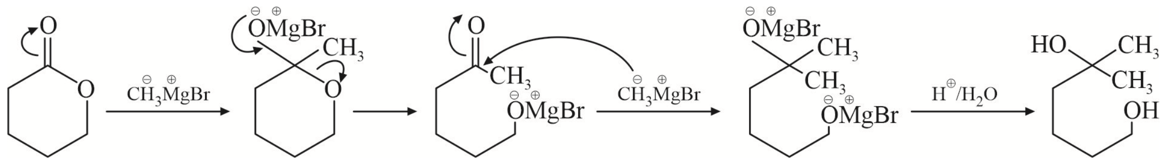


75.(3)

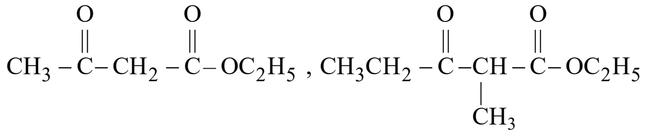


76.(3) For n = 3, we get 6 member ring

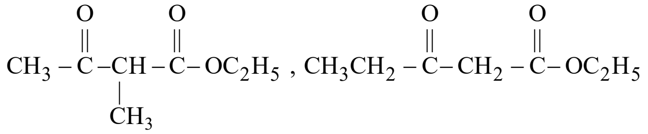
77.(2)



78.(4)

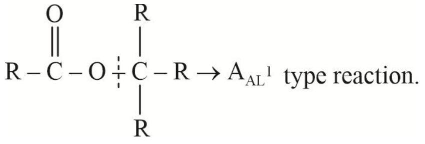


$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$, $CH_3CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$

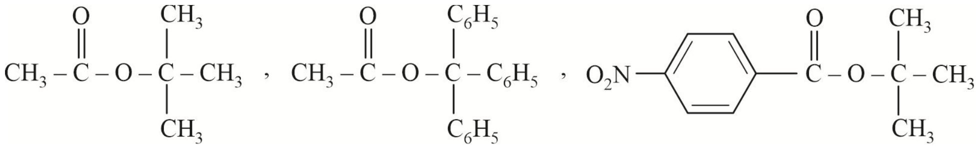


$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OC_2H_5$, $CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

79.(3)



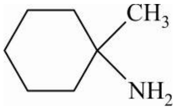
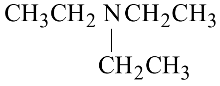
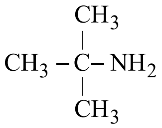
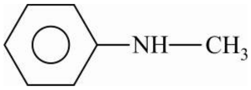
$R-\overset{O}{\overset{\|}{C}}-O\,\vdots\,\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-R\rightarrow A_{AL}{}^{1}$ type reaction.



$CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$, $CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{C_6H_5}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}-C_6H_5$,

Nitrogen Containing Organic Compounds

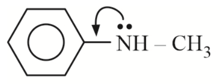
1.(B)

1-methylcyclohexylamine		1°
Triethylamine	 $CH_3CH_2\underset{CH_2CH_3}{\underset{\vert}{N}}CH_2CH_3$	3°
Tert-Butylamine	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-NH_2$	1°
N-methylaniline		2°

2.(D) $\underset{3}{CH_2}=\underset{2}{CH}-\underset{1}{CH_2}-NH-CH_3$ N-methylprop-2-en-1amine

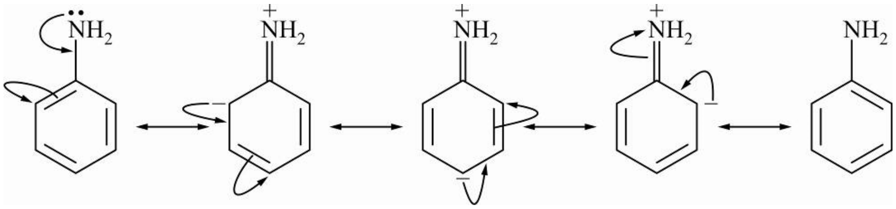
3.(C) In aqueous medium, protonated amine's stability depends on its solubility also so, 2° amine containing 2-hydrogen atoms are very well dissolved in water, so, 2° amine works as strong base in water.
In other cases

$N \equiv C - CH_2 - \ddot{N}H_2$
Inductive effect of CN



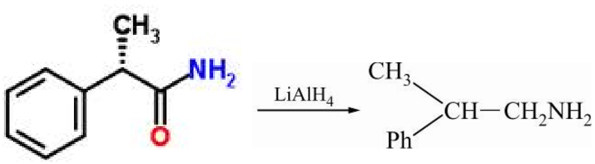
Lone pair is delocalised
by resonance

4.(A) Aniline is weakest base out of given option. Its long pair's delocalised by benzene ring through resonance.

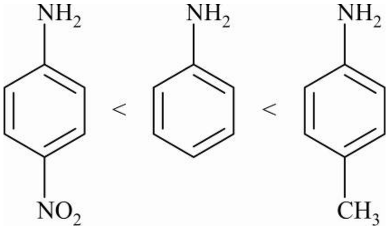


5.(B) $LiAlH_4$ is not suitable to reduce nitro group in aryl nitro compound

6.(D) $LiAlH_4$ reduce 2-phenylpropanamide into 2-phenylpropanamine.



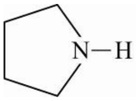
7.(D) $-NO_2$ group is electron withdrawing through – R & – I effect whereas $-CH_3$ group is electron donating through +H and + I effect, so, $-NO_2$ reduces and $-CH_3$ increase basic nature of aniline.



8.(B) 2° amines are most basic in aqueous solutions if methyl groups are attached with nitrogen atom. This is so because conjugate acid of 2° amine is more soluble than 3° amine's conjugate acid.

9.(D) Compounds with highly activated benzene ring can undergo diazo coupling reaction. Since nitrobenzene contains $-NO_2$ group which deactivate benzene ring cannot undergo diazo coupling reaction.

10.(C) Phenol is the weakest base since its lone pair is delocalised over benzene ring. Also lone pair exists on more electronegative atom (O) in comparison of aniline in which lone pair exists on relatively less electronegative(N) atom.

11.(D) 

is 2° amine without delocalization of lone pair on nitrogen atom, so, it is most basic among given options. In other cases lone pair on nitrogen atom is delocalized.

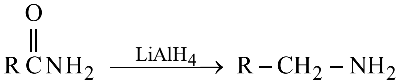
12.(A) In general, anions are more basic than neutral species.

$$H_2O \longrightarrow \bar{O}H + H^+ \; ; \; NH_3 \longrightarrow \bar{N}H_2 + H^+$$

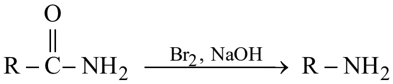
$$\bar{N}H_2 > \bar{O}H > NH_3 > H_2O$$

13.(B) $CH_3CH_2CH_3$ is most volatile since its molar mass is minimum, only dispersion forces exist in propane.

14.(ABC) $RCH_2CN \xrightarrow{LiAlH_4} RCH_2CH_2NH_2$

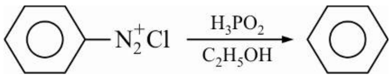

$R\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2$

$R-CH_2Br \xrightarrow[\text{(ii) hydrolysis}]{\text{(i) Potassium Phthalimide}} R-CH_2-NH_2$


$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2,\ NaOH} R-NH_2$

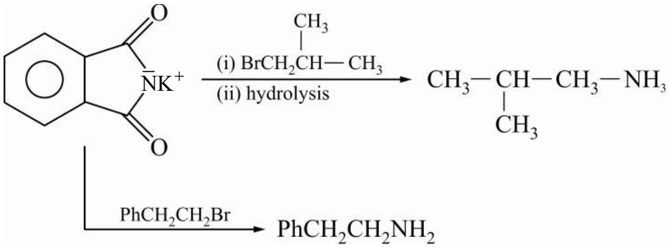
15.(ABC) Sn/HCl, Fe/HCl and H_2-Pd can reduce nitrobenzene into aniline.

16.(BC) Alcohol and H_3PO_2 can be used to reduce benzenediazonium chloride into benzene.

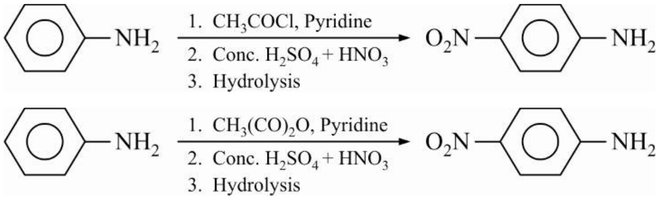


17.(ABC) $-NH_2$ group is activating and ortho-para directing, so, intermediates which are formed by ortho and para attack are valid intermediates.

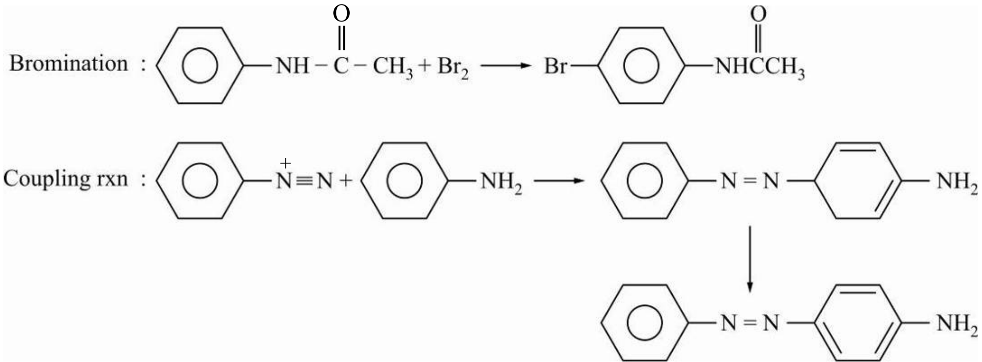
18.(AB) For Gabriel synthesis, haloalkanes should be primary which will produce primary amine.



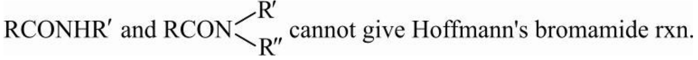
19.(AB)

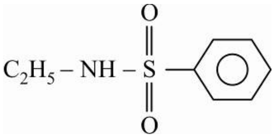


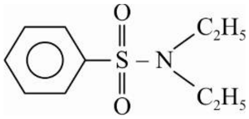
20.(AB)



21.(C)


RCONHR′ and RCON<R′, R″ cannot give Hoffmann's bromamide rxn.

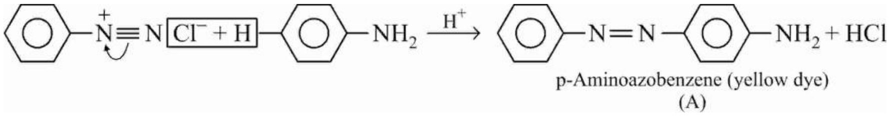
22.(A)  H atom on nitrogen is very acidic due to sulphonic group.

23.(B)  no acidic hydrogen **24.(D)**

25.(C) Bromobenzene doesn't give S_N2 reaction. **26.(A)**

27.(C) Benzoylation of compound containing an active hydrogen atom such as alcohols, phenols and amines with benzoyl chloride in the presence of dilute aq. NaOH solution is called Schotten Baumann reaction. The products formed are esters and amides.

28.(ABD) Aniline cannot be prepared by this method (C) because aryl halides do not undergo Nucleophilic substitution reaction with potassium phthalimide under mild conditions.

29.(D) 

p-Aminoazobenzene (yellow dye)
(A)

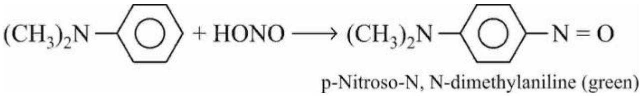
30.(A) H_3PO_2 and H_2O reduce the $-\overset{+}{N_2}\overset{-}{C}l$ group to $-H$.

31.(A) $CH_3CH_2CH_2NC + 2H_2O \xrightarrow{H^+} \underset{I}{CH_3CH_2CH_2NH_2} + \underset{II}{HCOOH}$

$II(HCOOH)$ reduces Tollen's reagent and Fehling's solution.

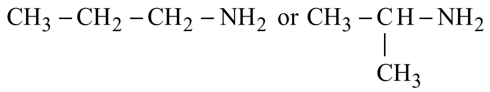
32.(BCD) Aromatic tertiary amines undergoes electrophilic substitution (S_E) with nitrosonium ion at p-position of the phenyl ring to form green-coloured p-nitrosoamines.

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$



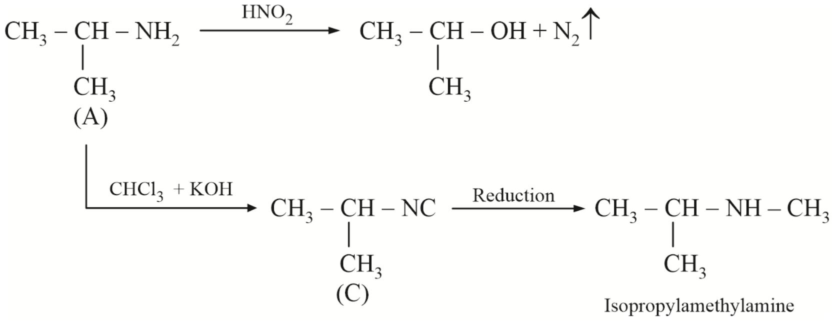
p-Nitroso-N, N-dimethylaniline (green)

33.(A) Only 1° aliphatic amines gives alcohol with HNO_2. C_3H_9N has two possible structure with $-NH_2$ groups (1°).

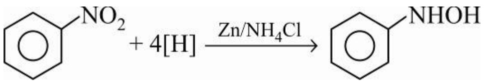


$$CH_3-CH_2-CH_2-NH_2 \text{ or } CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-NH_2$$

As (C) gives isopropylmethylamine thus it should be isopropyl amine not n-propyl amine.

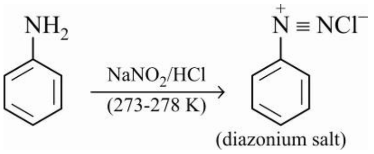


Isopropylamethylamine

34.(A) 

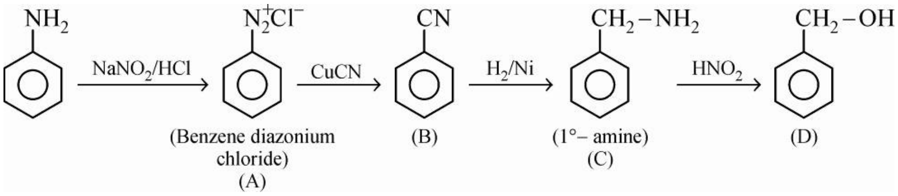
35.(B) In benzylamine, the electron pair present on the nitrogen is not delocalised with the benzene ring.

36.(ABD) Aryl amines react with nitrous acid to produce diazonium salts.

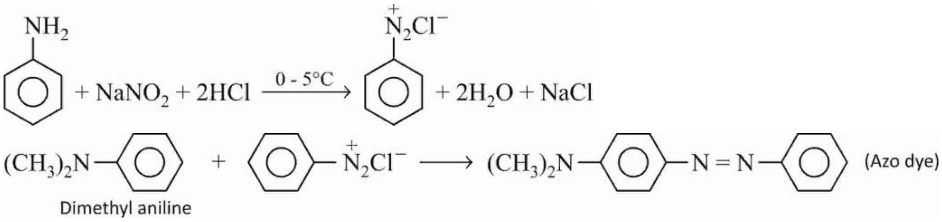


37.(B) $\underset{(\text{from } H_2SO_4)}{H^+} + H\underset{(\text{Base})}{\ddot{\underset{\cdot\cdot}{O}}} - NO_2 \longrightarrow [H_2O^+ - NO_2] \longrightarrow H_2O + NO_2^+$

38.(D)



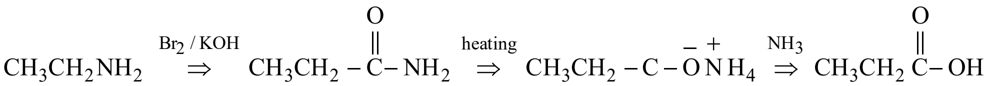
39.(C)



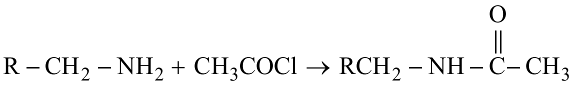
40.(D) The reaction conditions are for carbylamine reactions, so, product is isocyanide

$$RCH_2NH_2 + CHCl_3 \xrightarrow{C_2H_5OK^+} RCH_2NC$$

41.(A) Smallest pK_b value implies strongest base. In aqueous medium, solubility factor is also added which stabilize the conjugate acid due to which secondary amines are the strongest base in aqueous medium.

42.(C) 

$$CH_3CH_2NH_2 \overset{Br_2\,/\,KOH}{\Rightarrow} CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \overset{\text{heating}}{\Rightarrow} CH_3CH_2-C-\overset{-}{O}\overset{+}{N}H_4 \overset{NH_3}{\Rightarrow} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

43.(C) Acylation of amino group 

$$R-CH_2-NH_2 + CH_3COCl \rightarrow RCH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Thus, H is replaced by $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ due to which net change in molar mass of amine is $(43-1) = 42$

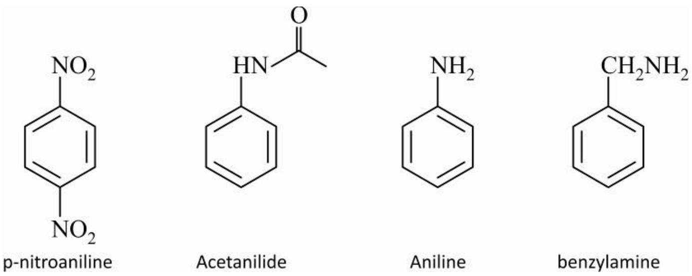
The change in molecular mass on acylation is $390-180 = 210$

So number of amine group present in reactant $= \dfrac{210}{42} = 5$

44.(C) Out of aliphatic amines bearing methyl groups, secondary amines are strongest base in aqueous medium.

45.(C) $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2NC + 3KCl + 3H_2O$

46.(D)



In the case of benzylmine, lone pair on nitrogen is not delocalised over benzene ring, lone pair is delocalised in other cases. Thus benzylamine is most basic.

47.(D) In the case of (A), (B) and (C), lone pair is delocalised over benzene ring but in benzylmine, lone pair is not delocalised over benzene ring. Thus it is most basic.

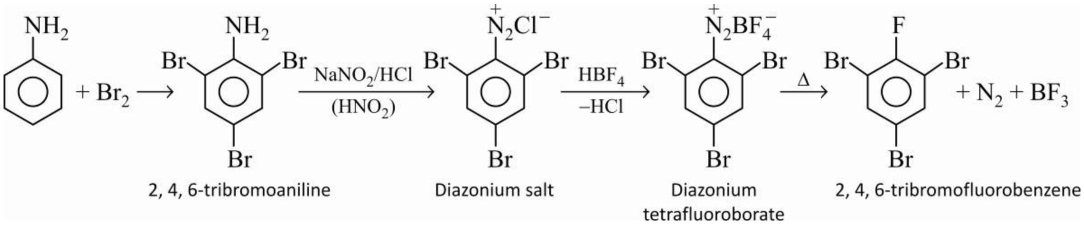
48.(C) Secondary amine one most basic due to the inductive effect of methyl group.

49.(A) The reaction $RCONH_2 + Br_2 + KOH \rightarrow RNH_2$ is known as Hoffmann-bromamide reaction.

RCONHBr and RNCO are important intermediate (Refer to Mechanism in text).

This reaction is used in the descent of series, i.e. for preparing a lower homologue from a higher one.

50.(D)



51.(A) Benzaldehyde reacts with primary aromatic amines to form Schiff's base (Benzylidene aniline).

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Aniline}}{C_6H_5NH_2} \rightarrow \underset{\text{Benzylidene aniline}}{C_6H_5HC = NC_6H_5} + H_2O$$

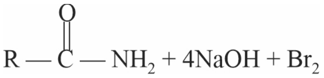
(Benzanilide)

52.(ACD) Basic strength (B) decreases as : cyclohexylamine > aniline > benzamide.
Lesser basicity in aniline and benzamide is due to conjugation of lone pair of electron of $-NH_2$ group.

53.(C) The correct answer is (C). The product (E) is 4-Methylbenzonitrile.

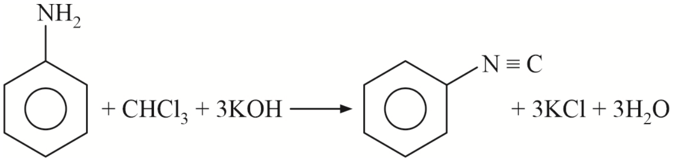
54.(C) $RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

55.(CD) Only primary amines (both aliphatic and aromatic) give Hoffmann's rearrangement.

56.(4) Balanced reaction is  $\longrightarrow R - NH_2 + 2NaBr + Na_2CO_3 + H_2O$

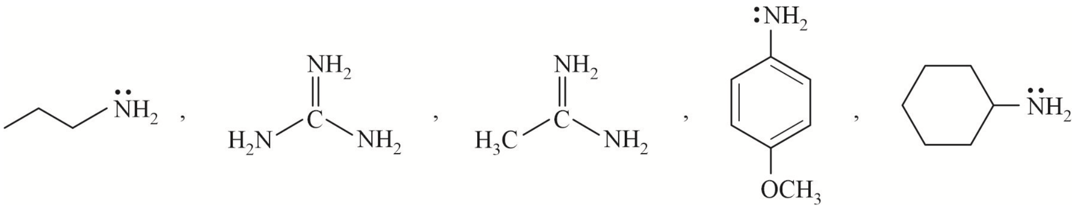
$$R - \overset{\overset{\large O}{\|}}{C} - NH_2 + 4NaOH + Br_2 \longrightarrow R - NH_2 + 2NaBr + Na_2CO_3 + H_2O$$

57.(3)

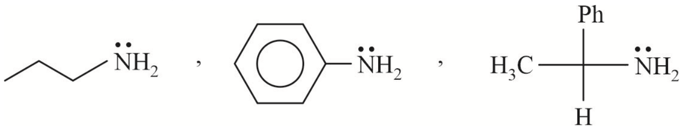


58.(4) **(a, c, e, f)**

59.(5)

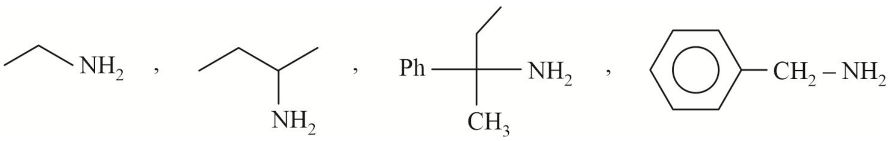


60.(3) Only 1° amines give carbylamines reaction.

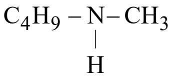


61.(5) (a, b, c, e, h)

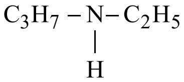
62.(4) Only 1° amine give Hofmann's mustard oil reaction



63.(6)



$C_4H_9 - \underset{\underset{H}{|}}{N} - CH_3$ (4 possible structures)

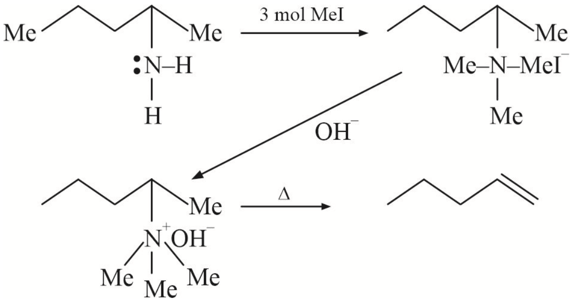


$C_3H_7 - \underset{\underset{H}{|}}{N} - C_2H_5$ (2 possible structures)

64.(4) (a, c, e, f)

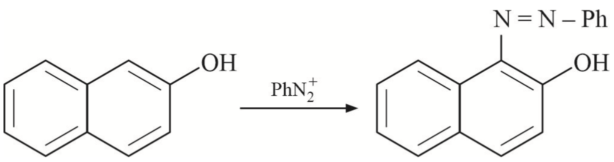
65.(5) Five primary amines are possible for the molecular formula $C_6H_{11}N$.

66.(2)

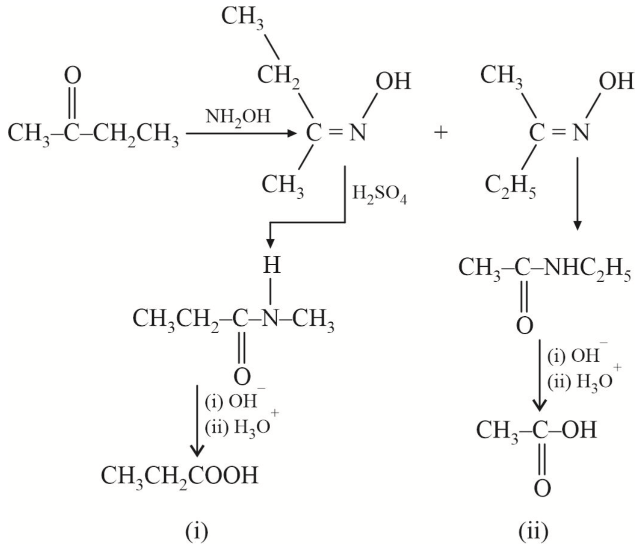


67.(4) No. of NH_2 groups $= \dfrac{348-180}{42} = 4$

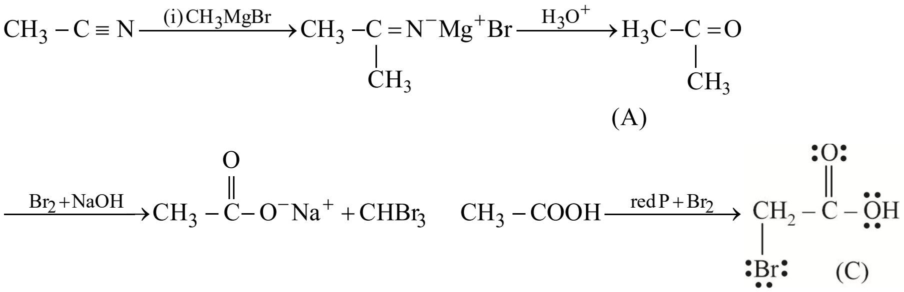
68.(1)



69.(14)



70.(14)



$$CH_3-C\equiv N \xrightarrow{(i)\,CH_3MgBr} CH_3-\underset{\substack{|\\ CH_3}}{C}=N^-Mg^+Br \xrightarrow{H_3O^+} H_3C-\underset{\substack{|\\ CH_3}}{C}=O \quad (A)$$

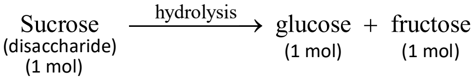
$$\xrightarrow{Br_2+NaOH} CH_3-\overset{\substack{O\\ \|}}{C}-O^-Na^+ + CHBr_3 \qquad CH_3-COOH \xrightarrow{red\,P+Br_2} \underset{\substack{|\\ :\ddot{Br}:}}{CH_2}-\overset{\substack{:O:\\ \|}}{C}-\ddot{O}H \quad (C)$$

Biomolecules & Polymers

1.(B) Glycogen has a structure similar to that of amylopectin but glycogen has more branches

2.(D)

3.(C)



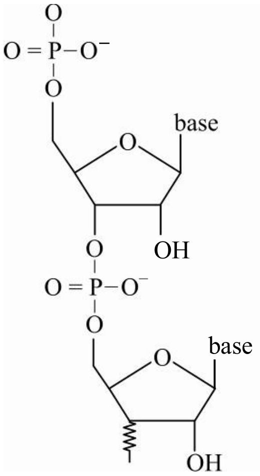
$$\underset{\substack{\text{(disaccharide)}\\ \text{(1 mol)}}}{\text{Sucrose}} \xrightarrow{\text{hydrolysis}} \underset{\text{(1 mol)}}{\text{glucose}} + \underset{\text{(1 mol)}}{\text{fructose}}$$

4.(C) α-helix structure is stabilized by hydrogen bonding.

5.(B) If acetal or ketal groups exists instead of hemiacetal or hemiketal, the carbohydrades are non-reducing, in case of (B), hemiacetal or hemiketal exist, so, it is non-reducing.

6.(B) Ascorbic acid is vitamin C.

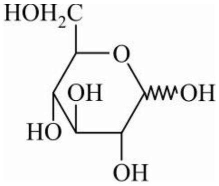
7.(A)



Thus linkage occurs at 5′ and 3′

8.(B) The phosphate + Sugar + Amino acid from a single unit which is called nucleotide and these units are monomer of nucleic acids.

9.(C) The cyclic structure of glucose is based on pyran



Since it contains hemiacetal group, both cyclic and noncylic form exist in aqueous solution, due to which it is reducing sugar. It contains total six carbon atoms, so it is called aldohexose. Open chain structure reacts with HI and produces n-hexane.

10.(A) Linkage of amino acids are called primary structure of proteins.

11.(C) Bases in DNA → Cystosine, Thymine, Adenine, Guanine

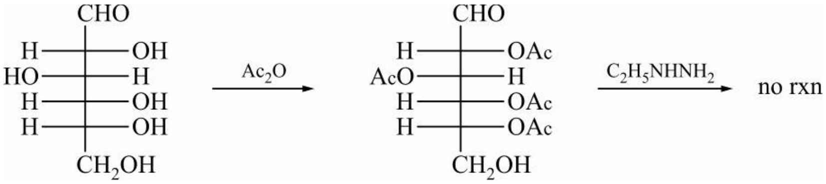
Bases in RNA → Cystosine, Uracil, Adenine & Guanine

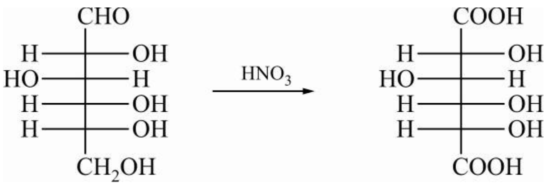
12.(D)

13.(D) Bases in DNA → Cystosine, Thymine, Adenine & Guanine.

14.(A) Anomers ⇒ Compounds which have opposite configuration on one carbon atom only.

15.(A) Cyclic structure of glucose contains five hydroxy group, so, acylation of cyclic glucose produces pentaacetate.





16.(B) Hydroxyl group on right at lowest chiral carbon atom indicates D-configuration.

17.(B) RNA contains ribose sugar and uracil.

18.(C) The numbering in carbohydrates starts from epimeric carbon atom, thus A contains β C1-C4 glycosidic linkage, B contains α C1-C6 glycosidic linkage and C contains α C1-C6 glycosidic linkage.

19.(D) Glycogen is stored by animals as energy source.

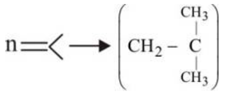
20.(A) Cis-polyisoprene is a natural polymer. Cellulose nitrate, cellulose acetate and vulcanized rubber are formed by reforming of natural polymers, so, these are semisynthetic polymers. **21.(B)**

22.(D) Amide linkages are degraded easily, so, it is biodegradable.

23.(A) In case of A, copolymer is formed by

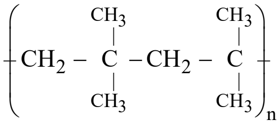
24.(C) Properties of low density polyethene
(i) Tough (ii) Hard (iii) Highly branched.

25.(A)



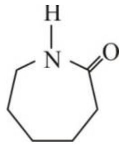
(Incorrect polymer structure given in question)

It should be

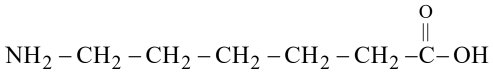


$$\left(-CH_2 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_2 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - \right)_n$$

26. (D)

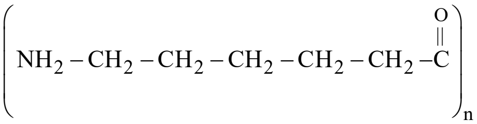


Caprolactum



$$NH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - OH$$

(Amino caproic acid)



$$\left(NH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} \right)_n$$

Nylon-6

27.(A) Dacron is a condensation polymer neoprene, teflon and Acrylonitrile are Addition polymers.

28.(A) Quinoline is not present in DNA **29.(A)** Refer NCERT, Class XII, Part-II, Page No-405

30(C) Lewis acids are most commonly used for cationic polymerisation.

31.(B) Molish's test is for carbohydrates. **32.(B)** Refer NCERT, Class XII, Part-II, Page No-419

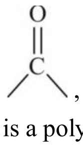
33.(D) Mutarotation, Refer NCERT, Class XII, Part-II, Page No-409

34.(C) Refer NCERT, Class XII, Part-II, Page No-432

35.(A) Biuret test is given by α-amino acids

36.(B) Nylon-6,6 is a polymer of Hexamethylene diamine and Adipic acid

37.(B) Carbohydrates is have



, -OH , -CHO.

38.(C) Buna-N is a polymer of $CH_2 = CH - C \equiv N +$ $CH_2 = CH - CH = CH_2$

39.(B) Polytetrafluoroethylene or Teflon is a tough material, resistance to heat and bad conductor of electricity. It is used for coating the cookware to make them non-sticky.

40.(C) Anomers (have different optical configuration at carbonyl carbon) **41.(A)** α- helical backbone

42.(D) Anomer (have different optical configuration at carbonyl carbon) **43.(C)** Cytosine and Thymine.

44.(C) Teflon (Monomer $CF_2 = CF_2$) **45.(C)** Nylon - 6,6

46.(A) C_5' and C_1' linkage of sugar molecule (Fact) **47.(D)** Refer NCERT, Class XII, Part-II, Page No-440

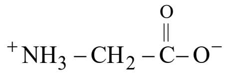
48.(B) Refer NCERT, Class XII, Part-II, Page No-448 **49.(A)** Refer NCERT, Class XII, Part-II, Page No-420

50.(A) Refer NCERT, Class XII, Part-II, Page No-420

51.(C) Nylons are formed by reaction of amines and carboxylic acids.

52.(C) Cellulose is a polymer of β-D- glucopyranose. So complete hydrolysis of cellulose will form D-Glucose

53.(B) Condensation reaction of monomers leads to formation of polymer

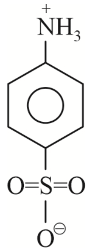
54.(C) Zwitter ions formed in 

$^{+}NH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - O^{-}$

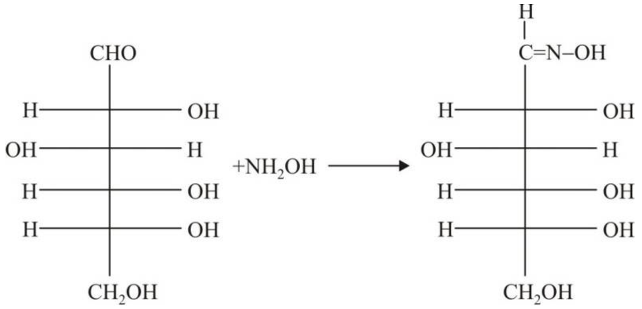
(a) $-NH_2, -COOH$

As well as in

(b) $-NH_2, -SO_3H$



55.(D)



56.(B) H-bonding (Bases are linked via hydrogen bonding) **57.(B)** Refer NCERT, Class XII, Part-II, Page No-449

58.(B) Sucrose is formed by the condensation of α -D-glucopyranose and β -D-fructofuranose.

59.(C) (+) Lactose is a reducing sugar and all reducing sugars show mutarotation.

60.(C) Denaturation does not change the primary structure of protein.

61.(A) Sucrose does not show mutarotation.

Mutarotation is the phenomenon of change in optical rotation shown by freshly prepared solutions of sugars. However, this property is not exhibited by all sugars. Only those sugars which have a free aldehyde $(-CHO)$ or ketone $(>C=O)$ groups are capable of showing mutarotation. Sucrose lacks free aldehyde or ketone group and is therefore incapable of showing mutarotation.

62.(D) Under alkaline conditions of the reagent, fructose gets converted into a mixture of glucose and mannose (Lobry de Bruyn van Ekenstein rearrangement) both of which contain the $-CHO$ group and hence reduce Tollen's reagent to give silver mirror test.

63.(C) DNA contains two types of nitrogeneous bases

Purine → Adenine (A) and guanine (G) Pyrimidine → Cytosine (C) and thymine (T)

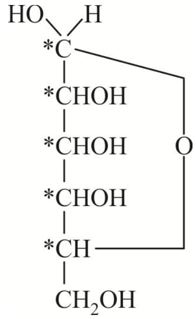
The purine and pyrimidine bases pair only in certain combination. Adenine pairs with thymine (A : T) by two hydrogen bonds and guanine with cytosine (G : C) by three hydrogen bonds.

64.(C) The constituent of nucleic acids are nitrogenous bases, sugar and phosphoric acid. The sugar present in DNA is D(−)-2-deoxyribose and the sugar present in RNA is D(−)-ribose. Due to these D(−)-sugar components, DNA and RNA molecules are chiral molecules.

65.(D) $\text{Proteins} \xrightarrow[\text{proteases}]{\text{pepsin}} \text{Polypeptides} \xrightarrow[\text{chemotrypsin}]{\text{trypsin}} \text{Amino acids}$

66.(C) Disulphide bond may be reduced to thiol by means of reagents i.e., $NaBH_4$, which shows the presence of thiol group in disulphide bond formation.

67.(A)



This structure of β-D-glucose has five asymmetric carbon atom.

68.(B) α-helix structure is formed when the chain of α-amino acids coil as a right handed screw because of the formation of hydrogen bonds between amide groups of the same peptide chain, i.e. NH group in one unit is hydrogen bonding. This H-bonding is responsible for holding helix in a position.

69.(A) Starch is also known as amylum which occurs in all green plants. A molecule of starch $\left(C_6H_{10}O_5\right)_n$ is built of a large number of α-glucose rings joined through oxygen atoms.

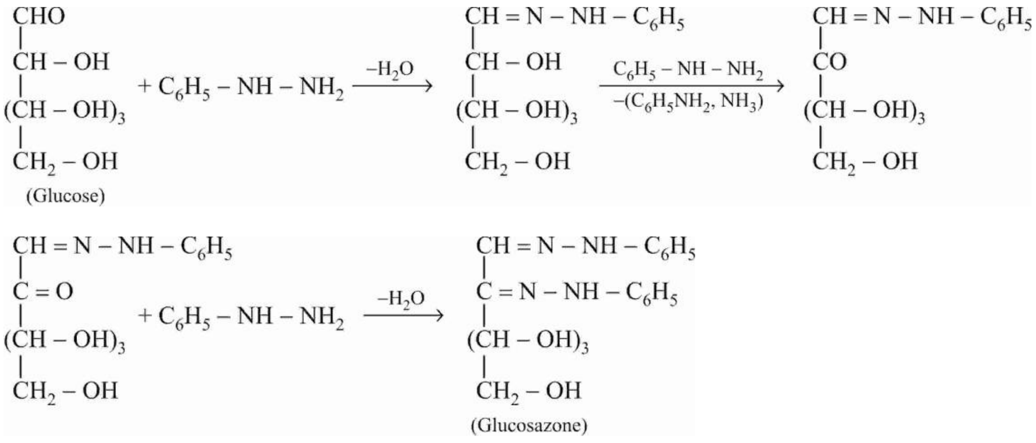
70.(A) Peptide bond is formed by the reaction of one $-COOH$ group of one amino acid with the $-NH_2$ group of another amino acid and represented as

$$-\overset{\overset{O}{\|}}{C}-\ddot{N}H- \longleftrightarrow -\overset{\overset{O^-}{|}}{C}=\overset{\oplus}{N}H-$$

As some double bond character is found between $C-N$ bond, the bond length of $C-N$ in protein should be smaller than the usual $C-N$ bond.

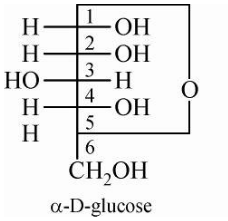
71.(A) Phenol and formaldehyde undergoes condensation polymerisation under two different conditions to give a cross linked polymer called bakelite.

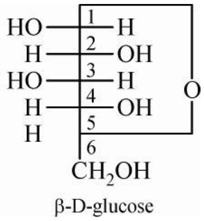
72.(D) Glucose first reacts with phenyl hydrazine giving phenylhydrazone. Then the adjacent $-CHOH$ group is oxidized by 2nd phenyl hydrazine molecule and itself is reduced to aniline. The resulting carbonyl group reacts with 3rd phenyl hydrazine molecule giving osazone.



73.(D) Haemoglobin is a globular protein of four subunits, each subunit having a heme moiety and a polypeptide chain (Two α and two β chains).

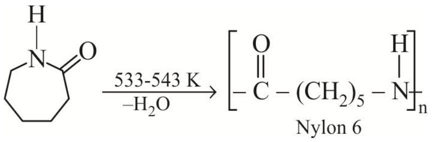
74.(D)


α-D-glucose


β-D-glucose

These isomers differ only in the orientation (or configuration) at C_1 atom.

75.(D)

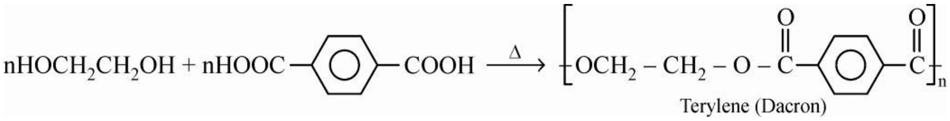


Nylon 6

76.(C) $\underset{\text{Glycine}}{nH_2N-CH_2-COOH}+\underset{\text{Aminocaproic acid}}{nH_2N-(CH_2)_5-COOH}\longrightarrow \underset{\text{Nylon 2-nylon 6}}{\left(NH-CH_2-CO-NH-(CH_2)_5-CO\right)_n}$

77.(D)
- **(A)** Neoprene rubber (elastomer)
- **(B)** PVC (thermoplastic polymer)
- **(C)** Nylon-6, 6 (fibre)
- **(D)** Novolac which further undergoes cross linking to produce Bakelite (thermosetting polymer)

78.(C)



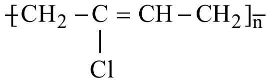
Terylene (Dacron)

79.(D) Neoprene is an addition polymer

80.(B) Nylon 6,6 is an example of fibres

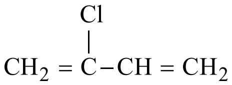
81.(B) Nylon-2-nylon-6 is formed

82.(A) Neoprene is :



$$\left[CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2\right]_n$$

It is polymer of chloroprene

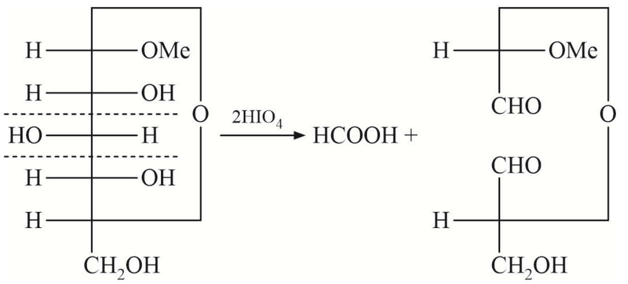


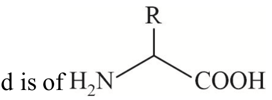
$$CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2$$

83.(B) Nylon-6, 6 is a copolymer

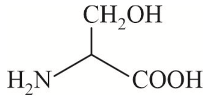
84.(C) Chain-growth polymers involve a series of reactions each of which consume a reaction particle and produce another similar one. The reactive particles may be free radicals or ions (cation or anion) to which monomers get added by a chain reaction. It is an important reaction of alkenes and conjugated dienes or indeed of all kinds of compounds that contains $C-C$ double bonds.

85.(2)



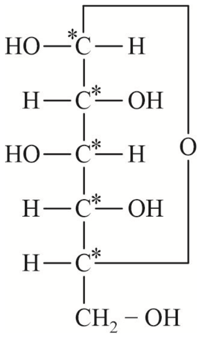
86.(3) α-amino acid is of  type.

Total number of C atoms in $C_3H_7NO_3 = 3$ and O atoms = 3, so R = CH_2OH



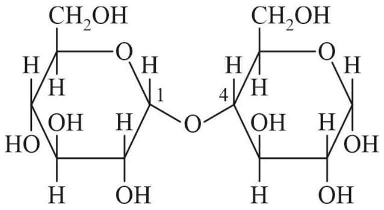
87.(3) The compound is a γ-lactone and has furanose structure. **88.(3)**

89.(5)



90.(2) Polyethylene and polypropylene are addition polymers.

91.(4)



Chemistry in Everyday Life

1.(D) Antiseptic medicines cannot be ingested.

2.(C) Combinations of estrogen and progestin work by preventing ovulation (the release of eggs from the ovaries) and used as contraceptive pills to control birth.

3.(A) Aspirin often used as an analgesic to relieve minor aches and pains, as an antipyretic to reduce fever, and as an anti-inflammatory medication.

4.(C) Chemists catagories drugs on the basis of molecular targets.

5.(A) Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

6.(A) Salvarsan was the first effective treatment discovered for syphilis.

7.(A) Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics. Those effective mainly against Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics.

8.(B) Tranquilizers are have antidepressant action on central nervous system.

9.(D) Bithionol (the compound is also called bithional) is added to soaps to impart antiseptic properties.

10.(B) Equanil is used in controlling depression and hypertension, so, it is called tranquilizer **11.(B)**

12.(C) Glycerol acts as moisturiser, so, it prevents soap to dry quickly. **13.(B)**

14.(C) Polyethylene glycol is formed by condensation of ethylene glycol, so, it is non-ionic.

15.(C) Vitamins are taken as nutrient in our diet, so, these are not the targeted molecules for drug functions **16.(C)**

17.(D) Sucralose is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature.
It does not provide calories.

18.(B) Artificial sweeteners are excreted unchanged, so, they don't provide any nutrition.

19.(BD) Majority of receptor proteins are embedded in cell membranes. Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

20.(B) Sodium hydrogen carbonate is used as baking powder. Sugar, table salt and sodium benzoate are the common preservatives used for food.

21.(BC) Iodine is a powerful antiseptic. Its 2-3 per cent solution in alcoholwater mixture is known as tincture of iodine. It is applied on wounds. Iodoform is also used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes.

22.(AB) Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers. These derivatives are called barbiturates. Barbiturates are hypnotic, *i.e.*, sleep producing agents.

23.(AB) Sulphapyridine and prontosil are sulphadrugs. Salvarsan resembles with prontosil in structure but not a sulphadrug.

24.(ABC) Iproniazid, phenelzine and equanil are antidepressants but Salvarsan is antibiotic.

25.(CD) Panicillin is a Penicillium fungus.Penicillin G has a narrow spectrum. Ampicillin and Amoxycillin are synthetic modifications of penicillins. These have broad spectrum. **26.(BD)**

27.(AD) The drug cimetidine (Tegamet), was designed to prevent the interaction of histamine with the receptors present in the stomach wall. This resulted in release of lesser amount of acid. Ranitidine (Zantac), was discovered later.

28.(AD) Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers.

29.(AD) Sodium salts of organic sulphonic acids are anionic detergents **30.(ACD)**

31.(A) Methylisocyanate $CH_3-N=C=O$ (MIC gas) gas was leaked from the storage tank of the union carbide plant in Bhopal gas tragedy.

32.(D) DDT is a non-biodegradable pollutant. It is the first chlorinated organic insecticide.

33.(D) **(A)** $NO+O_3 \longrightarrow NO_2+O_2$

$O_3+hv \longrightarrow O_2+O$

$NO_2+O \longrightarrow NO+O_2$

Net reaction $2O_3+hv \longrightarrow 3O_2$ Thus, ozone layer is depleted by oxides of nitrogen. Thus **(A)** is correct statement.

(B) Ozone layer is protective layer and absorbs harmful UV rays from the sun.
Thus, **(B)** is also correct statement.

(C) $Cl+O_3 \longrightarrow Cl\dot{O}+O_2$

$O_3+hv \longrightarrow \dot{O}+O_2$

$ClO+\dot{O} \longrightarrow Cl+\dot{O}_2$

Net reaction $2O_3+hv \longrightarrow 3O_2$

Thus, ozone layer is also depleted by reaction with freons. Thus **(C)** is also correct statement.

(D) It is a incorrect statement as ozone layer is permeable for IR rays. Thus, correct answer is **(D)**.

34.(C) Ozone layer permits the infrared radiation to pass through but doesn't permit the higher range of ultraviolet radiation to pass through.

35.(A) Somg is formed by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides. Somg mainly contains higher concentration of Peroxyacteyl nitrate (PAN) formed by the reaction of NO_2, O_3 and unsaturated hydrocarbons.

$$NO_2 \xrightarrow{hv} NO + O$$

$$O + O_2 \rightleftharpoons O_3$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO + O_3 + \text{unsaturated hydrocarbons} \rightarrow PAN$$

36.(A) During thunderstorm, there is formation of NO which changes to NO_2 and ultimately to HNO_3 (acidrain).

$$N_2 + O_2 \longrightarrow NO \xrightarrow{O_2} NO_2$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3 \qquad [pH < 7]$$

37. (B) Total mmol of H_2SO_4 taken = $60 \times \frac{1}{10} = 6$ mmol

$$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O;$$

mmol of H_2SO_4 neutralized by NH_4OH $= \frac{1}{2} \times 20 \times \frac{1}{10} = 1$ mmol

Thus, mmol of H_2SO_4 neutralized by ammonia gas = 6 – 1= 5 mmol

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$; it implies that 10 mmol of ammonia reacts with sulphuric acid.

$10 \text{ mmol } NH_3 \equiv 10 \text{ mmol N} \equiv 10 \times 14 = 140 \text{ mg N} \quad \therefore \quad \% \text{ of N} = \frac{140}{1000 \times 1.4} \times 100 = 10\%$

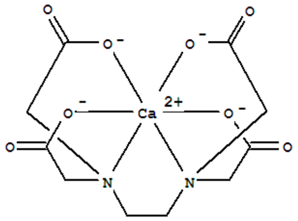
38.(C) $NaOH + HCl \rightarrow NaCl + H_2O$;

Acid neutralized by ammonia = $20 \times 0.1 - 15 \times 0.1 = 0.5$ mmol

$NH_3 + HCl \rightarrow NH_4Cl$; It implies that 0.5 mmol ammonia evolved from organic compounds.

$$\therefore \quad \% \text{ of N} = \frac{0.5 \times 14}{29.5} \times 100 = 23.7\%$$

39.(C)



40.(C) Antipyretic drugs reduces temperature, so, helpful in reducing fever.

41.(A) Chlorophyll is green pigment in plants but contains magnesium.

42.(A) The carbon and nitrogen present in the organic compound on fusion with sodium metal gives sodium cyanide (NaCN) soluble in water. This is converted in to sodium ferrocyanide by the addition of sufficient quantity of ferrous sulphate. Ferric ions generated during the process react with ferrocyanide to form prussian blue precipitate of ferric ferrocyanide.

$$Na + C + N \longrightarrow NaCN$$

$$6NaCN + FeSO_4 \longrightarrow \underset{\text{Sodium ferrocyanide}}{Na_4[Fe(CN)_6]} + Na_2SO_4$$

$$\underset{\text{Ferric ferrocyanide}}{Na_4[Fe(CN)_6] + Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3}$$

43.(C) The reaction of hydrogen and oxygen highly exothermic, due to which produced water be in gaseous state and works as propellant. **44.(B)**

45.(C) The given compound is the aspirin which works as analgestic **46.(B)**

47.(C) Aspartame is stable under cold conditions but unstable at cooking temperature.

48.(A) Dilute solutions of boric acid and hydrogen peroxide are weak antiseptics.

49.(B) Diphenylhydramine is employed as antihistamine drug.

50.(D) When chloroform is titrated with concentrated nitric acid, its hydrogen is replaced by nitro group.

$$CHCl_3 + HONO_2 \rightarrow \underset{\text{chloropicrin}}{CNO_2Cl_3} + H_2O$$

51.(D) It is cationic detergent.

52.(A) Ampicillin is a modification of penicillin and thus is not a natural antibiotic. These semisynthetic penicillin (SSP) like ampicillin, cloxacillin, etc. are produced by chemically combining specific side chains (in place of benzyl side chain of penicillin group) or by incorporating specific precurssors in the mould cultures. The aim of producing SSP's is to overcome penicillin's shortcomings such as poor oral efficacy, hyper sensitivity, susceptibility to penicillinase, narrow spectrum of activity, etc.

53.(A) $CH_3(CH_2)_{10}CH_2OH \xrightarrow{H_2SO_4} CH_3(CH_2)_{10}CH_2OSO_3H \xrightarrow{NaOH(aq)} CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$

Sodium lauryl sulphate (Anionic detergent)

54.(C) Fractional distillation is used if the difference in boiling points of two liquids is not much. This technique is used to separate different fractions of crude oil in petroleum industry.

Distillation under reduced pressure is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Glycerol can be separated from spent-lye in soap industry by using this technique

Simple distillation ⇒ This technique is used to separate volatile liquids from nonvolatile impurities or liquids having sufficient difference in their boiling points.

55.(B) In drinking water maximum permissible concentration of

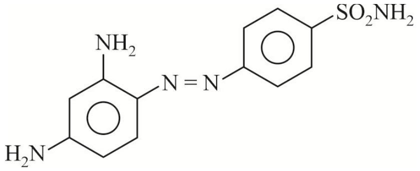
Lead about 50 ppb
Nitrate about 50 ppm
Iron about 0.2 ppm
Fluoride about < 1 ppm

High concentration of nitrate in drinking water can cause disease such as methemoglobinemia.

Read NCERT (XIth)-Chapter-14/Environmental Chemistry-Page-412.

56.(2) Valium and serotonin are tranquilizers.

57.(1) Prontosil



58.(3) Erythromycin, Tetracycline and Chloramphenicol are bacteriostatic antibiotics.

59.(2) Pencillin and chloramphenicol contain amide linkage.

60.(2) Chloroxylenol and Bithionol contain phenolic group.

61.(4) Aspartame, Saccharin, Sucrolose and Alitame are used artificial sweeteners.