Hints & Solutions

1

Solid State

Exercise 1 : WARM-UP
Topic-wise MCQs

1. **(c)** Both (a) and (b)
2. **(a)** Intermolecular distances are short in the solid state.
3. **(b)** Crystalline solids are anisotropic in nature that is some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals.
4. **(c)** Amorphous silicon is used as best photovoltaic material available for conversion of sunlight into electricity.
5. **(c)** Covalent bond force
6. **(b)** In graphite, the electrons are spread out between the sheets.
7. **(d)** Methane is a non-polar covalent molecular which forms molecular solid when solidified.
8. **(a)** The aqueous solution or melt has ions.
9. **(d)** Covalent solid have very high melting point due to network like structure and they are insulator in both solid and in molten state, e.g., diamond, SiO_2.
10. **(c)**
11. **(c)** Silicon carbide (SiC) is a covalent network solid. In this silicon atoms are connected with carbon atoms in a tetrahedral manner.
12. **(b)**

Molecule	Type of solid	Constituent particles	Melting point	Electrical Conductivity
SiO_2	Covalent or Network solid	Atoms	Very high	Insulator
MgO	ionic	ions	High	Insulator
H_2O(ice)	Molecular solid	molecule	low	Insulator
Ag(s)	Metallic solid	–	Fairly High	Conductor

13. **(d)** Ag $\Rightarrow$ Metallic solid

ZnS $\Rightarrow$ Ionic solid

$CO_2 \Rightarrow$ Molecular solid

$SO_2 \Rightarrow$ Molecular solid

HCl $\Rightarrow$ Molecular solid

$H_2O \Rightarrow$ Molecular solid

$SiO_2 \Rightarrow$ Network solid

AlN $\Rightarrow$ Network solid

14. (a) SiO_2 is a covalent network solid that forms a network of tetrahedral SiO_4^{4-} units.

MgO, CaF_2 and ZnS are ionic solids.

15. **(d)** HCl Polar molecular solid, H_2O hydrogen bonded molecular solid, CCl_4 non-polar molecular solid. SiO_2 is covalent or network solid.
16. **(c)** $a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$

are parameters of monoclinic unit cell.

17. **(b)** For tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90°$
18. **(d)** The *bcc* cell consists of 8 atoms at the corners and one atom at centre. Contribution of each atom at each corner is equal to $\frac{1}{8}$.

$$\therefore n = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

The *fcc* cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

$$\therefore n = 8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$$

19. **(a)** The number of octahedral voids is equal to number of spheres. The number of tetrahedral voids is double the number of spheres.
20. **(c)** Density $= \dfrac{(Z \times M)}{(a^3 \times NA)}$

$$N_A = \frac{4 \times 58.5}{(0.5 \times 10^{-7})^3 \times 6.023 \times 10^{23}} = 3.1 \text{ g/cm}^3$$

21. **(a)** Given: Atoms are present in the corners of cube = *A* and atom present at body centre = *B*. We know that a cubic unit cell has 8 corners. Therefore, contribution of each atom at the corner $= \frac{1}{8}$. Since number of atoms per unit cell is 8, therefore, total contribution $= 8 \times \frac{1}{8} = 1$. We also know thats atom is in the body centre, therefore number of atoms per unit cell = 1. Thus formula of the compound is *AB*.
22. **(b)** $A : B : C = \frac{1}{8} \times 8 : \frac{1}{2} \times 2 : \frac{1}{2} \times 4 = 1 : 1 : 2$

23. **(d)** Number of effective atoms in *fcc* arrangement

$$=\left(8\times\frac{1}{8}\right)+\left(6\times\frac{1}{2}\right)=4$$

Number of tetrahedral voids = 2 × 4 = 8

24. **(c)** RbCl, NaCl and LiCl share the same crystal structure with 6 : 6 coordination no. ratio. CsCl crystallises witn 8 : 8 C.N. ratio.

25. **(b)** The volume of the unit cell = $(2.88\ \text{Å})^3$

$= 23.9 \times 10^{-24}\ \text{cm}^3$.

The volume of 100 g of the metal

$$=\frac{M}{\rho}=\frac{100}{7.20}=13.9\ \text{cm}^3$$

Number of unit cells in this volume

$$=\frac{13.9\ \text{cm}^3}{23.9\times10^{-24}\ \text{cm}^3}=5.82\times10^{23}$$

26. **(d)** Metal M ions form ccp structure. Let number of ions of M be : X

No. of tetrahedral voids = 2x

No. of octahedral voids = x

Number of oxide ions will be $\frac{1}{2}\text{x}+\frac{1}{2}(2\text{x})=\frac{3}{2\text{x}}$

Formula of oxide $=\frac{\text{MxO}_3}{2\text{x}}=\text{M}_2\text{O}_3$

27. **(b)** Edge length (a) = 412.1 pm = 4.12×10^{-8} cm

Molecular mass (M) = 133 + 35.5 = 168.5 g mol^{-1}

$$d=\frac{Z\cdot M}{a^3\cdot N_A}$$

Since it is a *bcc* arrangement number of atoms per unit cell of CsCl, Z = 1.

$$d=\frac{1\times168.5g\ mol^{-1}}{\left(4.12\times10^{-8}cm\right)^3\times6.023\times10^{23}mol^{-1}}$$

$$=\frac{1\times168.5g\ mol^{-1}}{\left(6.994\times10^{-23}cm^3\right)\times6.023\times10^{23}mol^{-1}}$$

$$=\frac{168.50g}{42.12\ cm^3}=4.0\ \text{g cm}^{-3}$$

28. **(d)** Density (d) = 10 g cm^{-3}

Edge length (a) = 100 pm = 100×10^{-10} cm

Z = 4 as it is *fcc* crystal lattice.

$$d=\frac{Z\cdot M}{a^3\cdot N_A}\qquad\therefore\quad M=\frac{d\cdot a^3\cdot N_A}{Z}$$

$$=\frac{10\times\left(100\times10^{-10}\right)^3\times6.023\times10^{23}}{4}=1.506\ g$$

According to definition of Avogadro number 1.506 g of element contains 6.023×10^{23} no. of atoms.

$\therefore$ 1 g of element will contain $=\frac{6.023\times10^{23}}{1.506}$

$= 3.99 \times 10^{23}$ atoms $\approx 4 \times 10^{23}$ atom

Number of atoms in the crystal is 4×10^{23} atoms.

29. **(d)** Number of atoms per unit cell = 1

Atoms touch each other along edges. Hence $r=\frac{a}{2}$

(r = radius of atom and a = edge length)

Therefore % fraction $=\frac{\frac{4}{3}\pi r^3}{(2r)^3}=\frac{\pi}{6}$

30. **(a)** Let radius of the sphere = r

Area occupied by sphere in hexagonal close packing

$$\pi r^2+6\times\left(\frac{1}{6}\times\pi r^2\right)=2\pi r^2$$

Area of hexagonal $=6\times\left[\frac{\sqrt{3}}{4}\times(2r)^2\right]$

$$=6\times\frac{\sqrt{3}}{4}\times4r^2\ =6\sqrt{3}\times\text{r}^2$$

% occupied by $=\frac{2\pi r^2}{6\times\sqrt{3}\times r^2}\times100$

$$=\frac{2\times3.14}{6\times\sqrt{3}}\times100=60.43\%$$

31. **(a)** For b.c.c., $Z = 2$, Now, $d=\frac{ZM}{NV}$ and $V = a^3$

$$\therefore\ d=\frac{2\times56}{(6.02\times10^{23})\times(2.861\times10^{-8})^3}=7.92\ \text{g ml}^{-1}$$

32. **(c)** Mass of the unit cell = V × d = $a^3 \times d$

$= (5 \times 10^{-8})^3 \times 3.84 \times 6.023 \times 10^{23} = 289$ g

Mass of one furmula units of FeO = 56 + 16 = 72 u

$\therefore$ Number of formula units per unit cell $=\frac{289}{72}=4$

If means that there are 4 Fe^{2+} and 4 O^{2-} ions per unit cell.

33. **(a)** Following generalization can be easily derived for various types of lattice arrangements in cubic cells between the edge length (a) of the cell and (r) the radius of the sphere.

For simple cubic : $a = 2r$ or $r=\frac{a}{2}$

For body centred cubic : $a = \frac{4}{\sqrt{3}} r$ or $r = \frac{\sqrt{3}}{4} a$

For face centred cubic : $a = 2\sqrt{2} r$ or $r = \frac{1}{2\sqrt{2}} a$

Thus the ratio of radii of spheres for these will be

simple : *bcc* : *fcc* = $\frac{a}{2} : \frac{\sqrt{3}}{4} a : \frac{1}{2\sqrt{2}} a$

i.e. option (a) is correct answer.

34. **(a)** $d = \frac{ZM}{N_A a^3}$; Z = 4 for *fcc*

$$M = \frac{9.03 \times 6.02 \times 10^{23} \times 64 \times 10^{-24}}{4} = 86.97$$

35. **(d)** Given:

Edge Length (a) = 3.608×10^{-8} cm

Density of copper (d) = 8.92

In *fcc* crystal structure, the value of z is 4.

$$d = \frac{z \times M}{N_A \times a^3}$$

$$8.92 = \frac{4 \times M}{6.022 \times 10^{23} \times (3.608 \times 10^{-8})^3}$$

$$M = \frac{8.92 \times 6.022 \times 10^{23}}{4} \times 46.96 \times 10^{-24}$$

M = 63.1 g/mol (Molar Atomic Mass)

M = 63.1 u (Atomic Mass)

36. **(a)** In 14 types of Bravais lattices, body centred unit cell is present in cubic, tetragonal and orthorhombic crystal systems.

37. **(a)** Number of octahedral and tetrahedral voids formed by N closed packed atoms are N and 2N respectively. Hexagonal unit cell contains 6 atoms therefore, number of tetrahedral void = $2N = 6 \times 2 = 12$

Number of octahedral void = N = 6

38. **(d)** For *bcc*, $\sqrt{3}a = 4r \Rightarrow r = \frac{\sqrt{3}a}{4}$

Given, a = 288 pm

$$r = \frac{\sqrt{3}}{4} \times 288 \text{ m}$$

39. **(c)**

	Oh void (C)	:	HCP (A)
No. of ions ⇒	$6 \times \frac{75}{100}$	:	6
	$\frac{3}{4}$	:	1
	3	:	4 C_3A_4

40. **(a)** Diamond is like ZnS. In diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure (tetrahedral voids).

Total no. of atoms present per unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 8$$

(corners) (face centered) (inside body)

41. **(b)**

Unit cell	No. of atoms
Simple cubic	$\frac{1}{8} \times 8 = 1$
bcc	$\frac{1}{8} \times 8 + 1 \times 1 = 2$
fcc	$\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

42. **(a)** For triclinic crystal

$a \neq b \neq c$ Edge lengths

$\alpha \neq \beta \neq \gamma$ Axial angle

43. **(b)** For bcc Z = 2

Let mass of 1 atom of M is A, Crystal lattice,

Edge length (a) = 300 pm

Density (d) = 6g/cm^3

$$\therefore \quad 6\text{g}/\text{cm}^3 = \frac{Z \times A}{N_A (300 \times 10^{-10})}$$

$$= \frac{2 \times A}{27 \times 10^{-27} \times 6.023 \times 10^{23}}$$

∴ Atomic mass = 48.6g

$$\therefore \quad \text{Mole in 180g} = \frac{180}{48.6} = 3.7 \text{ moles}$$

Atoms of M = $3.7 \times 6 \times 10^{23} = 22.22 \times 10^{23}$ atoms

44. **(d)** atoms of A (left) in the unit cell after the removal of two opposite face atoms.

$$A \rightarrow 4 - \left(2 \times \frac{1}{2}\right) = 3$$

atoms of B present in the lattice is

$$B \rightarrow 12 \times \frac{1}{4} + 1 \times 1 = 4$$

So, Compound is A_3B_4

The value of x is 3.

45. **(c)** There are 4 formula units per unit cell.

$$d = \frac{z \times M}{a^3 \times N_A} \Rightarrow 43.1 = \frac{4 \times 58.5}{a^3 \times 6.02 \times 10^{23}}$$

$\Rightarrow a = 2.08 \times 10^{-8}$ cm $\Rightarrow a = 2.08 \times 10^{-10}$ cm

Also $a = 2\left(r_{Na^+} + r_{Cl^-}\right)$

$$\Rightarrow \quad r_{Na^+} + r_{Cl^-} = 1.04 \times 10^{-10} \text{ m}$$

∴ The answer is l.

46. **(a)** No. of tetrahedral voids = 2 × No. of atoms

$$X \rightarrow 6 \quad Y \rightarrow \frac{2}{3} \times 2 \times 6 = 8$$

$$\% X = \frac{16}{14} \times 100 = 42.8 \simeq 43\%$$

47. **(c)** Anions occupy ccp or fcc (B^-) = 4 B^- per unit cell

Cations occupy all octahedral voids (A^+) = $4A^+$ per unit cell

$\therefore$ Cell formula $\Rightarrow A_4B_4$.

Empirical formula $\Rightarrow$ AB

$\Rightarrow x = 1$

48. **(b)** $d = \dfrac{Z \times M}{a \times N_A}$

$$7.62 = \frac{4 \times M}{\left(0.4518 \times 10^{-7}\right)^3 \times 6.022 \times 10^{23}}$$

$M = 105.8$ g/mol = 106 g/mol

49. **(c)** For bcc,

$$4r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}}{4} \times 27$$

For fcc,

$$\Rightarrow a = 2\sqrt{2}r$$

$$= 2\sqrt{2} \times \frac{\sqrt{3}}{4} \times 27$$

$$= \frac{2 \times 1.41 \times 1.73 \times 27}{4} = 33 \text{ Å}$$

50. **(b)** Ga crystallizes in a hexagonal close packing.

No. of Ga atoms per unit cell $= \dfrac{1}{6} \times 12 + \dfrac{1}{2} \times 2 + 1 \times 3 = 6$

No. of tetrahedral voids = 2 × 6 = 12

No. of octahedral voids = 6

Total voids per unit cell = 18

Total voids per atom of Ga $= \dfrac{18}{6} = 3$

Total no. of atoms of Ga

$$= \frac{\text{Mass}}{\text{Molar mass}} \times N_A = \frac{0.581}{70} \times 6.023 \times 10^{23}$$

$\therefore$ Total no. of voids = 3 × total no. of atoms

$$= 3 \times \frac{0.581}{70} \times 6.023 \times 10^{23}$$

$$= 14.99 \times 10^{21} \approx 15 \times 10^{21}$$

51. **(a)** If number of lattice point = N

then effective octahedral voids = N

So, octahedral voids/lattice site = 1

52. **(b)** Copper crystallises is fcc unit cell with edge length, $a = 3.569$ Å

$$d = \frac{z \times M}{N_A (a)^3}$$

$$\Rightarrow d = \frac{4 \times 63.54}{1000 \times 6.022 \times 10^{23} (3.596 \times 10^{-10})^3}$$

$$\simeq 9077 \text{ kg m}^{-3}$$

53. **(c)** The coordination number of an atom in a body centered cubic structure is 8.

54. **(d)** Atom X are present in bcc lattice. For atom X, effective number of atoms in the unit cell = 2.

For molecule X_2, z = 1.

$$d = \frac{z \times M}{N_A \times a^3}$$

$$\Rightarrow 6.17 = \frac{1 \times M}{6 \times 10^{23} \times (300 \times 10^{-10})^3}$$

$\Rightarrow M = 100$ g/mol.

Number of molecules present in 200g of

$$X_2 = \frac{200 \text{ g}}{100 \text{ g / mol}} \times N_A \text{ molecules/mol}$$

= $2N_A$ molecules.

55. **(d)** $d = \dfrac{Z \times M}{N_A \times \text{Volume}}$

$$2.7 = \frac{Z \times 27}{6.02 \times 10^{23} \times [4.05 \times 10^{-8}]^3}$$

$Z = 4 \Rightarrow$ fcc unit cell

For fcc unit cell $4r = \sqrt{2}a$

$$r = \frac{1.414 \times 405}{4} = 143.1675 \text{ pm} = 143.17 \text{ pm}$$

56. **(c)** In fcc, tetrahedral voids are located on the body diagonal at a distance of $\dfrac{\sqrt{3}a}{4}$ from the corner. Together they form a smaller cube of edge length $\dfrac{a}{2}$. Therefore, distance between centres of two nearest tetrahedral voids in the lattice is also $\dfrac{a}{2}$.

57. **(b)** No. of lattice points in ccp structure = 4

$\therefore$ No. of atoms of B = 4

No. of octahedral voids = 4

No. of atoms of A $= \dfrac{1}{2} \times$ No. of *Oh* voids

$$= \frac{1}{2} \times 4 = 2$$

No. of atoms of O = No. of all Td voids

= 2 × No. of lattice points

= 2 × 4 = 8

Hence, A : B : O = 2 : 4 : 8 = 1 : 2 : 4

Therefore, the formula of the compound is AB_2O_4.

58. **(c)** Radius of atom A = r

$\therefore$ Radius of atom B = $2r$

Volume occupied by atoms in solid 2

$$= \frac{4}{3}\pi r^3 + \frac{4}{3}\pi(2r)^3 = 12\,\pi r^3$$

Relationship between body diagonal and radius of atom (r),

$$\sqrt{3}\,a = r + 2(2r) + r$$

$$a = \frac{6r}{\sqrt{3}}$$

$$\text{Packing efficiency} = \frac{\text{vol. of particles}}{\text{vol. of unit cells}}$$

$$\text{Packing efficiency} = \frac{12\pi r^3}{\left(\frac{6r}{\sqrt{3}}\right)^3} \times 100 = 90\%$$

59. **(d)** For bcc

$$\Rightarrow R = \frac{\sqrt{3}\,a}{4}$$

$$\therefore \text{Empty space at edge} = a - 2R = a - \frac{\sqrt{3}\,a}{2}$$

= diameter of sphere.

$$\therefore \quad r_{\text{sphere}} = \frac{a - \frac{\sqrt{3}}{2}a}{2} = \left(\frac{2-\sqrt{3}}{4}\right)a = 0.067\,a$$

60. **(d)** Here, A_2B_3 can also be written as A_4B_6.

No. of effective atoms in hcp lattice = 6.

So, 'B' forms hcp lattice and 'A' is present in tetrahedral voids.

Total tetrahedral voids = 12

$\therefore$ Fraction of tetrahedral voids occupied by A = 4/12 = $\frac{1}{3}$

61. **(d)** The given unit cell has atoms at all the corners and at two opposite face centres.

Thus, it is an end-centred unit cell.

62. **(c)** edge length a ≠ b ≠ c and axial angles $\alpha = \beta = \gamma = 90^\circ$

Possible variations

Primitive

Body centered

Face centered

End centred

63. **(c)** Volume of the cubic unit cell = a^3

$= (2r)^3$

$= 8x^3$

64. **(a)** An element has bcc structure with:

edge length (a) = 288 pm

No. of atoms (Z) = 2

$$\text{As, density } (d) = \frac{Z\,M}{N_A a^3}$$

Where, M = molar mass of element

N_A = Avogadro Constant

So,

$$7.2 \text{ g cm}^{-3} = \frac{2\,M}{(288\times10^{-10}\text{ cm})^3 \times (6.023\times10^{23}\text{ mol}^{-1})}$$

$$7.2g/\text{cm}^3 = \frac{2\,M}{14.33\text{ cm}^3\text{mol}^{-1}}$$

$$7.2\,g = 0.140\text{ M mol}$$

$$M = \frac{7.2\ g}{0.140\text{ mol}} = 51.42\,g/\text{mol}$$

By mole concept, 51.42 g of the element contains 6.022×10^{22} atom, 208 g of the element will contain

$$= \frac{6.022\times10^{23}\times208}{51.42}\text{atoms}$$

$= 24.22 \times 10^{23}$ atoms

65. **(c)** As, $d = \dfrac{ZM}{N_A\,a^3}$

Where, d = density

Z = No. of atoms = 1 for simple cubic lattice

M = Molar mass

N_A = Avogadro constant

a = edge length

$$\therefore \quad 7.2 = \frac{1\times250}{6.02\times10^{23}\times a^3}$$

$$a^3 = \frac{250}{6.02\times10^{23}\times7.2}$$

$$a = \left(\frac{250}{6.02\times7.2\times10^{23}}\right)^{1/3}$$

$a = 3.86 \times 10^{-8}$ cm

$$\therefore \quad \text{radius } (r) = \frac{a}{2} = 1.93\times10^{-8}\text{ cm} = 1.93\text{ Å}$$

66. **(a)** Number of A^{+y} ions = 2 × number of atoms per unit cell.

Number of B^{-x} ions = 2 (BCC) per unit cell.

$\Rightarrow$ Number of A^{+y} ions = 2 × 2 = 4

$\Rightarrow$ Formula = $A_4\,B_2$

67. **(a)** In CaF_2, the coordination numbers for $Ca^{+2} = 8$ and $F^- = 4$

68. **(d)** Body diagonal (*d*) of a cubic crystal of edge length (*a*) is given by,

$$d = a\sqrt{3}$$

putting $a = 400$ pm, we get

$$d = \sqrt{3} \times 400 \text{ pm} = 692.8 \text{ pm} \approx 693 \text{ pm}.$$

69. **(b)** Number of tetrahedral voids in the unit cell
= 2 × number of atoms = 2Z

70. **(b)** In AgI crystal, number of Ag^+ ions is equal to I^- ions. However, the number of tetrahedral voids are twice the number of atoms forming the cubic lattice.
$\therefore$ Number of tetrahedral voids occupied by Ag^+ ion is 50 %.

71. **(b)** ABAB.... is hexagonal close packing (*hcp*) in which space occupied = 74 % and, empty space = 26%.

72. **(c)** $40 \text{ g} = N_A$ atoms $\Rightarrow 4\text{g} = 0.1 \times N_A$ atoms
2 atoms form 1 unit cell in *bcc* crystal

$$\therefore 0.1 \times N_A \text{ atoms} = \frac{0.1 \times N_A}{2} \text{ unit cells}$$

73. **(a)** The number of spheres in one body centred cubic and in one face centred cubic unit cell is 2 and 4 respectively.

74. **(d)** Monoclinic crystals have two Bravais lattices—primitive and end centred.

75. **(c)** For *fcc*, radius of the atom = $\frac{a}{2\sqrt{2}}$

76. **(d)** **77.** **(b)** **78.** **(a)**

79. **(a)** Density, $p = \frac{Z \cdot M}{a^3 \cdot N_A}$

$a = 654 \text{ pm} = 654 \times 10^{-12} \text{ m} = 654 \times 10^{-10} \text{ cm}$

$$2.75 = \frac{Z \times 119}{\left(654 \times 10^{-10}\right)^3 \times \left(6.023 \times 10^{23}\right)} \quad Z = 3.89 \approx 4$$

Ionic solid has *fcc* system with coordination number = 6

80. **(a)** There are two atoms in a *bcc* unit cell.
So, number of atoms in 12.08×10^{23} unit cells
$= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}$ atoms.

81. **(c)** The coordination number is 8 : 8 for Cs^+ and Cl^-.

82. **(c)** The no. of atoms is a unit cell may be calculated by the the formula

$$Z = \frac{n_c}{8} + \frac{n_b}{1} + \frac{n_f}{2} + \frac{n_e}{4}$$

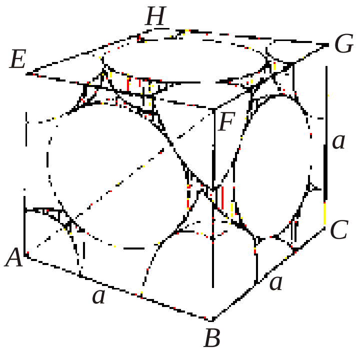
Where n_c = no. of atom at the corner
n_b = no. of atoms at body centre
n_f = no. of atoms at face centre
n_e = no. of atoms at edge centre.

An *fcc* crystal contains

$$= \frac{8}{8} + \frac{6}{2} = 4 \text{ atoms in a unit cell.}$$

83. **(b)** 14 kinds of Bravais lattices (space lattices) are possible in a crystal.

84. **(c)**



An isolated fcc cell is shown here. Each face of the cell is common to two adjacent cells. Therefore, each face centre atom contributes only half of its volume and mass to one cell. Arranging six cells each sharing the remaining half of the face centred atoms, constitutes fcc cubic lattice. e.g., Cu and Al.

85. **(c)** Match box exhibits orthorhombic geometry i.e., $a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$

86. **(b)** For orthorhombic system $\alpha = \beta = \gamma = 90°$

87. **(c)** Metal deficiency defect (cation is missing from lattice site); in Frenkel defect the smaller ion occupies the interstitial sites and Schottky defect equal number of cations and anions are missing. Interstitial defect an atom or molecule occupies interstitial sites so in these three defects the ratio of positive and negative ions (Stoichiometry) of a solid is not disturbed.

88. **(d)** Due to vacancy defect density of the substance will decrease.

89. **(c)** Frenkel defect is due to dislocation of ion from its usual lattice site to interstitial position.

90. **(d)** Ionic solids must always maintain electrical neutrality. Ionic solids show vacancy or interstitial defects as Frenkel and Schottky defect.

91. **(d)** When electrons are trapped in anion vacancies, these are called F-centre.

92. **(d)** The appearance of colour in solid alkali metal halide is due to presence of F-centre found as defect in the crystal structure.

93. **(a)** Stoichiometric Frenkel defects occur in those compound which have Low C.N. and Large difference in size of cations and anions

94. **(c)** Pink colour of LiCl crystal is due to metal excess defect and formation of anionic vacancies (F-Centre).

95. **(b)** Transition metals exhibit this defect due to metal deficiency. The compound obtained are non stoichiometric *e.g*. It is difficult to prepare ferrous oxide with the ideal composition of FeO; what we actually obtain is $Fe_{0.95}O$ or Fe_xO with x = 0.93 to 0.96

96. **(c)** AgBr exhibit Frenkel defect.

97. **(c)** 1 Cd^{2+} atom replace 2Ag^+ ions as a result cationic vacancy are created.

98. **(d)** Excess of lithium makes LiCl crystal pink.

99. **(b)** More is the Schottky defect in crystal more is the decrease in density.

100. **(b)** $Ni_{0.98}O = (Ni^{2+})_x\,(Ni^{3+})_{0.98-x}\,(O^{2-})_1$

Net charge = 0

$[x \times 2] + [(0.98 - x) \times 3] + [-2 \times 1] = 0$

$x = 0.94$

Fraction of nickel existing as

$$Ni^{2+} = \frac{0.94}{0.98} = 0.959 \approx 0.96$$

101. **(b)** AgBr shows both, Frenkel as well as Schottky defects.

102. **(a)** Impurity present in a crystal does not establish thermal equilibrium.

103. **(a)** Let moles of Fe^{2+} in $Fe_{0.93}O$ be x.

Thus, moles of $Fe^{3+} = 0.93 - x$.

For electrical neutrality,

$(+2)x + (+3)(0.93 - x) = +2 \;\Rightarrow\; x = 0.79$

$$\%\ Fe^{2+} = \frac{0.79}{0.93} \times 100 = 84.9\,\% \approx 85\%$$

104. **(c)** One Sr^{2+} replaces two K^+. It occupies one of the position and one void is created.

Moles of KBr given $= \dfrac{1}{119}$

Number of vacancies in 1 mole of KBr

$$= \frac{10^{-5}}{100} \times 6.023 \times 10^{23}$$

$\therefore$ Total vacancies in KBr

$$= \frac{10^{-7} \times 6.023 \times 10^{23}}{119} = 5.06 \times 10^{14} \approx 5 \times 10^{14}.$$

105. **(a)** AgBr shows both Schottky as well as Frenkel defects.

106. **(c)** In Frenkel defect some of ions (usually cations due to their small size) missing from their normal position, occupy position in interstitial sites.

107. **(c)** The crystal lattice has vacant anion sites, which are occupied by electrons. Anion sites occupied by electrons are called F-centres (F is abbreviated from Farbe, the German word for colour. These F-centres are associated with the colour of the compound and the more F-centres present, the greater the intensity of the coloration. F-centre containing solids are paramagnetic, photoconductors.

108. **(d)** $Fe_{0.93}O$ is a metal deficiency defect. In FeO, some Fe^{2+} ions are missing and the loss of positive charge is made up by Fe^{3+} ions.

109. **(b)** Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

110. **(b)** Schottky defect is shown by highly ionic compounds e.g. NaCl, KCl, KBr, AgBr, CsCl etc.

111. **(d)**

112. **(b)** On adding non-metal in metal, the metal becomes less tensile.

113. **(d)** Extrinsic semiconductor

114. **(d)** Intrinsic semiconductors are insulators at room temperature and become semiconductors when temperature is raised.

115. **(b)** Doping by electron deficient atoms create *p*-type semiconductors.

116. **(b)**

117. **(b)** The ordering of domain even after removal of magnetic field make ferromagnetic substance permanent magnet.

118. **(d)** Both obribtal motion and spin of electron contributes to the magnetic moment of electron.

119. **(c)** Rhenium oxide ReO_3 is like metallic copper in conductivity.

120. **(d)** $CCl_4 \rightarrow$ Non-conductor in solid and liquid phase.

Melting point of CCl_4 is –23 °C. It does not conduct electricity in both solid and liquid state.

121. **(c)** Quartz exhibits piezoelectricity and thus, can be used as a piezoelectric material.

122. **(a)** Ferromagnetism is maximum in Fe due to more number of unpaired electrons.

123. **(a)** $BaTiO_3$

124. **(c)**

125. **(c)** The doped silicon piece will become p-type.

Exercise 2 : ACCELERATOR

Topic-wise MCQs

1. **(d)** Ionic compounds are dissociated in solution state and form ions. Ions are good carrier of charge which make solution conducting.

2. **(d)** Crystals show good cleavage because their constituent particles are arranged in planes.

3. **(c)** Solid CH_4 is a molecular solid. In this, the constituent molecules are held together by van der Waal's forces.

4. **(a)** Si is an example of covalent crystalline solid among the given choices. Si atoms are covalently linked in tetrahedral manner.

5. **(b)** Amorphous solids are isotropic, because these substances show same properties in all directions.

6. **(b)**

7. **(c)** Polymorphism is a ability of a substances to show two or more crystalline structure.

8. **(c)** All metals and some alloys are metallic crystal.

9. **(a)** According to **Born-Lande** equation :

$$U = \frac{Z^+Z^-e^2AN}{4\pi e_\circ r_\circ}\left(\frac{1}{n}-1\right)$$

where,

A = Madelung constant (depends on type of crystal lattice)

N = Avogadro's number

Z^+, Z^- = magnitude of charge

$r_\circ$ = distance between ions

$e_\circ$ = permitivity of vaccum

Lattice energy is inversely proportional to interionic distance (r_o) i.e., ions should be of small size to give high lattice energy.

10. **(d)** Ionic crystals exhibit non-directional properties of the bond.

11. **(a)** Glass is a pseudo solid.

12. **(c)** AB is just like NaCl. Thus twelve A^+ are at edges and 1 within body of *fcc* i.e. in octahedral voids and six B^- at faces and 8 at corner.

13. **(c)** In fluorite structure each F^- ion is surrounded by four Ca^{++} ions whereas each Ca^{++} is surrounded by eight F^- ions, giving a body centred cubic arrangement. Thus the co-ordination number of Ca^{++} and F^- are 8 and 4 respectively.

14. **(b)** *hcp* is a closed packed arrangement in which the unit cell is hexagonal and coordination number is 12.

15. **(c)** ABAB...... is hexagonal close packing.

16. **(d)** It represents ccp arrangement.

17. **(b)** For body centred cubic lattice $Z = 2$

Atomic mass of unit cell = 133 + 80 = 213 a.m.u

Volume of cell = $(436.6 \times 10^{-10})^3\,\text{cm}^3$

$$\text{Density, } \rho = \frac{ZM}{a^3 N_A}$$

$$= \frac{2 \times 213}{(436.6 \times 10^{-10})^3 \times 6.02 \times 10^{23}} = 8.50\ \text{g/cm}^3$$

18. **(b)** Distance between K^+ and F^- $= \frac{1}{2} \times$ length of the edge

19. **(a)** For bcc structure, atomic radius, $r = \frac{\sqrt{3}}{4}a$

$$= \frac{\sqrt{3}}{4} \times 4.3 = 1.86$$

Since, r = half the distance between two nearest neighbouring atoms.

∴ Shortest interionic distance = 2 × 1.86 = 3.72

20. **(c)** In a *fcc* lattice, the distance between the cation and anion is equal to the sum of their radii, which is equal to half of the edge length of unit cell,

i.e. $r^+ + r^- = \frac{a}{2}$ (where a = edge length)

$r^+ = 95$ pm, $r^- = 181$ pm

Edge length = $2r^+ + 2r^- = (2 \times 95 + 2 \times 181)$ pm

= (190 + 362) pm = 552 pm.

21. **(b)** Number of tetrahedral voids (V_T) in a crystal is twice the number of atoms (n) in a crystal i.e.,

$$V_T = 2n$$

So, number of tetrahedral voids per atom is given by

$$V_T / n = 2$$

22. **(c)** A body-centred cubic system consists of all eight corners plus one atom at the centre of cube.

23. **(a)** For a face centred cubic structure,

No. of X atoms $= 8 \times \frac{1}{8} = 1$

No. of Y atoms $= 6 \times \frac{1}{2} = 3$

∴ Formula of the compound = XY_3

24. **(a)** ZnS has cubic close packed (ccp) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, S^{2-} ion is surrounded by four Zn^{2+} ions.

25. **(a)**

26. **(d)** In a unit cell, W atoms at the corner $= \frac{1}{8} \times 8 = 1$

O-atoms at the centre of edges $= \frac{1}{4} \times 12 = 3$

Na-atoms at the centre of the cube = 1

W : O : Na = 1 : 3 : 1

Hence, formula = $NaWO_3$

27. **(a)** Since MgO has a rock salt structure. In this structure each cation is surrounded by six anions and vice versa.

28. **(a)** Potassium crystallises in *bcc* lattice.

29. **(b)** The face centered cubic unit cell contains 4 atom

∴ Total volume of atoms $= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

30. **(c)** As CsCl is body-centred, $d=\sqrt{3}a/2$.

31. **(d)** $M=\dfrac{\rho\times a^3\times N_A\times 10^{-30}}{Z}$

$$=\frac{10\times(100)^3\times 6.02\times 10^{23}\times 10^{-30}}{4}=15.05$$

$\therefore$ Number of atoms in 100 g $=\dfrac{6.02\times 10^{23}}{15.05}\times 100$

$= 4\times 10^{25}$

32. **(d)** For *bcc*, $d=\dfrac{\sqrt{3}}{2}a$ or $a=\dfrac{2d}{\sqrt{3}}=\dfrac{2\times 4.52}{1.732}=5.219\text{Å}$

$= 522$ pm

$$\rho=\frac{Z\times M}{a^3\times N_A\times 10^{-30}}$$

$$=\frac{2\times 39}{(522)^3\times(6.023\times 10^{23})\times 10^{-30}}$$

$$=0.91\text{g}/\text{cm}^3=910\text{ kg m}^{-3}$$

33. **(d)** Packing fraction of bcc = 68%

Empty space = 100 – 68 = 32%

34. **(b)** Density $=\dfrac{nM}{N_A\times a^3}$

$$=\frac{4\times 58.5}{6.023\times 10^{23}\times(5.64\times 10^{-8})^3}=2.16\text{ g/cm}^3$$

35. **(d)** For an *fcc* crystal

$$r_{\text{cation}}+r_{\text{anion}}=\frac{\text{edge length}}{2}$$

$$110+r_{\text{anion}}=\frac{508}{2}$$

$$r_{anion}=254-110=144\text{ pm}$$

36. **(d)** For *bcc* structure $\sqrt{3}\,a=4r$

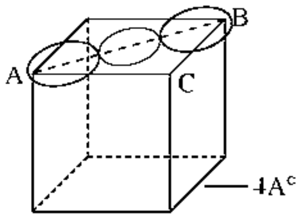
$$r=\frac{\sqrt{3}}{4}a=\frac{\sqrt{3}}{4}\times 351=152\text{ pm.}$$

37. **(c)** The *hcp* arrangement of atoms occupies 74% of the available space and thus has 26% vacant space.

38. **(b)** $(AB)^2=4^2+4^2$

$AB^2=32$

$4r=AB=\sqrt{32}$



$$r=\frac{\sqrt{32}}{4}=\frac{4\sqrt{2}}{4}=\sqrt{2}$$

x = distance between two atom = $2r=2\sqrt{2}$

$$\text{density}=\frac{\text{mass}}{V}=\frac{\text{mass of unit cell}}{\text{Volume of unit cell}}$$

$$=\frac{zM}{a^3\text{Na}}=\frac{4\times 197}{4^3\times 6.022\times 10^{23}}$$

$$=\frac{4\times 197}{64\times 10^{-24}\times 10^{23}\times 6.022}$$

$= 20.44\ g\text{ cm}^{-3}$

39. **(c)** Molecular formula = X_3Y_2

Y atom = ccp = 4

$$\text{X atom}=\frac{50\times 4}{100}+\frac{x\times 8}{100}\qquad\begin{bmatrix}\text{Td void}=8\\ \text{Oh void}=4\end{bmatrix}$$

$$\frac{X\dfrac{(50\times 4)}{100}+\dfrac{x\times 8}{100}}{2}Y_2$$

$$\therefore\ \frac{\dfrac{50\times 4}{100}+\dfrac{x\times 8}{100}}{2}=3$$

$$\text{or, }2+\frac{8x}{100}=6$$

$$\frac{8x}{100}=4$$

$\therefore$ x = 50%

40. **(a)** hcp contribution i.e (C) = 4

Total octahedral void = 4

‘A’ contribute = 4 × 50% = 2

Total tetrahedral void = 8

$\therefore$ ‘B’ contribute $=8\times\dfrac{2}{3}=\dfrac{16}{3}$

$\therefore$ $A_2\,B_{16/3}\,C_4$

$A_6\,B_{16}\,C_{12}$

By simplify we get

$A_3\,B_8\,C_6$

41. **(d)** Number of octahedral voids = x (where x = total number of atoms in the unit cell)

Number of tetrahedral Voids = 2x

$\Rightarrow$ Total number of ‘A’ atoms = x + 2x = 3x

Since all ‘B’ atoms occupy all the FCC centres:-

$\Rightarrow$ Total number of ‘B’ atoms $=\left[6\times\dfrac{1}{2}\right]+\left[8\times\dfrac{1}{8}\right]=4$

$\Rightarrow$ x = 4 so number of ‘A’ atoms = 3x = 3 × 4 = 12

So, the formula will be $A_{12}\,B_4$ or A_3B

42. **(c)** density (d) = $\frac{Z \times M}{N_A \times a^3}$

for Cu ; Z = 4 (for Fcc) $\Rightarrow$ a = x Å = x × 10^{-8} cm

$N_A = 6.0 \times 10^{23}$ mol^{-1} $\Rightarrow$ M = 63.5 g mal^{-1}

$$\Rightarrow \quad d = \frac{(4)(63.5)}{\left(6.0 \times 10^{23}\right)\left(x \times 10^{-8}\right)^3} = \frac{423.0}{x^3}$$

43. **(c)** $d = \frac{M \times Z}{N_A a^3}; Z = \frac{d N_A a^3}{M}$

$$\therefore \quad Z = \frac{0.613 \times 6.023 \times 10^{23} \times \left(5 \times 10^{-8}\right)^3}{23}$$

$= 20.06 \times 10^{-1} \simeq 2.0$

44. **(a)** No. of atoms present in 540 g of Ag $= \frac{540 N_A}{108} = 5N_A$

Effective no. of atoms in fcc = 4

In one unit cell, no. of Tetrahedral voids = 2 × 4 = 8

$\therefore$ No. of fcc unit cell formed by 5 N_A atoms $= \frac{5N_A}{4}$

$\therefore$ Total no. of tetrahedral voids created by $5N_A$ atoms

$= 8 \times \frac{5N_A}{4} = 10N_A$

45. **(b)** Face-centred cubic packing (fcc) and cubic close packing (ccp) has same packing efficiency.

46. **(d)** In a unit cell of fcc lattice, A is present at 8 corners and 6 faces.

$\therefore$ Effective no. of $A = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

C is present at body centre and 6 edges.

$\therefore$ Effective no. of C $= 1 + 6 \times \frac{1}{4} = \frac{5}{2}$

$\therefore \; C_{\frac{5}{2}} A_4 = C_5 A_8$

47. **(a)** 210 g of A contains $\left(\frac{N_A}{M_A} \times 210\right)$ no. of atoms A and

594 g of B contains $\left(\frac{N_A}{M_A} \times 594\right)$ no. of atoms B.

[M_A and M_b are the atomic weights of A and B, respectively].

Now, $\frac{N_A}{M_A} \times 210 = \frac{N_A}{M_B} \times 594$ or $\frac{M_B}{M_A} = \frac{594}{210}$

Effective no. of A atoms in fcc = 4 and that of B atoms in bcc = 2

$d_A = \frac{M_A \times 4}{N_A \times a^3}$ and $d_B = \frac{M_B \times 2}{N_A \times a^3}$; $d_A = 7 g / cm^3$

$\therefore \; \frac{d_B}{d_A} = \frac{M_B \times 2}{M_A \times 4}; \therefore d_B = 7 \times \frac{594}{210} \times 2 = 9.9 \text{ g} / cm^3$

48. **(c)** In the face centred unit cell, (fcc) the lattice points are present at the corners and face centres of unit cell.

49. **(a)** Aslo, number of tetrahedral voids = 2 × number of metal atoms in close packed structure

= 2 × 0.5 = 1 mol

Number of octahedral void = number of metal atoms in close packed structure

Total number of voids = tetrahcdral void + octahedral void

= (1 + 0.5) mol = 1.5 mol

50. **(b)** Given,

Radius of an atom (bcc) = 173.2 pm, = 1.732 × 10^{-8} cm

$\because$ For bcc structure

$\sqrt{3}.a = 4r$ where, a = edge-length

r = radius of atom.

and a^3 = V (volume of cubic unit cell).

$$a = \frac{4}{\sqrt{3}} \cdot r$$

$$a = \frac{4}{1.73} \times 1.732 \times 10^{-8} \text{ cm}$$

$a = 4 \times 10^{-8}$ cm

Therefore,

Volume (V) = $(a^3) = [10^{-8}]^3 \times 4^3$

64×10^{-24} cm$^3 \Rightarrow 6.4 \times 10^{-23}$ cm^3

51. **(d)** Given, body centered cubic (bcc) $Z = 2$

Edge length (a) = 400 pm = 400 × 10^{-10} cm

M (atomic mass) = 24 g mol^{-1}

$\because$ Density (d) = $\frac{Z \times M}{a^3 \times N_A}$

$$d = \frac{2 \times 24}{\left(400 \times 10^{-10}\right)^3 \times 6.022 \times 10^{23}}$$

$\Rightarrow \quad d = 1.25 \; g \; cm^{-3}$

52. **(d)** For bcc lattice : $Z = 2$, $a = \frac{4r}{\sqrt{3}}$

For fcc lattice : $Z = 4$, $a = 2\sqrt{2}r$

$$\therefore \quad \frac{d_{25\,°C}}{d_{900\,°C}} = \frac{\left(\frac{ZM}{N_A a^3}\right)_{bcc}}{\left(\frac{ZM}{N_A a^3}\right)_{fcc}} = \frac{2}{4}\left(\frac{2\sqrt{2}r}{\frac{4r}{\sqrt{3}}}\right)^3 = \frac{3\sqrt{3}}{4\sqrt{2}}$$

53. **(a)** $a = 2(r_+ + r_-)$

$\Rightarrow a = 2(102 + 181)$

$\Rightarrow a = 566$ pm

54. **(d)** No. of carbon atoms in fcc lattice = $8\times\frac{1}{8}+6\times\frac{1}{2}=4$

No. of tetrahedral voids = 4 × 2 = 8

No. of carbon atoms in tetrahedral voids $=8\times\frac{1}{2}=4$

$\therefore$ Total atoms = 4 + 4 = 8

55. **(a)**

	M1	**M2**	**O**
	50%	12.5%	ccp
	octahedral void	tetrahedral void	
	$\frac{50}{100}\times 4$	$\frac{12.5}{100}\times 8$	4
	2	1	4
Charge	$2x$	$1y$	4 × 2

So, $2x+y=8$

$x=2$; $y=4$ (among given options, only option (a) is possible)

56. **(d)** We know that, density $=\frac{Z(M)}{N_A\times a^3}$

Given that: $Z=4$ (fcc)

$M=63.5$ g

$N_A=6\times 10^{23}$

$a=x\times 10^{-8}$cm

After putting the values, we get

$$d=\frac{4\times 63.5}{6.022\times 10^{23}\times x^3\times 10^{-24}}=\frac{422\text{ g cm}^{-3}}{x^3}$$

57. **(a)** HI is a covalent molecule, and crystallize in a face centred cubic structure. Therefore HI molecules are present at the lattice points of the crystal.

58. **(c)** Let the number of Z atoms in the *ccp* arrangement = 100

Thus the number of tetrahedral sites = 200

Since all the tetrahedral sites are occupied by X atoms, the number of X atoms = 200

Hence ratio of X : Z = 2 : 1

Thus the formula is X_2Z.

59. **(d)** Since in NaCl type structure 4 formula units form a cell.

58.5 g of NaCl = 6.023×10^{23} atoms

1 g of NaCl $=\frac{6.023\times 10^{23}}{58.5}$ atoms

4 atoms constitute 1 unit cell

$\therefore$ $\frac{6.023\times 10^{23}}{58.5}$ atoms constitute

$=\frac{6.023\times 10^{23}}{58.5\times 4}=2.57\times 10^{21}$ unit cells.

60. **(b)** In ZnS structure, sulphide ions occupy all *fcc* lattice points while Zn^{2+} ions are present in alternate tetrahedral voids.

61. **(c)** $Z=\frac{V\times N_A\times\rho}{M}$

$$=\frac{4.2\times 8.6\times 8.3\times 10^{-24}\times 6.023\times 10^{23}\times 3.3}{155}=3.84=4$$

62. **(b)** Volume of unit cell = a^3

$=(3.04\times 10^{-8}\text{ cm})^3=2.81\times 10^{-23}\text{ cm}^3$

63. **(a)** Let the units of ferrous oxide in a unit cell = n,

molecular weight of ferrous oxide (FeO) = 56 + 16

= 72 g mol^{-1}

weight of n units $=\frac{72n}{6.023\times 10^{23}}$

Volume of one unit = (length of corner)^3

$=(5\text{Å})^3=125\times 10^{-24}\text{ cm}^3$

Density $=\frac{\text{wt. of cell}}{\text{volume}}$

$$4.09=\frac{72\times n}{6.023\times 10^{23}\times 125\times 10^{-24}}$$

$$n=\frac{3079.2\times 10^{-1}}{72}=42.7\times 10^{-1}=4.27\approx 4$$

64. **(c)** No. of *hcp* particles in 0.5 mole = $0.5\times 6.023\times 10^{23}$

$=3.011\times 10^{23}$

No. of Octahedral void (n) = 3.011×10^{23}

No. of Tetrahedral void ($2n$) = $2\times 3.011\times 10^{23}$

= 6.022×10^{23}

$\therefore$ Total no. of voids = $3.011\times 10^{23}+6.022\times 10^{23}$

= 9.033×10^{23}

65. **(a)** $\rho=\frac{ZM}{N_AV}$

$$Z=\frac{\rho N_AV}{M}=\frac{2\times 6\times 10^{23}\times(5\times 10^{-8})^3}{75}$$

Z = 2, which represents *bcc* structure

$$\therefore\ r=\frac{\sqrt{3}}{4}a=\frac{\sqrt{3}}{4}\times 5=2.165\text{Å}=216.5\text{ pm}$$

$\approx$ 217 pm

66. **(c)** Density $=\frac{Z\times M}{N_A\times a^3}$

$$9\times 10^3=\frac{4\times M}{\left(200\times\sqrt{2}\times 10^{-12}\right)^3 6\times 10^{23}}$$

$M=305.4\times 10^{-4}=0.0305\text{ kg mol}^{-1}$

67. **(d)** Packing efficiency

$$= \frac{\text{Area occupied by circles within the square}}{\text{Area of square}}$$

$$= \frac{2\pi r^2}{L^2} \times 100 = \frac{2\pi r^2}{(2\sqrt{2}r)^2} \times 100$$

$$= \frac{\pi}{4} \times 100 = 78.54\%$$

68. **(d)** The coordination number is 12.

69. **(d)** For *bcc* lattice body diagonal = $a\sqrt{3}$
The distance between the body centred atom and one corner atom in cube will be = $\frac{\sqrt{3}a}{2}$

70. **(a)** **71.** **(d)**

72. **(d)** In KCl, co-ordination number of cation and anion is 6 and 6 respectively. KCl is highly ionic so Schottky defect is common.

Note : Schottky defect is common in compounds having high coordination nummber while Frenkel defect is common in compounds with low coordination number.

73. **(a)** Schottky defects are found in solid.

74. **(d)** Frenkel defect does not lower the density of the crystal since the ions do not leave the crystal lattice.

75. **(d)** Schottky defect occurs in ionic crystals of type $A^+ B$, when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This defect generally appears in highly ionic compounds which have high coordination number. NaCl, KCl and CsCl all have high coordination numbers i.e., 6, 6 and 8 respectively. So, Schottky defect appear in all of the given compounds.

76. **(c)** Frenkel and Schottky defects are crystal defects. It arises due to dislodgement of cation or anion from their places in the crystal lattice.

77. **(c)** The vacancy created due to missing of equal no. of atoms or ions form normal lattice point is called Schottky defect. In this type of defect electrical neutrality of ionic crystal is maintained.

78. **(b)** When equal number of cations (Na^+) and anions (Cl^-) are missing from their regular lattice positions, we have schottky defect.

79. **(c)** One $CdCl_2$ creates one cationic vacancy by replacing one Ag^+ due to Cd^{2+} divalent cation.

Now, 10^{-4} mol % $CdCl_2$ per mole AgCl

= 10^{-4} mol $CdCl_2$ per 100 moles AgCl

= $10^{-2} \times 10^{-4} = 10^{-6}$ mol $CdCl_2$ per mole AgCl

= $10^{-6} \times 6.023 \times 10^{23}$

= 6.023×10^{17} $CdCl_2$ per mole AgCl

= 6.023×10^{17} Cd^{2+} ions per mole AgCl

= 6.023×10^{17} cationic vacancies per mole AgCl

80. **(b)** Zinc oxide is white in colour at room temperature on heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Excess of zinc in the crystal and its formula become ($Zn_{(1+x)}$ 0). The excess Zn^{2+} ions move to interstitial site and electrons to neighbouring interstitial site.

It is metal excess defect due to the pressure of extra cations at interstitial sites.

So, (I) and (III) are correct.

81. **(b)** NaCl has monovalent Na^+ ion. If $SrCl_2$ remains as impurity in NaCl then one Na^+ ion has to be absent in order to maintain electrical neutrality with divalent Sr^{2+}. Thus, it creats cationic vacancies.

82. **(d)**

83. **(b)** Schottky defect is caused if some of the lattice points are unoccupied. The points which are unoccupied are called vacancies or holes. The number of missing positive and negative ions are of similar size.

84. **(c)** Pure silicon doped with phosphorus is a *n*-type semiconductor, as *n*-type extrinsic semiconductor (Si) is made by doping the semiconductor with pentavalent element.

85. **(d)** The semiconductors formed by the introduction of impurity atoms containing one elecron less than the parent atoms of insulators are termed as *p*-type semiconductors. Therefore silicon containing 14 electrons is to be doped with boron containing 13 electrons to give a *p*-type semiconductor.

86. **(d)** For n-type, impurity added to silicon should have more than 4 valence electrons.

87. **(c)**

88. **(c)**

89. **(a)** *p*-type of semiconductors are produced

(i) due to metal deficiency defects

(ii) by adding impurity containing less electrons (i.e., atoms of group 13)

Ge belongs to Group 14 and In to Group 13. Hence on doping, p-type semicondutor is obtained.

90. **(a)** Ferromagnetism is due to spontaneous alignment of the magnetic dipoles in same direction.

91. **(d)** When insulators (non metal atoms) interact to form a solid, their atomic orbitals mix to form two bunch of orbitals, separated by a large band gap. Electrons cannot therefore be promoted to an empty level, where they could move freely.

92. **(d)**

93. **(c)** When polar crystal is subjected to a mechanical stress, electricity is produced – a case of piezoelectricity. Reversely, if electric field is applied, mechanical stress is developed. Piezoelectric crystal acts as a mechanical electrical transductor.

94. **(c)** Piezoelectric crystals are used in record player.

95. **(a)** An element containing an odd number of electrons is paramagnetic.

96. **(c)** In antifluorite structure the oxide ions (anions) form a face-centered cubic array and the metal ions (cations) occupy all the tetrahedral voids. Example : Na_2O

97. **(d)** Ferrimagnetic substance become para-magnetic on heating. This is due to randomisation of spins on heating.

98. **(c)** The conduction band is empty

99. **(a)** Lies towards the conduction band.

100. **(a)**

Exercise 3 : PREVIOUS YEARS MCQs

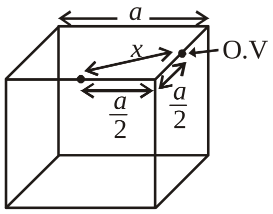
1. **(b)** For fcc,

$$r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}} = 0.3535a$$

Given, $a = 361$ pm

$r = 0.3535 \times 361 = 128$ pm

2. **(a)**



Distance between two octahedral voids

$$x = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \sqrt{\frac{a^2}{4} + \frac{a^2}{4}} = \frac{a}{\sqrt{2}}$$

3. **(d)** $d = \dfrac{Z \times M}{a^3 \times N_A}$

$Z = 2$; for bcc

$$5 \text{ g/cm}^3 = \frac{2 \times M}{(200 \times 10^{-10} \text{ cm})^3 \times 6.0 \times 10^{23}}$$

$\Rightarrow$ $M = 12$ g

12 g of element contain $= N_A$ atoms

300 g of element contains $= N_A \times \dfrac{300}{12} = 25\, N_A$

4. **(c)** Octahedral voids are present at body centre and edge centre.

Distance between octahedral void $= \dfrac{a}{\sqrt{2}}$

Length of body diagonal $= \sqrt{3}a$

$x = \sqrt{3}a \qquad a = \dfrac{x}{\sqrt{3}}$

Distance $= \dfrac{a}{\sqrt{2}} = \dfrac{x}{\sqrt{3} \times \sqrt{2}} = \dfrac{x}{\sqrt{6}}$ A

5. **(b)** Coordination number of an atom in BCC unit cell is 8.

6. **(a)** Brass is an alloy of copper and zinc metal and shoos substitutional impurity defect.

7. **(b)** CrO_2 is ferromagnetic solid whereas NaCl, C_6H_6, H_2O are diamagnetic solid

8. **(b)** $\rho = \dfrac{Z\,M}{N_A V}$

$$Z = \frac{\rho N_A V}{M} = \frac{8.92 \times 6.02 \times 10^{23} \times (362)^3 \times 10^{-30}}{63.55} = 4$$

$\therefore$ It has *fcc* unit cell.

9. **(d)** Diamond -crystalline solid, Glass, plastic and rubber amorphous solids

10. **(d)** Cu metal forms ccp crystal structure.

11. **(a)** Iodine molecules belongs to a class of non – polar molecular solids in which constituents molecule are held together by London or dispersion forces.

12. **(b)** In AB AB packing (*hcp*), spheres occupy 74%. 26% is empty.

13. **(b)** Tetragonal crystal system has 2 unit cell simple or primitive unit cell and body centred

14. **(b)** Density is given by

$d = \dfrac{Z \times M}{N_A a^3}$; where Z = number of formula units present in unit cell, which is 4 for *fcc*

a = edge length of unit cell. M = Molecular mass

$$2.72 = \frac{4 \times M}{6.02 \times 10^{23} \times \left(404 \times 10^{-10}\right)^3} \quad (\because\ 1\text{pm} = 10^{-10}\text{cm})$$

$$M = \frac{2.72 \times 6.02 \times (404)^3}{4 \times 10^7} = 26.99 = 27 \text{ g mole}^{-1}$$

15. **(b)** Packing fraction is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the total volume of the unit cell.

P.F. for *cpp* and *bcc* are 0.74 and 0.68 respectively.

So, the free space in *ccp* and *bcc* are 26% & 32% respectively.

16. **(a)** In crystalline solid there is perfect arrangement of the constituent particles only at 0 K. They have sharp M.P.

17. **(c)** Due to electrostatic force of attraction, the melting points and boiling points of ionic compounds are high.

18. **(d)** If in an ionic crystal of the type A^+, B^-, equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. The defect is called Schottky defect.

19. **(d)** For a *fcc* unit cell

$$r = \frac{\sqrt{2}a}{4}$$

$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2} \times 0.14 = 0.39 \approx 0.4 \text{ nm}.$$

20. **(d)** Frenkel defect is found in AgCl because there is a large difference between the size of Ag^+ and Cl^-. Hence the cation Ag^+ occupy the interstitial site by leaving a corresponding number of normal lattice site vacant.

21. **(a)**

22. **(c)** kg m^{-3}

23. **(a)** ZnS because it shows Frenkel defect.

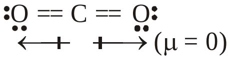
24. **(c)** The volume occupied by the face centred cubic unit cell

$$= z_{eff} \times \frac{4}{3}\pi r^3$$

$$= 4 \times \frac{4}{3}\pi r^3$$

$$= \frac{16}{3}\pi r^3$$

25. **(d)** Carbon dioxide is a non-polar solid because the bonds are linear and dipole moment point in opposite directions, cancel out the dipole moments, leaving a net polarity of zero.



$$:\ddot{O} == C == \ddot{O}: \quad (\mu = 0)$$

2

Solutions

Exercise 1 : WARM-UP

Topic-wise MCQs

1. **(b)**
2. **(a)**
3. **(b)** A gaseous solution is a solution in which the solvent is a gas.
4. **(c)**
5. **(b)** According to Henry's law

$$p \propto x$$

$$\Rightarrow \quad p = K_H x$$

As value of K_H rises solubility of gases decreases.

6. **(c)** Dissolution of gases in liquids is generally an exothernic process accompanied by a large decrease in volume. According to Le chatelier's principle, high pressure and low temperature favours the dissolution of a gas in a liquid.
7. **(b)** Exothermic and reversible process (according to Le-Chatelier principle, solubility of gases in liquids decreases with rise in temperature)
8. **(d)**
9. **(a)** As the value of Henry's law constant increases, the solubility of gas decreases.
10. **(c)**

Gas	Temperature	K_H / k bar
He	293	144.97
H_2	293	69.16
O_2	293	34.86
N_2	293	76.48

So, He has the highest Henry's law constant.

11. **(d)** CO_2 reacts with water and therefore is high soluble in water. So it greatly deviates from Henry's law in water.
12. **(d)** Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
13. **(d)** Since CO_2 is most soluble in water among the given set of gases. Therefore, CO_2 has the lowest value of Henry's law constant.
14. **(c)** Greater the Henry's constant (K_H), lower is the solubility at the same pressure.

$\therefore$ Order of $K_H : CO > O_2 > CO_2 > C_2H_2$

$\therefore$ Order of solubility : $C_2H_2 > CO_2 > O_2 > CO$.

15. **(d)** All get dissolved with the evolution of heat.
16. **(c)** Value of K_H depends upon nature of gases dissolved in water

Gas	Temperature	K_H / k bar
Ar	298 K	40.3
CO_2	298 K	1.67
CH_4	298 K	0.413
HCHO	298 K	1.83×10^{-5}

Hence correct order is $Ar < CO_2 < CH_4 < HCHO$.

17. **(a)** $P_{N_2} = 5 \times 0.8 = 4$ atm

$$P_{N_2} = K_H \times X_{N_2} \Rightarrow X_{N_2} = \frac{4}{1 \times 10^5} = 4 \times 10^{-5}$$

10 moles of water contain, 4×10^{-4} moles of N_2.

18. **(c)** The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x).

$p = K_H . x$

Where K_H is Henry's constant.

19. **(b)** At total pressure 5 atm, the partial pressure of

$N_2 = 5 \times 0.8 = 4$ atm

According to Henry's Law, $P_{N_2} = K_H \, x_{N_2}$

(x_{N_2}) is the mole fraction of nitrogen gas dissolved in water.

or, $x_{N_2} = \dfrac{4 \text{ atm}}{1 \times 10^5 \text{ atm}}$ or, $x_{N_2} = 4 \times 10^{-5}$

$$\frac{n_{N_2}}{n_{N_2}+n_{H_2O}} \simeq \frac{n_{N_2}}{n_{H_2O}} = 4\times10^{-5} \quad \left[\text{since } n_{H_2O} >> n_{N_2}\right]$$

$\therefore \quad n_{N_2} = 4\times10^{-5}\times10 = 4\times10^{-4}\,\text{mol}$

20. **(a)** According to Henry's law,

$P = K_H \,.\, X_{gas}$

$\because \quad X_{gas} + X_{H_2O} = 1 \Rightarrow X_{gas} = 1 - X_{H_2O}$

$\therefore \quad P = K_H(1 - X_{H_2O}) \Rightarrow P = K_H - K_H \,.\, X_{H_2O}$

$y = c + mx$; $m = -K_H \Rightarrow$ slope is negative and $c = K_H$

Therefore, the intercept on Y axis increases from w to z.

21. **(a)** According to Henry's law

$p = K_H\chi$

for χ constant : $p \propto K_H$

p has max partial pressures.

So it should have maximum K_H and s have minimum partial pressure, So K_H should be minimum.

22. **(d)** Moles of CO_2 dissolved

$= K \times P_{CO_2} \times V_{bottle} = 3\times10^{-2}\times4\times100 = 12$;

Mass of $CO_2 = 12 \times 44 = 528$ g

23. **(a)** $k_H = 100$ kbar $= 10^5$ bar, p = 1 bar

$p = k_H \times x_A$

$$x_A = \frac{p}{k_H} = \frac{1}{100\times10^3} = 10^{-5}$$

$$\text{Moles of water} = \frac{1000}{18} = 55.5$$

Weight of water = 1000 g ($\because$ 1000 mL = 1000 g)

$$\text{Mole fraction} = 10^{-5} = \frac{x}{55.5+x}$$

As 55.5 >>> x, thus neglecting x from denominator

$$10^{-5} = \frac{x}{55.5} \Rightarrow x = 55.5\times10^{-5}\,\text{moles}$$

or 0.555 millimoles.

24. **(d)**

(a) From Henry's law $p = K_H(x)$

Higher the value of K_H smaller will be the solubility of the gas, so γ is more soluble.

(b) Though solubility of gases will decrease with increase in temperature but this conclusion can not be drawn from the given table.

(c) For γ

$(p)_\gamma = (K_H)_\gamma \,.\, (x)_\gamma$

$$= 2\times10^{-5}\left[\frac{55.5}{55.5+\frac{1000}{18}}\right] = 10^{-5}\ \text{k bar} = 10^{-2}\,\text{bar}$$

(d) For $\delta \Rightarrow p_\delta = (K_H)_\delta \,.\, (x)_\delta$

$$= 0.5\left[\frac{55.5}{55.5+\frac{1000}{18}}\right] = 0.5\times0.5$$

$= 0.25\ k$ bar = 250 bar.

25. **(d)** According to Henry's law

$$\frac{P_1}{P_2} = \frac{S_1}{S_2}$$

$$\frac{500}{750} = \frac{0.01}{S_2}$$

$$\therefore \quad S_2 = \frac{750\times0.01}{500} = 0.015\ \text{g / L}$$

26. **(c)** $p = K_H \times x$

$$0.920\ \text{bar} = 46.82\times10^3\ \text{bar} \times \frac{\text{mol of } O_2}{\text{mol of } H_2O}$$

$$0.920 = 46.82\times10^3\times\frac{\text{mol of } O_2}{1000/18}$$

$\Rightarrow \quad 0.920 = 46.82 \times n_{O2} \times 18$

$\Rightarrow \quad n_{O2} = 1.09\times10^{-3} \quad \Rightarrow \quad$ milli mol of $O_2 = 1$

27. **(a)** P_{O_2} (over water) = 20 kPa

K_H for $O_2 = 8.0\times10^4$ kPa

If X_{O_2} is the mole fraction of O_2 in solution, then according to Henry's law,

$$P_{O_2} = K_H(X_{O_2}) \Rightarrow X_{O_2} = \frac{20}{8.0\times10^4} = 2.5\times10^{-4}$$

Mass of 1 kg of water containing O_2 = 1 L

$\therefore$ Molarity of O_2 in solution $= 25\times10^{-5}$ M

28. **(d)** Solubility is directly proportional to pressure.

29. **(b)** According to Raoult's law "The partial pressure of a volatile component of a solution is directly proportional to its mole fraction in solution at any temperature".

$p = p^o x$

where, p = Partial pressure of component

$P°$ = Vapour pressure of component in pure form

x = mole fraction of component in solution.

30. **(b)**

31. **(c)** These two components A and B follows the condition of Raoult's law if the force of attraction between A and B is equal to the force of attraction between A and A or B and B.

32. **(c)** Relative lowering of vapour pressure depends upon the mole fraction of solute.

i.e., $\frac{P^\circ - P}{P^\circ}$ = mole fraction of solute

33. **(d)** Solutions in cases I and II are saturated and that in III is unsaturated.

34. **(c)** For high v.p. concentration of solute should be low and temperature should be high.

35. **(d)** $P = P_A^\circ + P_B^\circ = 300$ torr.

36. **(a)** Given $V.P_P = 80$ torr

$V.P_Q = 60$ torr

$P_{total} = V{\cdot}P_P \times x_P + V{\cdot}P_Q \times x_Q$

$= \left[80 \times \frac{3}{5} + 60 \times \frac{2}{5}\right] = 16 \times 3 + 12 \times 2$

$P_{total} = 48 + 24 = 72$ torr

37. **(d)** $P = P_A X_A + P_B X_B = P_A X_A + P_B (1 - X_A)$

$\Rightarrow P_A X_A + P_B - P_B X_A$

$\Rightarrow P_B + X_A (P_A - P_B)$

38. **(c)** $P_A = P_T x_A$

$P_A = P_T x_1$

$\therefore P_A = P_A^0 x_2 \Rightarrow P_T = \frac{P_A^0 x_2}{x_1}$

39. **(a)** Given $V.P_M = 800$ torr

$V.P_N = 600$ torr

$P_{total} = V{\cdot}P_M \times x_M + V{\cdot}P_N \times x_N$

$= 800 \times \frac{2}{5} + 600 \frac{3}{5} = 320 + 360 = 680$ torr

40. **(c)** The total pressure will be the sum of pressures of air and benzene 400 + 220 = 620 torr.

41. **(b)** Vapour pressure of aqueous solution (p) = 34.65 mm Hg

Mole fraction of non volatile solute is = 0.02

Mole fraction of water = 1 – 0.02 = 0.98

Vapour pressure of pure water (p°) = $\frac{p}{x} = \frac{34.65}{0.98} = 35.36$

42. **(a)** $p^\circ{}_A = 70$ mmHg, $x_B = 0.2$

$P_T = 84$ mm Hg, $x_A = 1 - x_B = 0.8$

$P_T = p^\circ{}_A x_A + p^\circ{}_B x_B \Rightarrow 84 = 70 \times 0.8 + p^\circ{}_B \times 0.2$

$\Rightarrow p^\circ{}_B = \frac{28}{0.2} = 140$ mm Hg.

43. **(b)** $p_A^\circ = ?$, Given $p_B^\circ = 200$ mm of Hg, $x_A = 0.6$, $x_B = 1 - 0.6 = 0.4$, $P = 290$ of Hg

$P = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$

$\Rightarrow 290 = P_A^\circ \times 0.6 + 200 \times 0.4 \;\therefore\; p_A^\circ = 350$ mm of Hg.

44. **(c)** $P_{Total} = P_A^0 x_A + P_B^0 x_B = 50 \times 0.3 + 100 \times 0.7 = 85$ torr

$P_2 = y_B \times P_{Total} \Rightarrow 70 = y_B \times 85 \Rightarrow y_B = \frac{70}{85} = \frac{14}{17}$

45. **(c)** Total V.P.,

$P = P_A^0 X_A + P_B^0 X_B = P_A^0 X_A + P_B^0 (1 - X_A)$

$= (P_A^0 - P_B^0) X_A + P_B^0$

Thus, $P_B{}^\circ = 114$ torr ; $P_A^0 - P_B^0 = 52$

or $P_A^0 = 166$ torr

Hence $P = 166 \times \frac{1}{2} + 114 \times \frac{1}{2} = 140$ torr

46. **(a)** 40% Hydrogen contains 40g Hydrogen gas and 60g of Oxygen gas.

$n_{H_2} = \frac{40}{2} = 20$; $n_{O_2} = \frac{60}{32} = 1.8$

$\chi_{H_2} = \frac{n_{H_2}}{n_{Total}} = \frac{20}{20 + 1.8} = \frac{20}{21.8} = 0.92$

$p_{H_2} = \chi_{H_2} \cdot P_{Total} = 0.92 \times 2.2 = 2.02$ bar

47. **(d)** Mole fraction of substance A in liquid phase = 0.2

The Raoult's law equation is:

$P_T = 0.8$; $P_A = P_T \times X_A$; $P_A = 0.4$

$P_A = \left(P_A^\circ\right) \times X_A \Rightarrow 0.4 \text{ atm} = P_A^\circ \times 0.2$

$\Rightarrow P_A^\circ = \frac{0.4}{0.2} = 2$ atm

48. **(d)** An ideal solution follows Raoult's law over a wide range of concentration and has zero enthalpy and volume of mixing of the components.

49. **(d)** Ethanol has hydrogen bonding while acetone has dipole-dipole forces. Thus, their mixture would form a non-ideal solution.

50. **(d)** $CH_3OH + CH_3COOH$ mixture solution is an example of ideal solution which obey Raoult's law and $\Delta H_{mix} = 0$.

51. **(a)** In ethyl chloride and ethyl bromide the intermolecular attraction is mostly Van der Waal's force. Therefore, A–B interactions are almost same as A–A and B–B.

$\therefore \quad \Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$

Acetone breaks the H-bonding in ethanol on mixing. So, the acetone-ethanol mixture shows positive deviation.

Phenol-aniline mixture has stronger H-bonding than A–A and B–B. So, negative deviation is observed.

Chloroform-acetone mixture has dipolar interactions among A–B. Hence, negative deviation is observed.

52. **(d)** Benzene and toluene have very similar molecular structure. Thus, they form an ideal solution.

53. **(d)** C_2H_5I and C_2H_5OH form non-ideal solution, because of hydrogen bonding in ethyl alcohol.

54. **(d)** $C_2\ H_5OH$ and C_6H_6 give positive deviation.

55. **(d)** Solution with negative deviation has

$P_T < P_{A0}\,X_A + P_{B0}\,X_B$ (Raoult's Law) $\Rightarrow P_A < P_{A0}\,X_A$ and $P_B < P_{B0}\,X_B$

If vapour pressure decreases so boiling point increases, due to stronger intermolecular forces.

56. **(d)** Conditions for real solutions showing negative deviation from Raoult's law are as follows :

$\Delta H_{mix} < 0$ and $\Delta V_{mix} < 0$

57. **(d)** CCl_4 is non-polar and $CHCl_3$ is polar.

58. **(a)** On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

59. **(b)** Positive deviations are shown by such solutions in which solvent-solvent and solute-solute interactions are stronger than the solute-solvent interactions.

In pure methanol, there exists intermolecular H–bonding.

On adding benzene, its molecules come between ethanol molecules, thereby breaking H-bonds which weaken intermolecular forces. This results in increase in vapour pressure.

60. **(c)** Acetone and chloroform shows negative deviation from Raoult's law. When these are mixed, the hydrogen bonding takes place between the two molecular species due to which escaping tendency of either liquid molecules becomes less and boiling point of solution increases.

61. **(b)** Solution

62. **(a)** The molal depression constant or cryoscopic constant is a characteristic property of a solvent.

63. **(b)** $\Delta T_b = K_b \times m$

$$\Rightarrow K_b = \frac{\Delta T_b}{m}$$

64. **(b)** Blood cells neither swell nor shrink in isotonic solution. As isotonic solutions have equal concentration therefore there is no flow of solvent occurs and hence solvent neither enters nor flow out of the blood cells.

65. **(a)** Isotonic solutions have same molar concentration at given temperature provided the van't Hoff factor (i) is same.

66. **(b)**

67. **(b)** $\Delta T_b = K_b \times i \times m$

Where ΔT_b = Elevation in boiling point

K_b = molal elevation constant

i = vant Hoff factor

$\therefore \quad \Delta T_b \propto$ molality.

68. **(c)** Properties which depend upon the number of particles irrespetive of their nature (ions or molecules) are called colligative properties. Thus amongst the given choices only osmotic pressure is a colligative property.

69. **(b)** Solvent molecules only.

70. **(a)** $CaCl_2$ acts as a non-volatile solute and results in depression in freezing point. Thus, snow fall is reduced and prevents blocking of roads in the polar region.

71. **(b)** Low concentration of oxygen in the blood and tissues of people living at high altitude is due to low atmospheric pressure. Because at high altitude, the partial pressure of oxygen is less than at the ground level. This decreased atmospheric pressure causes release of oxygen from blood.

72. **(a)** Molecular masses of polymers are best determined by osmotic pressure method. Firstly because other colligative properties give so low values that they cannot be measured accurately and secondly, osmotic pressure measurements can be made at room temperature and do not require heating which may change the nature of the polymer.

73. **(c)** During osmosis water flows through semipermeable membrane from lower concentration to higher concentration.

74. **(a)** According to Boyle-van't Hoff law,

$$\pi \propto C \qquad \text{(at constant temp)}$$

75. **(b)** Among the given options, $CaCl_2$ solution will produce maximum (three) ions per molecule, so it will show minimum freezing point.

76. **(d)** $\dfrac{P^0 - P_s}{P^0}$ = molality × $(1 - \alpha + x\alpha + y\alpha)$ the value of

$P° - P_s$ is maximum for $BaCl_2$.

77. **(b)** $4K^+ + [Fe\,(CN)_6]^-$

n = 5 i.e., i = 5

78. **(d)** $\Delta T_f = iK_f m$

As $m = 0.1$ molal for all given solutions, thus, lower the value of i, lower will be the depression in freezing point (ΔT_f) and higher will be the freezing point of the solution.

For $Al_2(SO_4)_3$; $i = 5$

For $BaCl_2$; $i = 3$

For $AlCl_3$; $i = 4$

For NH_4Cl ; $i = 2$

Thus, 0.1 molal NH_4Cl will have highest freezing point.

79. **(a)** Isotonic mixtures have equal osmotic pressure so there won't be any flow of liquid between the blood cells and blood.

80. **(d)** Depression in freezing point of benzene takes place.

81. **(a)** $K_f = \frac{RT_f^2 M_1}{1000\Delta H_f}$;

ΔH_f = latent heat of fusion = 180 J/g

$= \frac{8.314\times(290)^2\times 1}{1000\times 180}$ T_f = Freezing temperature = 290K

$= 3.88 \text{ K kg mol}^{-1} M_1$

82. **(b)** Molality of the solution $= \left(\frac{x}{78}\right)\times\frac{1000}{500} = \frac{x}{39}(m)$

$\Delta T_f = m(K_f)_{H_2O}$

$\therefore \frac{x}{39} = \frac{1}{1.86} \quad \therefore x = \frac{39}{1.86} = 20.96$

83. **(c)** Molecular mass of phosphorous

$= \frac{1000\times K_f\times W_{solute}}{\Delta T_f\times W_{benzene}}$

$= \frac{1000\times 5.12\times 2.48}{1.02\times 100} = 124.5 = (P)_x$

or, $x = \frac{124.5}{31} = 4$

84. **(b)** Greater is the effective molarity (i × C), higher the ΔTf value and lower the freezing point.

(i) 0.1 M NaCl = i × C = 2 × 0.1 = 0.2

(ii) 0.05 MBaCl2 = i × C = 3 × 0.05 = 0.15

(iii) 0.1 MNH2CSNH2 = i × C = 1 × 0.1 = 0.1

(iv) 0.025 MKNO3 = i × C = 2 × 0.025 = 0.50

Thus, order is (i) < (ii) < (iii) < (iv)

85. **(b)** As $\Delta T_f = K_f$

For,

$$\begin{array}{lcccc} & HX & \rightleftharpoons & H^+ & + & X^- \\ t = 0 & 1 & & 0 & & 0 \\ t = eq & (1-0.20) & & 0.20 & & 0.20 \end{array}$$

Total no. of moles = 1 – 0.20 + 0.20 + 0.20 = 1 + 0.20 = 1.2

∴ $\Delta T_f = 1.2 \times 1.86 \times 0.5 = 1.1160 \;\; 1.12$ K

86. **(d)** $\Delta T_f = K_f \times m$

$M = \frac{1000\times K_f\times w_2(\text{solute})}{\Delta T_f\times w_1(\text{solvent})}$

$= \frac{1000\times 1.86\times 1.8}{0.465\times 40} \Rightarrow M = 180$

Molecular formula = (empirical formula)$_n$

$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180}{30} = 6$

87. **(c)** If compound dissociates in solvent $i > 1$ and on association $i < 1$.

88. **(c)** $i = 1 + (n-1)\alpha$

$i = 1 + (3-1)\alpha$

$i = 1 + 2\alpha$

89. **(a)** Isotonic solutions are those which have same concentration.

90. **(a)** Lowering in vapour pressure depends on mole fraction of the solute.

So, 'a' having highest mole fraction as compare to all given options.

91. **(a)** Moles of urea $= \frac{12}{60} = 0.2$

Moles of sucrose $= \frac{68.4}{342} = 0.2$

Both are non electrolyte hence lowering of V.P. will be same.

92. **(d)** Urea does not give ions in the solution.

93. **(d)** $i = \frac{\pi_{obs}}{\pi_{cal}}$

94. **(d)** $\Delta T_b = k_b.m$

$\Delta T_b = k_b \times \frac{\text{weight of solute}\times 1000}{\text{molecular weight of solute}\times\text{weight of solvent}}$

$0.75 = 2.5\times\frac{1.5}{M}\times\frac{1000}{50}$

$M = \frac{2.5\times 1.5\times 1000}{0.75\times 50} = 100$

95. **(a)** $\Delta T_f = K_f\frac{1000W_2}{M_2W_1} = \frac{1.86\times 1000\times 68.5}{342\times 1000} = 0.372$

$T_f = T°_f - \Delta T_f$

$T_f = -0.372°C$

96. **(b)** Given $K_f = -1.86ºC\, m^{-1}$, mass of solute = 5.00 g, mass of solvent = 45.0 g and $\Delta T_f = -3.82°C$

$\Delta T_f = i\times K_f.m$

$3.82 = i\times 1.86\times\frac{5\times 1000}{142\times 45}$

∴ $i = 2.62$ (Molecular mass of Na_2SO_4 = 142 g)

97. **(b)** $$\left[\frac{P^\circ - P}{P^\circ}\right]\times 100 = \frac{w_2}{M_2}\times\frac{M_1}{w_1}\times 100 = 10$$

$$\frac{w_2}{60}\times\frac{18}{180}\times 100 = 10 \quad \text{or} \quad w_2 = 60\text{ g}$$

Thus, 60 g of the solute must be added to 180 g of water so that the vapour pressure of water is lowered by 10%.

98. **(b)** $\frac{P^\circ - P_s}{P^\circ}$ = Mole fraction of solute = x_2

99. **(a)** Lowering is always positive

100. **(c)** According to Raoult's law

$$\frac{p^\circ - p}{p^\circ} = x_B \left[\begin{array}{l} x_B = \text{Mole fraction of solute} = \frac{.2}{.2+.8} = \frac{1}{5} \\ p = 60 \text{ mm of Hg}\end{array}\right]$$

$$\frac{p^\circ - p}{p^\circ} = \frac{1}{5} \quad \text{or} \quad 4p^\circ = (p)\times 5$$

$$\Rightarrow p^\circ = \frac{60\times 5}{4} = 75 \text{mm of Hg}$$

Exercise 2 : ACCELERATOR
Topic-wise MCQs

1. **(c)** More the value of K_H (Henry's law constant) less will be the solubility.

$\therefore$ Order of K_H

$Ar > CO_2 > CH_4 > HCHO$

So, the order of solubility

$HCHO > CH_4 > CO_2 > Ar$

2. **(d)** According to Henry's law :-

$P = x\,K_H$

For N_2 :- $P_{N_2} = x_{N_2} K_H(N_2)$

For O_2:- $P_{O_2} = x_{O_2} K_H(O_2)$

We have, $P_{N_2} = P_{O_2}$, $K_H(N_2) = 76.48$ k bar,

$K_H(O_2) = 34.86$ k bar

$$\Rightarrow \frac{x_{N_2}}{x_{O_2}} = \frac{\left(\frac{P_{N_2}}{K_H(N_2)}\right)}{\left(\frac{P_{O_2}}{K_H(O_2)}\right)} = \frac{\frac{P}{N_2}}{K_H(N_2)} \times \frac{K_H(O_2)}{\frac{P}{O_2}}$$

$$= \frac{K_H(O_2)}{K_H(N_2)} = \frac{34.86}{76.48} = 0.45$$

3. **(c)** Total pressure of air over water = 1 atm.

Partial pressure of N_2 and O_2 are

$$P_{N_2} = \frac{1\times 79}{100} = 0.79 \text{ atm}$$

$$P_{O_2} = \frac{1\times 21}{100} = 0.21 \text{ atm}$$

Applying Henry's law

$P_{N_2} = K_H.x$

$$X_{N_2} = \frac{P_{N_2}}{K_{N_2}} = \frac{0.79}{8.54\times 10^4} = 9.25\times 10^{-6}$$

$$X_{O_2} = \frac{P_{O_2}}{K_{O_2}} = \frac{0.21}{4.56\times 10^4} = 4.60\times 10^{-6}$$

Proportion of N_2 and O_2

$\Rightarrow$ $9.25\times 10^{-6} : 4.60\times 10^{-6}$

$\Rightarrow$ $2:1$.

4. **(d)** According to Henry's Law,

$p = K_H \times x$

p = partial pressure

K_H = Henry constant

x = mole fraction

given

p = 1 bar

$K_H = 0.4 \times 10^3$ bar [1k bar = 10^3 bar] $\therefore p = K_H x$

1 bar = 0.4×10^3 bar $\times$ x

$$x = \frac{1}{0.4\times 10^3}$$

$$\frac{n_{methane}}{n_{methane} + n_{H_2O}} = \frac{1}{0.4\times 10^3}$$

$n_{methane} << n_{H2O}$

$$\therefore \frac{n_{methane}}{n_{H_2O}} = \frac{1}{0.4\times 10^3}$$

$$\frac{n_{methane}}{n_{H_2O}} = \frac{1}{0.4\times 10^3} \qquad \left[n_{H_2O} = \frac{1000}{18} = 55.55 \text{ mol}\right]$$

$$= \frac{55.55}{0.4\times 10^3} = 138\times 10^{-3}$$

$$\boxed{n_{methane} = 1.38\times 10^{-1}}$$

5. **(a)** $$n_{CHCl_3} = \frac{25.5}{119.5} = 0.213$$

$$n_{CH_2Cl_{22}} = \frac{40}{85} = 0.47$$

$$P_T = P_A^o\ X_A + P_B^o\ X_B$$

$$= 200 \times \frac{0.213}{0.683} + 41.5 \times \frac{0.47}{0.683}$$

$$= 62.37 + 28.55 = 90.92$$

6. **(a)** $P^o_{benzene} = 75$ mm Hg

$P^o_{toluene} = 22$ mmHg

Mole of benzene $= \frac{23.4}{78} = 0.3$ mol

Mole of toluene $= \frac{64.4}{92} = 0.7$ mol

Mole fraction of benzene $= \frac{0.3}{1.0} = 0.3$

Mole fraction of toluene = 1 – 0.3 = 0.7

Partial pressure of benzene = 0.3 × 75 = 22.5 mmHg

Partial pressure of toluene = 0.7 × 22 = 15.4 mmHg

Total pressure of solution = 22.5 + 15.4 = 37.9 mmHg

Mole fraction toluene $= \frac{15.4}{37.9} = 0.406$

Mole fraction of toluene in vapour phase approximately 0.406.

7. **(d)** As, $p_{total} = x_1 p°_1 + x_2 p°_2$

$= (1 - x_2)p°_1 + x_2 p°_2$

$\therefore\ \ p_{total} = p°_1 + (p°_2 - p°_1)x_2$ ...(i)

Now, $p_{total} = 475$ torr

$p°_1 = 280.7$ torr (for liquid A)

$p°_2 = ?$ (for liquid B)

For mole fraction of liquid B :

$$X_2 = \frac{n_2}{n_1 + n_2} = \frac{5.555}{5.555 + 0.714} = \frac{5.555}{6.269} = 0.8861$$

So, using equation (i) we get –

$475 = 280.7 + (p°_2 - 280.7)\ 0.8861$

$475 - 280.7 = 0.8861\ p°_2 - 280.7 \times 0.8861$

$$\frac{194.3 + 248.72}{0.8861} = p_2^\circ$$

$$\frac{443}{0.8861} = p_2^\circ = 500$$

8. **(d)** At 1 atmospheric pressure the boiling point of mixture is 80°C.

At boiling point the vapour pressure of mixture, p_T = 1 atmosphere = 760 mm Hg.

Using the relation,

$p_T = p_A^\circ x_A + p_B^\circ x_B$, we get

$p_T = 520x_A + 1000(1 - x_A)$ $\{\because p_A^o = 520$ mm Hg ,

$p_B^\circ = 1000$ mm Hg , $x_A + x_B = 1\}$

or $760 = 520x_A + 1000 - 1000x_A$ or $480x_A = 240$

or $x_A = \frac{240}{480} = \frac{1}{2}$ or 50 mol. percent

i.e., the correct answer is (d)

9. **(a)** $p_{Total} = p_A^\circ x_A + p^\circ_B x_B$

$$= p^\circ_{Heptane}\ x_{Heptane} + p^\circ_{Octane}\ x_{Octane}$$

$$= 105 \times \frac{25/100}{\frac{25}{100} + \frac{35}{114}} + 45 \times \frac{35/114}{\frac{25}{100} + \frac{35}{114}}$$

$$= 105 \times \frac{0.25}{0.25 + 0.3} + 45 \times \frac{0.3}{0.25 + 0.3}$$

$$= \frac{105 \times 0.25}{0.55} + \frac{45 \times 0.3}{0.55} = \frac{26.25 + 13.5}{0.55} = 72\ \text{kPa}$$

10. **(b)** $p_{total} = \overset{\circ}{p}_A x_A + \overset{\circ}{p}_B x_B$

$$550 = \overset{\circ}{p}_A \times \frac{1}{4} + \overset{\circ}{p}_B \times \frac{3}{4}$$

$$\overset{\circ}{p}_A + 3\overset{\circ}{p}_B = 550 \times 4 \qquad \text{...(i)}$$

In second case

$$p_{total} = \overset{\circ}{p}_A \times \frac{1}{5} + \overset{\circ}{p}_B \times \frac{4}{5}$$

$$\overset{\circ}{p}_A + 4\overset{\circ}{p}_B = 560 \times 5 \qquad \text{...(ii)}$$

Subtract (i) from (ii)

$$\therefore\ \overset{\circ}{p}_B = 560 \times 5 - 550 \times 4 = 600$$

$$\because\ \ \overset{\circ}{p}_A = 400$$

11. **(c)** When $A = 1$ mole, $B = 3$ mole

$$X_A = \frac{1}{4}$$

$$X_B = \frac{3}{4}$$

$$P_{Total} = P_A^0 X_A + P_B^0 X_B$$

$$550 = P_A^0\left(\frac{1}{4}\right) + P_B^0\left(\frac{3}{4}\right)$$

$$2200 = P_A^0 + 3P_B^0 \qquad ...(1)$$

When one mole of *B* added

$$X_A = \frac{1}{5}$$

$$X_B = \frac{4}{5}$$

$$560 = P_A^0 X_A + P_B^0 X_B$$

$$560 = P_A^0\left(\frac{1}{5}\right) + P_B^0\left(\frac{4}{5}\right)$$

$$2800 = P_A^0 + 4P_B^0 \qquad ...(2)$$

Substracting [eq. (2) – eq. (1)]

$$P_B^0 = 600$$

Putting the value of in eq. (1)

$$2200 = P_A^0 + 3 \times 600$$

$$P_A^0 = 2200 - 1800 = 400$$

The ratio $P_A^0 : P_B^0$

$= 400 : 600 = 2 : 3.$

12. **(a)** According to Raoult's law,

$P_T = x_A p^\circ_A + x_B p^\circ_B$

Given, $P_{T_1} = 500$ mm Hg

$n_A = 1$ and $n_B = 2$ $\therefore$ $x_A = 1/3$ and $x_B = 2/3$

$$\Rightarrow 500 = \frac{1}{3}p_A^\circ + \frac{2}{3}p_B^\circ \quad \Rightarrow 1500 = p_A^\circ + 2p_B^\circ \qquad ...(i)$$

Also given that, one more mole of *B* is added to the solution, the pressure of the ideal solution increases by 25 mm Hg.

$\therefore$ $P_{T_2} = 500 + 25 = 525$ mm Hg

Also, $n_B = 3$

$\therefore$ $x_A = 1/4$ and $x_B = 3/4$

$$525 = \frac{1}{4}p_A^\circ + \frac{3}{4}p_B^\circ \quad \Rightarrow 2100 = p_A^\circ + 3p_B^\circ$$

Subtract (i) and (ii),

$p^\circ_B = 600$ mm Hg

$p^\circ_A + 2p^\circ_B = 1500 \quad \Rightarrow \quad p^\circ_A = 300$ mm Hg.

13. **(c)**

14. **(d)** A solution containing *A* and *B* components shows negative deviation when *A–A* and *B–B* interactions are weaker than that of *A–B* interactions. For such solutions.

ΔH = –ve and ΔV = –ve

15. **(b)**

16. **(b)** For this solution, intermolecular interactions between *n*-heptane and ethanol are weaker than *n*-heptane-*n*-heptane & ethanol-ethanol interactions. Hence the solution of *n*-heptane and ethanol is non-ideal and shows positive deviation from Raoult's law.

17. **(a)** *A–A* and *B–B* type interaction are nearly same as *A–B* interaction, hence they form ideal solution and follows Raoult's law.

18. **(a)** $\dfrac{p^\circ - p}{p^\circ} = x_{\text{solute}}$

Given, $p^\circ = 0.8$ atm, $p = 0.6$ atm, $x_{\text{solute = ?}}$

$$\frac{0.8 - 0.6}{0.8} = x_{\text{solute}} \text{ or } \frac{0.2}{0.8} = x_{\text{solute}},$$

or $x_{\text{solute}} = 0.25$

19. **(a)** $\pi = \text{iCRT}$

$$\left(= \frac{\text{n}}{\text{v}} = \frac{\text{weight}}{\text{Molar mass} \times \text{volume (1 kg = 1000 g)}}\right)$$

$$= \frac{1 \times 2}{60000 \times 0.2} \times 0.083 \times 300 = 0.00415 \text{ bar}$$

($\because$ 1 bar = 10^5 Pa)

So, 0.00415×10^5 Pa = 415 Pa

20. **(c)** Moles of urea = $\dfrac{5}{60}$; moles of fructose = $\dfrac{5}{180}$;

$$C_{\text{urea}} = \frac{0.08 \times 1000}{100} \Rightarrow 0.833$$

moles of sucrose = $\dfrac{5}{342}$;

$$C_{\text{sucrose}} = 0.0146 \times \frac{1000}{100} = 0.146$$

moles of KCl(effective)

$$= 2 \times \frac{5}{74.5} = \frac{5}{37.25};\ \frac{0.134 \times 1000}{100} = 1.34$$

$\pi \propto C$

This order is $\pi_4 > \pi_1 > \pi_2 > \pi_3$

21. **(b)** KNO_3 is a strong electrolyte which dissociates into two ions. Therefore, its van't Hoff factor is 2. Acetic acid (CH_3COOH) is a weak electrolyte, it does not dissociate completely. So, its van't Hoff factor is less than that of KNO_3

$\therefore$ Osmotic pressure of 0.1 M KNO_3 >

Osmotic pressure of 0.1 M CH_3COOH

22. **(a)** The solution which provide same number of ions are isotonic.

$Ca(NO_3)_2 \longrightarrow Ca_2^{+} + 2\ NO_3^{-}$

Total ions produced = 3

$Na_2SO_4 \longrightarrow 2\ Na^{+} + SO_4^{2-}$

Total ions produced = 3

$\therefore$ 0.1 M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4 are isotonic.

23. **(a)** $\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1 + n_2}$ or $\frac{n_2}{n_1 + n_2} = \frac{640 - 630}{640} = \frac{0.0156}{1}$

or 1 mole i.e., 78g benzene contains solute = 0.0156 mol

$\therefore$ Molality of solution $= \frac{0.0156 \times 10^3}{78} = 0.2\ m$

24. **(a)** As both the solutions are isotonic hence there is no net movement of the solvent occurs through the semipermeable membrane between two solutions.

25. **(a)** Concentration of particles in $CaCl_2$ solution will be maximum as $i = 3$ for $CaCl_2$ and $i = 2$ for KCl.

Glucose and Urea do not dissociate into ions, as they are nonelectrolytes.

26. **(a)** Depression in freezing point $\propto$ No. of particles.

(when concentration of different solutions is equal)

$Al_2(SO_4)_3$ provides five ions on ionisation

$Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$

while KCl provides two ions

$KCl \longrightarrow K^{+} + Cl^{-}$

$C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$ are not ionised so they have single particle in solution.

Hence, $Al_2(SO_4)_3$ have maximum value of depression in freezing point or lowest freezing point.

27. **(b)** $\Delta T_f = K_f \times m = 1.86 \times 0.5 = 0.93°C;\ T_f = -0.93°C$

28. **(d)** Boiling temperature is a temperature at which vapour pressure is equal to the atmospheric pressure when external pressure is equal to 1 atm.

29. **(c)** Solvent molecules flow from low concentration solution to high concentration solution.

30. **(d)** $M = \frac{WRT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 200 \times 10^{-3}}$

$= \frac{31.374 \times 10^6}{514} = 61038$ g

31. **(c)** For dilute solution, $\frac{\Delta P}{P^\circ} \Rightarrow \frac{n_{solute}}{n_{solvent}}$

For solution in A, $\frac{\Delta P_A}{P_A^\circ} = \frac{W/M}{W_A/M_A} = \frac{W}{M} \times \frac{M_A}{W_A}$ ... (i)

For solution in B, $\frac{\Delta P_B}{P_A^\circ} = \frac{W}{M} \times \frac{M_B}{W_B}$ ... (ii)

From (i) and (ii), $\frac{\Delta P_A / P_A^\circ}{\Delta P_B / P_B^\circ} = 2 = \frac{M_A W_B}{M_B W_A} = \frac{M_A}{M_B}$

$(W_A = W_B)\ M_A = 2M_B$

32. **(b)** Lowering of vapour pressure depends on mole fraction of the solute.

$\chi_{urea} = \frac{0.2}{55.55} = 0.03$

$\chi_{sugar} = \frac{0.4}{55.55} = 0.07$

So, urea is half of the sugar.

33. **(a)** Relative lowering of vapour pressure $= \frac{P^\circ - P_s}{P^\circ}$

1 atm = 760 mm

$= \frac{760 - 684}{760} = \frac{76}{760} = 0.1$

34. **(a)** $\frac{P_0 - P_s}{P_0} = \frac{20}{100}$

$\frac{20}{100} = \frac{w/40}{114/114 + w/40}$

$w = 10$g.

35. **(a)**

$$\underset{\text{(Colligative property)}}{\text{Freezing point depression}} \propto \underset{\text{(Van't Hoff factor, i)}}{\text{number of solute particles}}$$

Acetic acid dissociates in water so 2i will be the van't Hoff factor. Acetic acid and benzoic acid will dimerise in benzene so $\frac{i}{\alpha}$ will be the actual van't Hoff factor.

Glucose does not dissociate in water so i will be the actual van't Hoff factor.

Thus, Acetic acid in water will have the highest van't Hoff factor and thus highest depression in the freezing point.

36. **(a)** A = 0.1 M, B = 0.01 M, C = 0.001 M

Value of i increases as solution becomes dilute so the correct order is: $i_A < i_B < i_C$

37. **(c)** For association i < 1.

38. **(d)**

39. **(b)** $\pi V = nRT$

$\frac{500V_1}{105.3V_2} = \frac{nR \times 283}{nR \times 298}; \frac{V_1}{V_2} = \frac{1}{5}$ So, $V_2 = 5V_1$.

40. **(b)** $\pi = CRT$

$$\pi = \frac{w \times R \times T}{mV} = \frac{68.4 \times 0.0821 \times 273}{342} = 4.48\, atm.$$

41. **(b)** $C = \frac{5}{342} \times \frac{1}{100} \times 1000 = \frac{50}{342}$ mol/L.

$$\pi = \frac{50}{342} \times 0.082 \times 423 = 5.07\, atm.$$

42. **(b)** $\pi = \frac{n}{V} RT \Rightarrow M_P = \left(\frac{m}{V}\right) \frac{RT}{\pi}.$

43. **(c)** $\pi = CRT, C = \frac{\pi}{RT} = \frac{0.0821}{0.0821 \times 300} = 0.033 \times 10^{-2}$

44. **(b)** Isotonic solution $= \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$

$$= \frac{w_1}{342 \times 1} = \frac{6}{60 \times 1} = \frac{342 \times 6}{60} = 34.2.$$

45. **(c)** Given,

$T_b° = 373.\ 15$, $K_b = 0.52$ K kg mol^{-1}

$T_b = 373.\ 202$

$T_f° = 273.15$, $K_f = 1.86$ K kg mol^{-1}

$\therefore \quad (T_b - T_b°) = m \times K_b$

$m = 0.1$

Again, $(T_f° - T_f) = m \times K_f$

$(273.15 - T_f) = 0.1 \times 1.86$

$273.15 - 0.186 = T_f$

$\therefore \quad T_f = 272.964$

46. **(a)** Given, $\Delta T_b = 0.01$ K

Molality = 0.01 m

$K_b = 0.52$ K kg mol^{-1}

We know, $\Delta T_b = i\, K_b\, m$

$$i = \frac{\Delta T_b}{K_b m} = \frac{0.01}{0.52 \times 0.01} = 1.92$$

47. **(d)** Given

$\Delta T_b = 0.052$ K

$\Delta T_b = K_b \times m$

$0.052 = 0.52 \times m$

$m = 0.1$

$\Delta T_f = m\, K_f = 0.1 \times 1.86 = 0.186$

Freezing point of solution = 273 – 0.186 = 272.81 K.

48. **(a)** Given, weight of benzoic acid = x g

Molar mass of benzoic acid = 122 g mol^{-1}

Weight of benzene = 49g

Molar mass of benzene = 78 g mol^{-1}

depression in freezing point (ΔT_f) = 1.12 K

degree of association (α) = 88% = 0.88

K_f for benzene = 4.9 k kg mol^{-1}

For association,

$$\text{Van't Hoff factor (i)} = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$= 1 + \left(\frac{1}{2} - 1\right) \times 0.88$$

$i = 0.56$

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

$$1.12 = 0.56 \times 4.9 \times \frac{x \times 1000}{122 \times 49} \left[m = \frac{\text{weight of solute} \times 100}{\begin{matrix}\text{Molecular} \times \text{Weight} \\ \text{Weight of} \quad \text{of} \\ \text{solventsolute}\end{matrix}} \right]$$

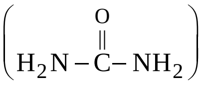
$x = 2.44$ g

49. **(c)** Osmotic pressure (π) = CRT

Given,

Weight of urea = 6g

Molecular weight of urea



$$\left(H_2N - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2\right)$$

$= 4 \times 1 + 2 \times 14 + 12 + 16 = 60$ g mol^{-1}

$\therefore \quad$ Number of mole of urea $= \frac{\text{Weight}}{\text{Molecular weight}}$

$$\Rightarrow \frac{6}{60} = 0.1 \text{ mole}$$

$$\text{concentration (C)} = \frac{\text{mole}}{\text{volume}}$$

$$= \frac{0.1}{0.5} \quad [1\text{ L} = 10^3 \text{ mL}]$$

(C) = 0.2 mole/liter

$\pi = 0.2 \times 0.082 \times 300$

$\pi = 4.92$ atm

50. **(c)** $\Delta T_f = 0.0405$ K

Concentration of formic acid (HCOOH) solution

= 0.5 ml/L

= 0.5 × 1.05 g/L = 0.525 g/L $\quad (\because d_{HCOOH} = 1.05$ g/ml)

No. of moles of HCOOH in 1 L solution

$$= \frac{0.525}{46} = 0.0114 \qquad (\because MW_{HCOOH} = 46)$$

Molality (m) of HCOOH = 0.0114 mol/kg

(considering $d_{H2O} = 1\text{kg/L}$)

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

$$\therefore \quad i = \frac{\Delta T_f}{K_f m} = \frac{0.0405}{1.86 \times 0.0114} = 1.91 \approx 1.9$$

∴ The van't Hoff factor of the formic acid solution is nearly 1.9.

51. **(c)** Given : $\frac{(K_b)_A}{(K_b)_B} = \frac{1}{8}$

$$\frac{(\Delta T_B)_A}{(\Delta T_B)_B} = \frac{(K_b)_A \cdot m}{(K_b)_B \cdot m} = \frac{1}{8} \quad \Rightarrow \quad \frac{x}{y} = \frac{1}{8}$$

∴ $y = 8$ (nearest integer)

52. **(a)** From Raoult law

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No.of moles of solute}}{\text{No. of moles of solvent+ No. of moles of solute}}$$

When the concentration of solute is much lower than the concentration of solvent,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$\Delta T_b = K_b \times m$

$$m = \frac{\text{Number of moles of the solute}}{\text{Mass of solvent in grams}} \times 1000$$

$$\Delta T_b = K_b \times \frac{\text{Number of moles of the solute}}{\text{Mass of solvent in grams}} \times 1000$$

Number of moles of solute

$$= \frac{\Delta T_b \times \text{Mass of solvent in grams}}{K_b \times 1000} = \frac{2 \times 100}{0.76 \times 1000} = 0.26,$$

Number of moles of solvent $= \frac{100}{18} = 5.56$

From equation (i) we get, $\frac{760 - p}{760} = \frac{0.26}{5.56}$

On solving, $p = 724.46 \approx 724$

53. **(c)** Isotonic solutions have same osmotic pressure

$\pi_{\text{glucose}} = \pi_{\text{unknown solute}}$

$$\therefore \quad \frac{m_1}{M_1} = \frac{m_2}{M_2} \quad \text{or} \quad \frac{5}{180} = \frac{2}{M_2} \Rightarrow M_2 = 72$$

54. **(b)** Moles of ascorbic acid $= \frac{10.2\text{g}}{176\text{g mol}^{-1}} = 0.058\,\text{mol}$

$\Delta T_f = (x \times 10^{-1})\ °\text{C}$

$$\Delta T_f = K_f.\text{molality} = 3.9 \times \frac{0.058}{150} \times 1000 = 1.5\ °\text{C}$$

$= 15 \times 10^{-1}\ °\text{C}$

55. **(c)** Mass of C_2H_5OH = density × volume

$= 62.5 \times 0.8 = 50$ g

$\Delta T_f = K_f \times m$ [m = molality]

$$0.9 = 2 \times \frac{1.8 \times 1000}{M_w \times 50}$$

$$M_w = \frac{2 \times 1.8 \times 1000}{0.9 \times 50} = 80$$

56. **(d)**

57. **(a)** $\frac{p^\circ - p_s}{p^\circ} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} \Rightarrow \frac{P^\circ - \frac{P^\circ}{2}}{P^\circ} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$

$$\Rightarrow \quad n_{\text{solute}} = n_{\text{solvent}} / 2 = \frac{100}{2 \times 18} = 2.77$$

58. **(c)** According to Raoult's law

$$\frac{p^\circ - p}{p^\circ} = x_B \quad \left[\begin{array}{l} x_B = \text{Mole fraction of solute} = \frac{0.2}{0.2 + 0.8} = \frac{1}{5} \\ p = 60 \text{ mm of Hg} \end{array}\right]$$

$$\frac{p^\circ - p}{p^\circ} = \frac{1}{5} \quad \text{or} \quad 4p^\circ = (p) \times 5$$

$$\Rightarrow p^\circ = \frac{60 \times 5}{4} = 75 \text{mm of Hg}$$

59. **(c)** Elevation in boiling point and depression in freezing point are colligative properties and their value depends only on the amount of solute present in the solution.

$\Delta T_b = iK_b m\,;\ \Delta T_f = iK_f m$

$$\frac{4}{4} = \frac{K_b 1.5}{K_f\, 4.5} \quad \Rightarrow \quad \frac{K_b}{K_f} = 3$$

60. **(c)** $K_4[Fe(CN)_6] \rightleftarrows 4K^+ + [Fe(CN)_6]^-$

and $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

∴ van't Hoff factor is 5 for both $Al_2\ (SO_4)_3$ and $K_4[Fe(CN)_6]$

61. **(a)** The solution which provide same number of ions are isotonic.

$$Ca\,(NO_3)_2 \longrightarrow Ca^{2+} + 2\,NO_3^-$$

Total ions produced = 3

$Na_2SO_4 \longrightarrow 2\,Na^+ + SO_4^{2-}$

Total ions produced = 3

∴ 0.1 M $Ca\,(NO_3)_2$ and 0.1 M Na_2SO_4 are isotonic.

62. **(c)** $\Delta T_b = K_b \times m$

Elevation in boiling point is a colligative property, which depends upon the no. of particles (concentration of solution). Thus, greater the number of particles, greater is the elevation in boiling point and hence, greater will be its boiling point.

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

$\Delta T_b = 3 \times 0.01 \times K_b$

63. **(a)** $K_4[Fe(CN)_6]$ and $Al_2(SO_4)_3$ both dissociates to give 5 ions or $i = 5$

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

and $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$

64. **(c)** $T_b = 100.18$ $K_b = 0.52$

$T_f = ?$ $K_f = 1.86$

$\Delta T_b = K_b m$

$0.18 = 0.52\,m$

$$m = \frac{0.18}{0.52} = 0.34$$

$\Delta T_f = 1.86 \times 0.34 = 0.6324 \approx 0.64$

65. **(a)** 7.5 mol; $\Delta T_f = K_f m$

$$\Delta T_f = K_f \frac{n_2 \times 1000}{w_1} \Rightarrow 14 = 1.86 \times \frac{n_2 \times 1000}{1000}$$

$n_2 = 7.5$ mol

66. **(b)** $$\Delta_A T_b = \frac{2}{M_A \times 100} \times 1000 \times K_b$$

$$\Delta_B T_b = \frac{8}{M_B \times 100} \times 1000 \times K_b$$

Given, $\Delta_A T_b = \Delta_B T_b$

$$\Rightarrow \frac{2}{M_A} = \frac{8}{M_B} \Rightarrow M_B = 4M_A$$

67. **(b)** $\underset{\text{Solute}}{w} = 2.5$ g $K_b = 0.52$ K kg

$w_{\text{solvent}} = 75$g M = Mol. Wt. of solute

$T_b^{\circ} = 373.15$K

$\Delta T_b = 0.385$ K

$$\Delta T_b = \frac{K_b \times 10^3 w_{\text{solute}}}{M_{\text{solute}} \times w_{\text{solvent}}}$$

$$0.385 = 0.52 \times \left(\frac{2.5}{M} \times \frac{1000}{75}\right)$$

$M = 45$ g mol^{-1}.

68. **(c)** Van't Hoff factor $(i) = \dfrac{\text{observed colligative properties}}{\text{calculated colligative properties}}$

Observed colligative properties = $\Delta T_f(1)$

Calculated colligative properties,

$\Delta T_f(2) = m \times K_f$

$= 0.5 \times 1.86 = 0.93$

$$\therefore\ i = \frac{\Delta T_f(1)}{\Delta T_f(2)} = \frac{\Delta T_f(1)}{0.93}$$

$\Rightarrow \Delta T_f(1) = 1.075 \times 0.93 \approx 1$

69. **(d)** $p^{\circ} = x$kPa

Let p is the vapour pressure of non-volatile solute.

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\Rightarrow \frac{x - p}{x} = \frac{1}{1 + 55.55} = \frac{1}{56.55}$$

$\Rightarrow 56.55x - 56.55p = x$

$$\Rightarrow p = \frac{55.55x}{56.56} = 0.982\,x$$

70. **(a)** (i) $i = \dfrac{\text{No. of particles after ionisation}}{\text{No. of particles before ionisation}}$

(ii) $\Delta T_b = i \times K_b \times m$

$$\begin{array}{lccc} CuCl_2 & \longrightarrow & Cu^{2+} & + 2Cl^- \\ 1 & & 0 & 0 \\ (1-\alpha) & & \alpha & 2\alpha \end{array}$$

$$i = \frac{1 + 2\alpha}{1},\ i = 1 + 2\alpha$$

Assuming 100% ionization

So, $i = 1 + 2 = 3$

$$\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16 \quad \left[m = \frac{13.44}{134.4} = 0.1\right]$$

71. **(d)** $\left(\underset{1-0.3}{HX} \rightleftharpoons \underset{0.3}{\overset{+}{H}} + \underset{0.3}{X^-},\ i = 1.3\right);$

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

$\Delta T_f = 1.85 \times 0.2 \times 1.3 = 0.481^{\circ}$C

$\therefore\ T_f = T_f^{\circ} - \Delta T_f = 0 - 0.481^{\circ}C = -0.481^{\circ}C$

72. **(d)** Let x is the atomic weight of XY and y is the atomic weight of XY_3.

$\Delta T_f = m \times K_f$

$$\Rightarrow m = \frac{\Delta T_f}{k_f} = \frac{5.333}{2}$$

$$\Rightarrow \frac{\text{weight} \times 1000}{\text{Molecular weight of XY} \times \text{Weight of solvent}} = 2.6665$$

$$\Rightarrow \frac{10 \times 1000}{M_{xy} \times 50} = 2.665$$

$$\Rightarrow M_{xy} = \frac{200}{2.665} = 75$$

Again for XY_3 compound.

$$M_{xy3} = 1\frac{10 \times 1000}{1.1428 \times 50}\left[m = \frac{\Delta T_f}{k_f} = \frac{2.2857}{2} = 1.1428\right]$$

$M_{xy3} = 175$

$\therefore \quad x + y = 75$ ...(i)

$x + 3y = 175$ ...(ii)

By solving equation (i) and (ii) we get

$x = 25$

$y = 50$

73. **(b)** As per the formula relative lowering of vapour pressure:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

Where, p_1 is vapour pressure of the solvent = 12.078 kPa

$p_1{}^0$ is the vapour pressure of pure solvent = 12.3 kPa

n_1 is no. of moles of solvent

n_2 is no. of moles of solute

$$\therefore \frac{12.3 - 12.078}{12.3} = \frac{n_2}{n_1}$$

$$i.e., 0.0180 = \frac{n_2}{n_1}$$

as $n_1 = \frac{1000}{18}$ (for H_2O as solvent)

$\therefore \quad n_1 = 555.5$

$\therefore \quad 0.0180 \times 55.5 = n_2 = 0.999 \approx 1$

$$\therefore \text{ Molality } (m) = \frac{n_2}{\text{Mass of solvent (kg)}}$$

$$= \frac{1}{1 \text{ kg of water}} = 1 \text{ mol/kg}$$

74. **(d)** The depression in freezing point is calculated as :

$\Delta T_f = T°_f - T_f$

Where, $T°_f$ is the freezing point of pure solvent which is 273.16 K

T_f is the freezing point of the solution which is 272.814 K

m is molality

k_f is freezing point depression constant

So, $\Delta T_f = 273.15 \text{ K} - 272.814 \text{ K}$

$\Delta T_f = 0.336 \text{ K}$

As, $\Delta T_f = k_f m$

$$\therefore \quad m = \frac{\Delta T_f}{k_f}$$

$$\therefore \quad m = \frac{0.336 \text{ K}}{1.86 \text{ K kg mol}^{-1}}$$

$m = 0.18065 \text{ mol/kg}$

$$\text{As, molality (m)} = \frac{\text{no. of moles of solute}}{\text{Mass of solvent in kg}}$$

and as Mass of solvent = 21.5 g = 0.0215 kg

$$\therefore \quad \text{no. of moles of solute} = 0.18065\frac{\text{mol}}{\text{kg}} \times 0.0215 \text{ kg}$$

$\therefore \quad$ no. of moles of solute = 0.00388 mol

$$\text{As, Molar mass of solute} = \frac{\text{mass of solute}}{\text{no. of moles of solute}}$$

$$\therefore \quad \text{Molar mass of solute} = \frac{0.2}{0.00388} = 51.5 \text{ g/mol}$$

75. **(b)** $\pi = \frac{nRT}{V}$ or $T = \frac{\pi V}{nR}$

10% (w/v) aqueous solution of glucose means 10 g glucose is present in 100 mL of H_2O

$$= \frac{14 \times 100 \times 10^{-3} \times 180}{0.082 \times 10} = 307.3 \text{ K}$$

76. **(d)** $\Delta T_f = iK_f m$

$$\begin{array}{ccc} \text{KBr} & \longrightarrow \text{K}^+ + & \text{Br}^- \\ 1 & 0 & 0 \\ (1-\alpha) & \alpha & \alpha \end{array}$$

$i = 1 + \alpha$

Here $\alpha = 0.8$ (80% ionization)

$i = 1.8$

$\Delta T_f = (1.8)(1.86)(0.4) = 1.339$

$T_f = -1.339°\text{C}$

77. **(a)** $\Delta T_f = iK_f m \Rightarrow i = \frac{\Delta T_f}{K_f m}$

$$= \frac{2}{5 \times \left(\frac{2.44/122.12}{30/1000}\right)} = 0.6$$

Now, $2C_6H_5COOH(\text{benzene}) \rightarrow (C_6H_5COOH)_2(\text{benzene})$

Initial 1 mol 0 mol

After association $1 - x$ mol $\frac{x}{2}$ mol

Where, x = degree of association

Thus, total moles at equilibrium (after association)

$$= (1-x) + \frac{x}{2} = 1 - \frac{x}{2}$$

$$\text{Thus, } i = \frac{\text{Moles after association}}{\text{Moles before association}}$$

$$= \frac{1-\frac{x}{2}}{1} = 1 - \frac{x}{2}$$

$\Rightarrow$ Degree of association $(x) = 2(1 - i)$

$= 2(1 - 0.6) = 0.8$ or 80 %

78. **(d)** Osmotic pressure is a colligative property. Hence resulting osmotic pressure of the solution is given by

$\pi_T = \pi_1 + \pi_2 + \pi_3$ ....

$\pi_T = 1.64 + 2.46 = 4.10$ atm.

79. **(d)** Addition of solute to water decreases the freezing point of water (pure solvent).

$\therefore$ When 1% lead nitrate (solute) is added to water, the freezing point of water will be below 0°C.

80. **(b)** As $\Delta T_f = K_f \cdot m$

$\Delta T_b = K_b \cdot m$

Hence, we have $m = \frac{\Delta T_f}{K_f} = \frac{\Delta T_b}{K_b}$

or $\Delta T_f = \Delta T_b \frac{K_f}{K_b}$

$\Rightarrow [\Delta T_b = 100.18 - 100 = 0.18°\text{C}]$

$$= 0.18 \times \frac{1.86}{0.512} = 0.654°\text{C}$$

As the Freezing Point of pure water is 0°C,

$\Delta T_f = 0 - T_f$

$0.654 = 0 - T_f$

$\therefore$ $T_f = -0.654$

Thus the freezing point of solution will be – 0.654°C

81. **(d)** Given $\alpha = 30\%$ i.e., 0.3

$$\text{HA} \longrightarrow \text{H}^+ + \text{A}^-$$

$1 - \alpha$ α α

$1 - 0.3$ 0.3 0.3

$i = 1 - 0.3 + 0.3 + 0.3$

$i = 1.3$

$\Delta T_f = 1.3 \times 1.86 \times 0.1 = 0.2418$

$T_f = 0 - 0.2418 = -0.2418$ °C

82. **(b)** Sodium sulphate dissociates as

$$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{--}$$

hence van't hoff factor $i = 3$

Now $\Delta T_f = i K_f . m$

$= 3 \times 1.86 \times 0.01 = 0.0558$ K

83. **(b)** For isotonic solutions

$\pi_1 = \pi_2$

$C_1 = C_2$

$$\frac{5/342}{0.1} = \frac{1/M}{0.1}$$

$$\frac{5}{342} = \frac{1}{M}$$

$$\Rightarrow M = \frac{342}{5} = 68.4 \text{ gm/mol}$$

84. **(b)** $\Delta T_f = i \times K_f \times m$

Given $\Delta T_f = 2.8$, $K_f = 1.86$ K kg mol^{-1} $i = 1$

(ethylene glygol is a non- electrolyte)

wt. of solvent = 1 kg

Let of wt of solute = x

Mol. wt of ethylene glycol = 62

$$2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1}$$

or $x = \frac{2.8 \times 62}{1.86} = 93$ gm

85. **(d)** The salt that ionises to least extent will have highest freezing point. [i.e., minimum ΔT_f]

86. **(b)** $\pi V = CRT$

$$\frac{\pi_1}{\pi_2} = \frac{C_1 T_1}{C_2 T_2}$$

$\pi_1 = P, \pi_2 = 2\ atm.\ C_1 = C,\ C_2 = \frac{C}{2}$

$T_1 = 600\,K$, $T_2 = 700\,K$

$$\frac{P}{2} = \frac{2 \times C \times 600}{C \times 700}$$

$$P = \frac{24}{7}.$$

87. **(b)** $AlCl_3$ furnishes more ions than $CaCl_2$ and thus possess higher boiling point i.e., $T_1 > T_2$.

88. **(a)** Van't Hoff equation is

$\pi V = inRT$

For depression in freezing point.

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

For elevation in boiling point.

$\Delta T_b = i \times K_b \times m$

For lowering of vapour pressure,

$$\frac{P^\circ_{\text{solvent}} - P_{\text{solution}}}{P^\circ_{\text{solvent}}} = i\left(\frac{n}{N+n}\right).$$

89. **(b)** $\Delta T_f = i.K_f.m$; $0.0054 = i \times 1.8 \times 0.001$

$i = 3$ so it is $[Pt(NH_3)_4Cl_2]Cl_2$.

90. **(c)** Given, $W = 500$ cc $= 500$ g

($\because$ density of water = 1g/cc)

As, Density $= \dfrac{\text{Weight}}{\text{Volume}}$

Weight = Density × Volume $= \dfrac{1\text{g}}{\text{cc}} \times 500\,\text{cc} = 500\,\text{g}$

w = amount of urea = ?

$K_f = 1.86°\text{C}$; $\Delta T_f = 0.186°\text{C}$

M = Molecular mass of urea = 60

$$M = \frac{1000 \times K_f \times w}{W \times \Delta T_f}$$

$$60 = \frac{1000 \times 1.86 \times w}{500 \times 0.186}$$

$60 = 20 \times w$

$$\therefore \quad w = \frac{60}{20} = 3\text{g}$$

91. **(d)** $\Delta T_f = 0 - (0.00732°\text{C}) = 0.00732$

$\Delta T_f = i \times K_f \times \text{m}$

$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.00732}{1.86 \times 0.002} = 1.97 \approx 2$$

92. **(d)** $\Delta T_b = K_b \dfrac{w}{M} \times \dfrac{1000}{W}$

$$0.52 = 0.6 \times \frac{3}{M} \times \frac{1000}{200} \left(W = 200 \times 1\right)$$

$$M = \frac{1.8 \times 5}{0.52} = 17.3\text{g mol}^{-1}$$

93. **(b)** ΔT_f = freezing point of water – freezing point of solution

$= 0°\text{C} - (-1.1°\text{C}) = 1.1°$

We know that, $\Delta T_f = i \times K_f \times m$

$1.1 = i \times 1.86 \times 0.2$

$$\therefore \quad i = \frac{1.1}{1.86 \times 0.2} = 2.95$$

But we know, $i = 1 + (n - 1)\,\alpha$

$2.95 = 1 + (3 - 1)\,\alpha = 1 + 2\alpha \Rightarrow \alpha = 0.975$

van't Hoff factor (i) = 2.95, 'Degree of dissociation = 0.975,' Percentage degree of dissociation = 97.5

94. **(b)** Given $k_b = x$ K kg mol^{-1}

$\Delta T_b = k_b \times m$

$\therefore \quad y = x \times m$

$$\text{m} = \frac{\text{y}}{\text{x}}$$

We know

$\Delta T_f = k_{f\times} m$

On substituting value of m,

$$\Delta T_f = \frac{\text{yz}}{\text{x}}$$

95. **(a)** $\Pi_{\text{sol}^n} = \text{iC}_{\text{NaCl}}\text{RT} + \text{iC}_{\text{glucose}}\text{RT}$

Van't Hoff of factor (i) for NaCl

$\text{i} = 1 + (\text{n} - 1)\,\alpha$

For NaCl (n) = 2

$\text{i} = 1 + 0.94 = 1.94$

$$\Pi_{\text{sol}^n} = 1.94 \times \frac{0.01}{0.5} \times 0.082 \times 300 + 1 \times \frac{0.03}{0.5} \times 0.082 \times 300$$

$$= \frac{0.082 \times 300}{0.5}(1.94 \times 0.01 + 0.03)$$

$$= \frac{0.0494 \times 0.082 \times 300}{0.5}$$

$\Pi_{\text{sol}^n} = 2.43$ atm.

96. **(a)** Using formula,

$\Delta \text{T}_\text{b} = \text{k}_\text{b} \times \text{molality}$

$(100.17 - 100)°\text{C} = 0.512°\text{C kg mol}^{-1} \times \text{molality}$

$$\text{molality} = \frac{0.17}{0.512}\text{m}$$

Now, depression in freezing point is given by,

$\Delta \text{T}_\text{f} = \text{k}_\text{f} \times \text{molality}$

$$\Delta \text{T}_\text{f} = 1.86°\text{C kg X } \frac{0.17}{0.512}\text{m} = 0.62°\text{C}$$

Thus, the freezing point of the solution

$= 0°\text{C} - 0.62°\text{C} = -0.62°\text{C}$.

97. **(b)** Given,

W_B (mass of ethylene glycol) = 31 g

W_A (mass of water) = 600 g

K_f (for water) = 1.86 K kg mol^{-1}

and M_B (for $C_2H_6O_2$) = 62

$$\because \quad \Delta T_f = K_f \cdot \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

$$\therefore \quad \Delta T_f = \frac{1.86 \times 31 \times 1000}{62 \times 600} = 1.55K$$

98. **(b)** According to Raoult's law

$$\frac{\Delta p}{p^\circ} = \frac{n}{n+N} \text{ (mole fraction of solute)}$$

$$\frac{10}{p^\circ} = 0.2 \therefore p^\circ = 50 \text{ mm of Hg}$$

For other solution of same solvent

$$\frac{20}{p^\circ} = \frac{n}{n+N} \text{ (Mole fraction of solute)}$$

$$\Rightarrow \frac{20}{50} = \text{Mole fraction of solute}$$

$\Rightarrow$ Mole fraction of solute = 0.4

As mole fraction of solute + mole fraction of solvent = 1

Hence, mole fraction of solvent = 1 – 0.4 = 0.6

99. **(a)** The vapour pressure of a solution of glucose in water can be calculated using the relation

$$\frac{p^\circ - p_s}{p_s} = \frac{\text{Moles of glucose in solution}}{\text{Moles of water in solution}}$$

$$\text{or} \quad \frac{17.5 - p_s}{p_s} = \frac{18/180}{178.2/18} \qquad [\because p^\circ = 17.5]$$

$$\text{or} \quad 17.5 - p_s = \frac{0.1 \times p_s}{9.9} \text{ or } p_s = 17.325 \text{ mm Hg.}$$

Hence (a) is correct answer.

100. **(a)** Given vapour pressure of pure solvent (P°) = 121.8 mm Hg; Weight of solute (w) = 15 g

Weight of solvent (W) = 250 g; Vapour pressure of solution (P) = 120.2 mm Hg and Molecular weight of solvent (M) = 78

From Raoult's law

$$= \frac{P^o - P}{P^o} = \frac{w}{m} \times \frac{M}{W}$$

$$\frac{121.8 - 120.2}{121.8} = \frac{15}{m} \times \frac{78}{250}$$

$$\text{or} \quad m = \frac{15 \times 78}{250} \times \frac{121.8}{1.6} = 356.2$$

101. **(d)** $\frac{P^\circ - P}{P^\circ} = \frac{n}{N} \quad \Rightarrow \quad \frac{640 - 600}{640} = \frac{2.5/x}{39/78}$

$$x = \frac{640 \times 78 \times 2.5}{39 \times 40} = 80$$

Exercise 3 : PREVIOUS YEARS MCQs

1. **(a)** $\Delta T_f = K_f \times \text{m}$

$$\text{m} = \frac{0.5 \text{ mol}}{1 \text{ kg}} = 0.5 \text{ mol/kg}$$

$\Delta T_f = 1.86°\text{C kg/mol} \times 0.5 \text{ mol/kg}$

$\Delta T_f = 0.93°\text{C}$

2. **(d)** According to Henry's law,

$S = K_H \times p$

$= 0.159 \times 0.242 = 0.0384$

$= 3.84 \times 10^{-2} \text{ mol dm}^{-3}$

3. **(c)** Relative lowering of vapour pressure $= \frac{\Delta p}{P_1^\circ} = x_2$

$$= \frac{w_2 M_1}{M_2 W_1}$$

Given : $= \frac{\Delta p}{P_1^\circ} = 0.050$

$w_2 = 4$ g

$M_1 = 18 \text{ g/mol}^{-1}$

$W_1 = 54$ g

$$0.050 = \frac{4 \times 18}{M_2 \times 54}$$

$$M_2 = \frac{3 \times 18}{0.050 \times 54} = 20 \text{ g/mol}^{-1}$$

4. **(d)** Solutions in which solute - solute and solvent-solvent interactions are almost similar to solute-solvent interactions are known as ideal solution.

5. **(b)** $\Delta T_b = i_1 m_1 k_b + i_2 m_2 k_b$

$$= 1 \times \frac{2}{0.5} \times 0.52 + \frac{1 \times 2}{0.5} \times 0.52 = 4.16$$

$(T_b)_{\text{solution}} = 373.16 + 4.16 = 377.3\text{K}$

6. **(a)** At high altitudes, the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

7. **(c)** For an ideal solution, $\Delta H = 0$, $\Delta V = 0$

Hence, option (c) is incorrect.

8. **(d)**

	Compounds	**Number of particles (*i*)**
(a)	$[Co(H_2O)_6]Cl_3$	4
(b)	$[Co(H_2O)_5Cl]Cl_2.H_2O$	3
(c)	$[Co(H_2O)_4Cl_2]Cl.2H_2O$	2
(d)	$[Co(H_2O)_3Cl_3].3H_2O$	1

9. **(a)** The value of Henry's constant (K_H) increases with increase in temperature.

10. **(c)** $K_b = \frac{0.1 \times 180 \times 100}{1.8 \times 1000} = 1 \text{ K/m}$

11. **(c)**

$$\Delta T = K_f m = \frac{K_f \times W_2 \times 1000}{M_2 W_1} = 5.12 \times \frac{1}{250} \times \frac{1000}{51.2} = 0.4\text{K}$$

12. **(d)** According to Henry's law,
solubility $= k \times p = 1.4 \times 10^{-3} \times 0.5$ mol/L
$= 7 \times 10^{-4}$ mol/L
Number of moles in 100 mL $= 7 \times 10^{-5}$
Mass of oxygen $m = 7 \times 10^{-5} \times 32\text{g} = 2.24$ mg

13. **(a)** $\pi = \text{iCRT}$

$$\left(= \frac{\text{n}}{\text{v}} = \frac{\text{weight}}{\text{Molar mass} \times \text{volume (1 kg = 1000 g)}} \right)$$

$$= \frac{1 \times 2}{60000 \times 0.2} \times 0.083 \times 300 = 0.00415 \text{ bar}$$

$(\because 1 \text{ bar} = 10^5 \text{ Pa})$

So, 0.00415×10^5 Pa = 415 Pa

14. **(a)** A solution of acetone in ethanol shows positive deviation from Raoult's law. It is because ethanol molecules are strongly hydrogen bonded. When acetone is added, these molecules break the hydrogen bonds and ethanol becomes more volatile. Therefore its vapour pressure is increased.

15. **(c)** $\dfrac{\text{P}^{\text{o}} - \text{P}_s}{\text{P}^{\text{o}}} = \dfrac{n}{N} = \dfrac{w}{m} \times \dfrac{\text{M}}{W}$

$$0.1 = \frac{12}{m} \times \frac{18}{108} \Rightarrow m = \frac{12 \times 18}{0.1 \times 108} = 20$$

16. **(b)** Moles of glucose $= \dfrac{18}{180} = 0.1$

Moles of water $= \dfrac{178.2}{18} = 9.9$

Total moles = 0.1 + 9.9 = 10

$p_{\text{H}_2\text{O}}$ = Mole fraction × total pressure

$$= \frac{9.9}{10} \times 760 = 752.4 \text{ Torr}$$

17. **(a)** $\dfrac{0.80 - 0.6}{0.80} = x_\text{B};\ x_\text{B} = 0.25$

18. **(a)** Maximum lowering of vapour pressure will be given by the substance which give maximum number of particles in solution.

19. **(d)** 0.1 molar $\approx$ 0.1 mol is present in 1L
Given volume = 200 mL $\approx$ 0.2L
No. of mole in 0.2 L liquid

$$= \frac{2}{1} \times 0.1$$

= 0.02 mol of CO_2
$V = 0.02 \times 22.4 = 0.448\text{L}$

20. **(d)** Ethyl alcohol and water, after mixing, can very easily become a homogeneous mixture, because the two liquids are miscible, soluble in all proportions. The dipoles on the ethanol and water molecules cause the formation of hydrogen bonds between the molecules.

21. **(b)** $\text{T}_\text{f} = \text{i.K}_\text{f}.\text{m}$
Given, $\text{T}_\text{f} = \text{T}^\circ_\text{f} - \text{T}_\text{f}$
$= 0 - (-0.680)$
$= +0.680°\text{C}$
$\text{m} = 0.2$
$\text{K}_\text{f} = 1.86$
Thus, $0.680 = \text{i} \times 0.2 \times 1.86$

$$\text{i} = \frac{0.680}{0.2 \times 1.86} = 1.83$$

22. **(d)** mol dm^{-3} atm^{-1}

23. **(a)** $\text{Ba(NO}_3)_2 \longrightarrow \text{Ba}^{2+} + 2\text{NO}_3^-$

n mol 0 0
n-nα nα 2nα

Total moles of particles $= \text{n} - \text{n}\alpha + \text{n}\alpha + 2\text{n}\alpha = \text{n}(1 + 2\alpha)$

Vant Haff factor $(i) = \dfrac{\text{n}(1 + 2\alpha)}{\text{n}}$

$$2.74 = \frac{\text{n}(1 + 2\alpha)}{\text{n}} = 1 + 2\alpha$$

$$\alpha = \frac{2.74 - 1}{2} = 0.87$$

24. **(a)** $\Delta\text{T}_\text{b} = \dfrac{\text{K}_\text{b} \times \text{W}_2 \times 1000}{\text{W}_1 \times \text{M}_2}$

$$\text{M}_2 = \frac{\text{K}_\text{b} \times \text{W}_2}{\Delta\text{T}_\text{b} \times \text{W}_1}$$

25. **(d)** The solubility of NaBr changes slightly with temperature.

26. **(a)** Osmotic pressure, $\pi = \text{CRT}$ or $\pi = \dfrac{\text{w}}{\text{MV}}\text{RT}$
where, C = concentration of solution.
Given, w = 34.2 g, V = 1L, M = 342 g mol^{-1}
T = 20 °C, C = 20 + 273 = 293 °K

$$\therefore\ \pi = \frac{\text{w}}{\text{MV}}\text{RT}$$

$$= \frac{342.2 \text{ g}}{342 \text{ g mol}^{-1}} \times \frac{0.082 \text{ L atm K}^{-1}\text{mol}^{-1} \times 293 \text{ K}}{1 \text{ L}}$$

= 2.40 atm.

27. **(d)** Number of total ions present in the solution is known as van't Hoff factor.
Urea is a molecular solid hence, does not undergo association or dissociation therefore, has the lowest value of van't Hoff factor (i).

28. **(a)** van't Hoff equation is $\pi = \dfrac{\text{n}}{\text{V}}\text{RT}$

3

Ionic Equilibria

Exercise 1 : WARM-UP

Topic-wise MCQs

1. **(d)** Base accepts protons and acid donates protons.

2. **(d)** $(CH_3)_3$ B - is an electron deficient, thus behave as a lewis acid.

3. **(c)** Boron in B_2H_6 is electron deficient

4. **(a)** Bronsted base is a substance which accepts proton. In option (a), H_2O is accepting proton, *i.e.*, acting as a base.

5. **(c)** HSO_4^- accepts a proton to form H_2SO_4.

Thus, H_2SO_4 is the conjugate acid of HSO_4^-.

$$\underset{\text{base}}{HSO_4^-} \xrightarrow{+H^+} \underset{\substack{\text{conjugate acid}\\ \text{of } HSO_4^-}}{H_2SO_4}$$

6. **(a)**

(i) $$\underset{\text{acid}_1}{H_3PO_4} + \underset{\text{base}_2}{H_2O} \longrightarrow \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{H_2PO_4^-}$$

(ii) $$\underset{\text{acid}_1}{H_2PO_4^-} + \underset{\text{base}_2}{H_2O} \longrightarrow \underset{\text{base}_1}{HPO_4^{2-}} + \underset{\text{acid}_2}{H_3O^+}$$

(iii) $$\underset{\text{base}_1}{H_2PO_4^-} + \underset{\text{acid}_2}{OH^-} \longrightarrow \underset{\text{acid}_1}{H_3PO_4} + \underset{\text{base}_2}{O^{2-}}$$

Hence, only in (ii) reaction $H_2PO_4^-$ is acting as an acid.

7. **(d)** $[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$ involves lose and gain of electrons. H_2O is coordinated to Cu by donating electrons (LHS). It is then removed by withdrawing electrons.

8. **(d)** BF_3 is an electron deficient molecule and thus, it can accept a pair of electrons.

In stannic chloride and stannous chloride, the Sn atom has vacant *d*-orbitals. Sn can increase its covalency to 6 by accepting pair of electrons. Thus $SnCl_2$ and $SnCl_4$ can also act as Lewis acids.

9. **(c)** Dissociation of a weak acid in water :

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{A^-(aq)}$$

If HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+, and the solution will mainly contain A^- and H_3O^+ ions. Hence, the equilibrium moves in the direction of formation of weaker acid and weaker base.

Similarly, this is true for dissociation of a weak base also.

10. **(c)** Strong base has higher tendency to accept the proton. Increasing order of base and hence the order of accepting tendency of proton is

$$I^- < HS^- < NH_3 < RNH_2$$

11. **(b)** Because NH_3 after losing a proton (H^+) gives NH_2^-

$$NH_3 + H_2O \rightleftharpoons NH_2^- + H_3O^+$$

(Conjugate acid-base pair differ only by a proton)

12. **(b)** $HA \longrightarrow H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}, \quad \because\ [H^+] = 10^{-pH}$$

$\therefore$ $[H^+] = 10^{-5}$; and at equilibrium $[H^+] = [A^-]$

$$\therefore\ K_a = \frac{10^{-5} \times 10^{-5}}{0.0015} = 2 \times 10^{-8}$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-8}}{.005}} = \sqrt{4 \times 10^{-6}} = 2 \times 10^{-3}$$

Percentage ionization = 0.2

13. **(b)** Given $[OH^-] = 10^{-3}$

$\therefore$ $pOH = 3$

$\because$ $pH + pOH = 14$

$\therefore$ $pH = 14 - 3 = 11$

14. **(a)** Given $[H_3O^+] = 1 \times 10^{-10}$ M

at 25° $[H_3O^+][OH^-] = 10^{-14}$

$$\therefore\ [OH^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

Now, $[OH^-] = 10^{-pOH} = 10^{-4}$

$\therefore$ $pOH = 4$

15. **(a)** Given $K_a = 1.00 \times 10^{-5}$, $C = 0.100$ mol for a weak electrolyte, degree of dissociation

$$(\alpha) = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1 \times 10^{-5}}{0.100}} = 10^{-2} = 1\%$$

16. **(b)** The value of ionic product of water changes with the temperature.

17. **(b)** Acidic strength $\propto \sqrt{K_a}$

18. **(b)** $pK_a = -\log K_a$

Smaller the value of pK_a, stronger will be acid

$\therefore$ Acid having pK_a value of 10^{-8} is strongest acid.

19. **(b)** $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}} = \sqrt{\dfrac{3.14 \times 10^{-4}}{1.96 \times 10^{-5}}} = 4:1$

20. **(a)** $K = c\alpha^2 = 0.1 \times \left(\dfrac{1.34}{100}\right)^2 = 1.8 \times 10^{-5}$

21. **(b)** CH_3COOH is weak acid while NaOH is strong base, so one equivalent of NaOH can not be neutralized with one equivalent of CH_3COOH. Hence the solution of one equivalent of each does not have pH value as 7. Its pH will be towards basic side as NaOH is a strong base. Hence, conc. of OH^- will be more than the conc. of H^+.

22. **(c)** On dilution $[H^+] = 10^{-6}$ M $= 10^{-6}$mol

Now dissociation of water cannot be neglected,

Total $[H^+] = 10^{-6} + 10^{-7} = 11 \times 10^{-7}$

$pH = -\log [H^+] = -\log (11 \times 10^{-7}) = 5.98$

23. **(d)** $\because$ pH = 1 ; $H^+ = 10^{-1} = 0.1$ M

pH = 2 ; $H^+ = 10^{-2} = 0.01$ M

$\therefore M_1 = 0.1 \quad V_1 = 1$

$M_2 = 0.01 \quad V_2 = ?$

From $M_1V_1 = M_2V_2$

$0.1 \times 1 = 0.01 \times V_2$

$V_2 = 10$ litres

$\therefore$ Volume of water added = 10 – 1 = 9 litres

24. **(a)** Molarity (M) = 10M. HCl is a strong acid and it is completely dissociated in aqueous solutions as :

$HCl\,(10) \rightleftharpoons H^+(10) + Cl^-$.

So, for every moles of HCl, there is one H^+. Therefore, $[H^+] = [HCl]$ or $[H^+] = 10$.

$pH = -\log[H^+] = -\log[10] = -1$.

25. **(d)** No. of moles of NaOH $= \dfrac{4}{40} = 0.1$

[Molecular weight of NaOH = 40]

No. of moles of $OH^- = 0.1$

Concentration of $OH^- = \dfrac{0.1}{1 \text{ litre}} = 0.1 \text{mol / L}$

As we know that, $[H^+][OH^-] = 10^{-14}$

$\therefore \quad [H^+] = 10^{-13} \quad (\because OH^- = 10^{-1})$

26. **(c)** $M_1V_1 = M_2V_2$

$1 \times 0.10 = M_2 \times 100 \Rightarrow M_2 = 0.001 = 10^{-3}$

$$\begin{array}{ccccc} BOH & \rightleftharpoons & B^+ & + & OH^- \\ C & & 0 & & 0 \\ C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$K_b = \dfrac{C\alpha \times C\alpha}{C(1-\alpha)} \Rightarrow K_b = C\alpha^2$

$\Rightarrow \alpha = \sqrt{K_b / C} \qquad (\because 1-\alpha \approx 1)$

$[OH^-] = C\alpha = \sqrt{\dfrac{K_b}{C}} \times C = \sqrt{K_b C}$

$= \sqrt{10^{-5} \times 10^{-3}} = 10^{-4}$

$\therefore pH + pOH = 14 \Rightarrow \therefore pH = 14 - 4 = 10$

27. **(b)** K_w depends upon temperature as it is an equilibrium constant.

28. **(b)** The solution with lowest pH will have the highest value of pOH.

$[H^+]$ order: (A) > (D) > (C) > (B)

pH order : (B) > (C) > (D) > (A)

pOH order : (A) > (D) > (C) > (B)

29. **(c)** Number of meq. of the acid = 0.04 × 100 = 4

Number of meq. of the base = 0.02 × 100 = 2

$\therefore$ Number of meq. of the acid left on mixing = 4 – 2 = 2

Total volume of the solution = 200 mL

$\therefore$ No. of meq of the acid present in 1000 mL of the solution = 10

or No. of eq. of the acid in 1000 mL of the solution

$= \dfrac{10}{1000} = 0.01$

Since the acid is monobasic and completely ionises in solution

0.01 N HCl = 0.01 M HCl

Thus $[H^+] = 0.01$

$\therefore$ $pH = -\log(0.01) = -(-2) = 2$

30. **(c)** 0.001 M NaOH

$[OH^-] = 10^{-3}$

$pOH = -\log[OH^-] \Rightarrow pOH = 3$

$pH + pOH = 14 \Rightarrow pH = 11$

31. **(d)** For acidic buffer,

$pH = pK_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

$= 4.57 + \log \left(\dfrac{0.1}{0.01}\right) = 5.57$

32. **(d)** Dimethylammonium acetate is a salt of weak acid and weak base whose pH can be calculated as

$pH = 7 + \dfrac{1}{2}(pK_a - pK_b)$

$= 7 + \dfrac{1}{2}(4.77 - 3.27) = 7.75$

33. **(d)** $[OH^-] = 0.01$ M $= 10^{-2}$ M

$pOH = -\log[OH^-] = -\log(10^{-2}) = 2$

$pH = 14 - pOH = 12$

34. **(d)** HCl cannot accept H^+ therefore cannot act as Bronsted base.

35. **(c)** When a proton is removed from an acid, we obtain its conjugate base.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$HF \rightleftharpoons H^+ + F^-$$

36. **(c)** Meq. of HCl $= 75 \times \frac{1}{5} \times 1 = 15$

Meq. of NaOH $= 25 \times \frac{1}{5} \times 1 = 5$

Meq. of HCl in resulting solution = 10

Molarity of $[H^+]$ in resulting mixture $= \frac{10}{100} = \frac{1}{10}$

$$pH = -\log[H^+] = -\log\left[\frac{1}{10}\right] = 1.0$$

37. **(a)** g eq of NaOH $= 0.1 \times V = 0.1V$

g eq of HCl $= 0.01 \times V = 0.01V$

g eq of NaOH > g eq. HCl

hence, resultant solution should be basic, hence from the eqn

$M_1V_1 - M_2V_2 = MV$

$0.1V - 0.01V = MV$

$$M = \frac{0.09}{2} = 0.045 = 4.5 \times 10^{-2}$$

Now, pOH $= -\log[OH^-]$

$= -\log 4.5 \times 10^{-2} = 1.34$

$\because$ pH + pOH = 14

$\therefore$ pH = 14 – 1.34 = 12.65

38. **(c)** Na, CO_3 from basic solution.

39. **(b)** BF_3 acts as Lewis acid.

40. **(b)** $$HCl(aq.) + NaOH(aq.) \rightarrow NaCl(aq.) + H_2O(\ell)$$

Initial	50 mm	30 mm	–	–
Final	20 mm		20	20

$$[HCl] = \frac{20}{80} = \frac{1}{4}M = 2.5 \times 10^{-1}M$$

$pH = -\log 2.15 \times 10^{-1} = 1 - 0.33979 = 0.6021$

$\Rightarrow$ pH $= 6021 \times 10^{-4}$.

41. **(d)** K_a of Butyric acid $= 2 \times 10^{-5}$

$pK_a = -\log K_a = -\log(2 \times 10^{-5}) = 4.7$

The pH of butyric acid is calculated as:

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log c = \frac{1}{2}(4.7)\frac{1}{2}\log(0.2)$$

$= 2.35 + 0.35 = 2.7$

pH $= 27 \times 10^{-1}$.

42. **(c)** C – concn. of salt, NH_4Cl, produced by neutralization of NH_4OH and HCl.

NH_4Cl, no. of moles = 2m mol $= 2 \times 10^{-3}$ mol

$$[NH_4Cl] = \frac{2m\,mol}{(20+40)ml} = \frac{1}{30}M$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

$$= 7 - \frac{1}{2} \times (+5) - \frac{1}{2}\log\left(\frac{1}{30}\right) = 7 - \frac{5}{2} + \frac{1.48}{2} = 5.24$$

43. **(c)** $$\underset{\text{(phosphorus acid)}}{H_3PO_3} \xrightarrow{-H^+} \underset{\text{conjugate base }(x)}{H_2PO_3^-}$$

$$\underset{\text{(oleum)}}{H_2S_2O_7} \xrightarrow{-H^+} \underset{\text{conjugate base }(y)}{HS_2O_7^-}$$

44. **(c)** NH_3, $\bar{O}H$, CO are acting as Lewis bases because they have lone pair of electrons in them.

Whereas, C_2H_4 has one double bond that means it has pielectrons which are electron rich.

45. **(a)** 12

Moles of HCl = 0.4m × 0.1L = 0.04 moles

For NaOH:-

Moles of NaOH = 0.5 M × 0.1 L = 0.05 moles

HCl and NaOH react in 1 : 1 Ratio

$HCl + NaOH \rightarrow NaCl + H_2O$

NaOH is in excess since 0.05 moles of NaOH react with 0.04 moles of HCl

0.05 moles – 0.04 moles = 0.01 moles of NaOH remaining

The total volume after mixing – 100ml of HCl + 100 ml
of NaOH + 800 ml of
distilled water
$\Rightarrow$ 1000 ml or 1 L

so the concentration of NaOH $= \frac{0.01 \text{ moles}}{1L} = 0.01$ m

pOH $= -\log[OH^-]$

pOH $= -\log[0.01] = 2$

As we know pH + pOH = 14

pH = 14 – pOH = 14 – 2 = 12

46. **(b)** Balanced stoichiometric equation is:

$P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^-$

conjugate of $H_2PO_2^-$ is H_3PO_2.

H_3PO_2 is hypophosphorous acid.

47. (d) $\underset{\text{chloric acid}}{HClO_3} \rightleftharpoons \underset{\text{Conjugate base}}{ClO_3^- + H^+}$

48. (a) Lewis acids = $AlCl_3$, H^+, Co^{3+}, Mg^{2+}, BF_3.

49. (c) Acidic solutions (pH < 7) are Black coffee, Lemon juice, Human Saliva, Tomato juice.

50. (b) Conjugate acid of $HCO_3^- = H_2CO_3$ (has an extra H^+)
Conjugate base of $HCO_3^- = CO_3^{2-}$ (has an less H^+)

51. (a) $H_3O^+ \longrightarrow H^+ + \underset{\text{conjugate base}}{H_2O}$

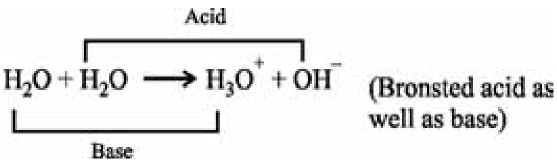
52. (c) $\underset{0.01\ (N)}{Ca(OH)_2}$ ’! $Ca^{2+} + 2OH^-$

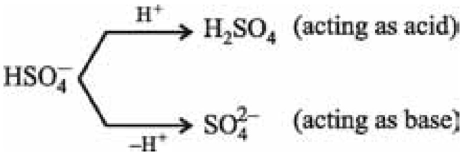
At 298K, pH = 14 – pOH = 14 – [– log (0.01)]
$= 14 + \log 10^{-2} = 14 - 2 = 12$

53. (c) Base have pH value more than seven. Distilled H_2O is neutral, HCl is acidic, NaOH and NH_3 both are base but, NaOH is a strong base among the given options. Therefore, it has highest pH.

54. (b) HF is weakest acid, thus, F^- is the strongest conjugate base.

55. (d)





56. (d) Molecular mass of NaOH = 23 + 16 + 1 = 40

$$\text{Molarity} = \frac{\text{Mass of solute (in g)}}{\text{Molecular mass of the solute} \times \text{Volume of solution (in L)}} = \frac{0.04 \times 1000}{40 \times 100} = 10^{-2}$$

$OH^- = 10^{-2}$ mol/L

So, pOH = $-\log[OH^-]$

pOH + pH = 14 or pH = 14 – 2 = 12

57. (a) With increase in temperature, K_w of water increases
So, degree of dissociation of water increases.
∴ pH as well as pOH of water decreases.
At 80°C, pH ≈ 6.93.

58. (b) $\underset{\text{Hydrazoic acid}}{N_3H} \rightleftharpoons N_3^- + H^+$

59. (b) I^- is electron donor. Hence it is Lewis base.

60. (d) Strongest Bronsted base has weakest conjugate acid.
∵ HOCl is weakest acid among HOCl, $HClO_2$, $HClO_3$ and $HClO_4$.
∴ Conjugate base of HOCl (i.e. OCl^-) is strongest Bronsted base.

61. (c) Proton donors are acids. Thus conjugate base of an acid has one H^+ less than the acid.

$$\underset{\text{Acid}}{HBr} \longrightarrow \underset{\text{Conjugate base}}{Br^-} + H^+$$

62. (d) Buffering action is maximum when
[Salt] = [Acid]
i.e., $pH = pK_a$

63. (b) $PbS \rightleftharpoons \underset{S}{Pb^+} + \underset{S}{S^-}$
$K_{sp} = S \times S = S^2$

64. (c) Solubility of weak electrolyte decreases in solvent having common ion. So solubility of AgI in NaI solution is less than in pure water because of common ion effect.

65. (d) HNO_2 is a weak acid and $NaNO_2$ is salt of that weak acid and strong base (NaOH).

66. (a) The pOH of a buffer consisting of NH_3 (*i.e.*, NH_4OH) and salt NH_4Cl (salt) is given by the equation

$$pOH = pK_b + \log\frac{[\text{ammonia}]}{[\text{salt}]} = 5.0 + \log\frac{[0.1]}{[1.0]}$$

$= 5.0 - \log 10 = 5 - 1 = 4.0$
∴ pH = 14 – pOH = 14 – 4.0 = 10

67. (d) For acidic buffer $pH = pK_a + \log\left[\frac{\text{salt}}{\text{acid}}\right]$

or $pH = pK_a + \log\frac{[A^-]}{[HA]}$

Given $pK_a = 4.5$ and acid is 50% ionised.
$[HA] = [A^-]$ (when acid is 50% ionised)
∴ $pH = pK_a + \log 1$
∴ $pH = pK_a = 4.5$
pOH = 14 – pH = 14 – 4.5 = 9.5

68. (a) Lets take an example of an acidic buffer CH_3COOH and CH_3COONa.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$;

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

when few drops of HCl are added to this buffer, the H^+ of HCl immediatly combine with CH_3COO^- ions to form undissociated acetic acid molecules. Thus there will be no appreciable change in its pH value. Like wise if few drops of NaOH are added, the OH^- ions will combine with H^+ ions to form unionised water molecule. Thus pH of solution will remain constant.

69. **(b)** $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$K_{sp} = [Mg^{++}][OH^-]^2$

$1.0 \times 10^{-11} = 10^{-3} \times [OH^-]^2$

$$[OH^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

$\therefore$ pOH = 4

$\therefore$ pH + pOH = 14

$\therefore$ pH = 10

70. **(d)** pH or $[H^+]$ of a buffer does not change with dilution.

71. **(b)** According to Henderson-Hasselbalch equation

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$4 = 5 - \log 1.3 + \log\frac{[CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

$$\log\frac{[CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = \log 1.3 - 1 = \log\frac{1.3}{10}$$

$$\therefore \log A - \log(B) = \log\left(\frac{A}{B}\right)$$

$$\frac{[CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = 0.13$$

72. **(b)** $\underset{}{Cr(OH)_3(s)} \rightleftharpoons \underset{s}{Cr^{3+}(aq.)} + \underset{3s}{3OH^-(aq.)}$

$(s)\ (3s)^3 = K_{sp}$

$27s^4 = K_{sp}$

$$s = \left(\frac{K_{sp}}{27}\right)^{1/4} = \left(\frac{1.6 \times 10^{-30}}{27}\right)^{1/4}$$

73. **(b)** Solubility product is the product of ionic concentration in a saturated solution of an electrolyte at a given temperature.

74. **(c)** Let binary electrolyte be *AB*

$\underset{s}{AB} \rightleftharpoons \underset{s}{A^+} + \underset{s}{B^-}$

Hence, solubility product of *AB*

$K_{sp} = [A^+]\,[B^-]$

$S = [s]\,[s] \Rightarrow s = S^{1/2}$

75. **(b)** Given pH = 12

or $[H^+] = 10^{-12}$

Since, $[H^+]\,[OH^-] = 10^{-14}$

$$\therefore \quad [OH^-] = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$Ba(OH)_2 \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{2s}{2OH^-}$

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

$2s = 10^{-2}$

$$s = \frac{10^{-2}}{2}$$

$$K_{sp} = 4s^3 = 4 \times \left(\frac{10^{-2}}{2}\right)^3 = 5 \times 10^{-7}$$

76. **(b)** $K_{sp} = [Fe^{3+}].[3OH^-]$

So molar solubility of $Fe^{3+} = s$ and $[3OH^-] = 3s$

$Fe(OH)_3 \rightleftharpoons \underset{[s]}{Fe^{3+}} + \underset{[3s]}{3OH^-}$

$1.0 \times 10^{-38} = [s]\,[3s]^3$

$1.0 \times 10^{-38} = s^4 \times 27$

$$s^4 = \frac{1.0 \times 10^{-38}}{27}$$

$s^4 = 3.703 \times 10^{-40}$

$$s = \left(3.703 \times 10^{-40}\right)^{\frac{1}{4}} = 1.386 \times 10^{-10}$$

77. **(d)** In deionized water no common ion effect will take place so solubility of AgCl will be maximum in it.

$KCl \longrightarrow K^+ + Cl^-$

$HCl \longrightarrow H^+ + Cl^-$

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$

78. **(a)** $Bi_2S_3 \rightleftharpoons \underset{2s}{2Bi^{3+}} + \underset{3s}{3S^{2-}}$

$K_{sp} = (2s)^2\,(3s)^3 = 108\,(s)^5$

$$(s)^5 = \frac{1.08 \times 10^{-73}}{108} \Rightarrow s = 10^{-15}$$

79. **(b)** $AgBr \rightleftharpoons Ag^+ + Br^-$

$K_{sp} = [Ag^+]\,[Br^-]$

For precipitation to occur

Ionic product > Solubility product

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1L $AgNO_3$ solution

$\therefore$ Number of moles of Br^- needed from KBr = 10^{-11}

$\therefore$ Mass of KBr = $10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

80. **(b)** $AB \longrightarrow \underset{s}{A^+} + \underset{s}{B^-}$

$K_{sp} = s \times s = s^2$

$$\Rightarrow \quad s = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}\ \text{mol L}^{-1}.$$

81. **(d)** $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$\quad s \qquad\qquad s \qquad 2s$

$NaOH \longrightarrow Na^+ + OH^-$

Total $[OH^-] = 2s + 0.1 \approx 0.1$

Ionic product $= [Ni]^{2+}[OH]^2$

$2 \times 10^{-15} = s(0.1)^2$

$s = 2 \times 10^{-13}$

Solubility of $Ni(OH)_2 = 2 \times 10^{-13}$ M

82. **(d)** $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$t = 0 \qquad 0 \qquad 0$

At eqm. $\qquad s \qquad 2s$

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

$0.1 \qquad 0.1 \quad 0.1$

Due to common ion effect of NaF, solubility of CaF_2 is further supressed. Therefore, the concentration of F^- will be mainly due to NaF.

$K_{sp} = [Ca^{2+}]\,[F^-]^2$

$K_{sp} = (s)\,(0.1 + 2s)^2 \quad 0.1 + 2s \approx 0.1$

$$s = \frac{K_{sp}}{(0.1)^2} = \frac{5.3 \times 10^{-11}}{(0.1)^2} = 5.3 \times 10^{-9}\ \text{mol L}^{-1}$$

83. **(a)** $Ca(OH)_2 \quad Ca^{2+} + 2OH^-$

pH = 9, pOH = 14 – 9 = 5

$[OH^-] = 10^{-5}$

$$\left[Ca^{2+}\right] = \frac{10^{-5}}{2}$$

$$K_{sp} = [Ca^{2+}]\,[OH^-]^2 = \left(\frac{10^{-5}}{2}\right) \times (10^{-5})^2$$

$= 0.5 \times 10^{-15}$

84. **(a)** Solubility of $BaSO_4 = 2.42 \times 10^{-3}\ gL^{-1}$

$$\therefore \quad s = \frac{2.42 \times 10^{-3}\ gl^{-1}}{233g\ mol^{-1}} = 1.038 \times 10^{-5}\ \text{mol L}^{-1}$$

$K_{sp} = s^2 = (1.038 \times 10^{-5})^2 = 1.08 \times 10^{-10}\ mol^2\,L^{-2}$

85. **(c)** $\underset{}{Ag_2C_2O_4(s)} \rightleftharpoons \underset{2s}{2Ag^+(aq)} + \underset{s}{C_2O_4^{2-}(aq)}$

$K_{sp} = [Ag^+]^2\,[C_2O_4^{2-}]$

$[Ag^+] = 2.2 \times 10^{-4}$ M

Given that:

$\therefore$ Concentration of $C_2O_4^{2-}$ ions,

$$\left[C_2O_4^{2-}\right] = \frac{2.2 \times 10^{-4}}{2} M = 1.1 \times 10^{-4} M$$

$\therefore \quad K_{sp} = (2.2 \times 10^{-4})^2\,(1.1 \times 10^{-4})$

$= 5.324 \times 10^{-12}$

86. **(d)** $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

$0.1M \qquad 0 \qquad 0$

$0 \qquad 0.1M \qquad 0.1 + S$

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$a \qquad 0 \qquad 0$

$a - S \qquad S \qquad S + 0.1$

$K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-] = S\,(0.1 + S)$

Q K_{sp} is small, S is neglected with respect to 0.1 M

Hence, $1.6 \times 10^{-10} = S \times 0.1$

$S = 1.6 \times 10^{-9}$ M

87. **(b)** MY $M^+ + Y^-$

$K_{sp} = s^2 = 6.2 \times 10^{-13}$

$s = \sqrt{6.2 \times 10^{-13}}$

$s = 7.87 \times 10^{-7}\ \text{mol L}^{-1}$

$NY_3 \rightleftharpoons N^{3+} + 3Y^-$

$K_{sp} = s \times (3s)^3 = 27s^4 = 6.2 \times 10^{-13}$

$$s = \left(\frac{6.2 \times 10^{-13}}{27}\right)^{1/4}$$

$s = 3.89 \times 10^{-4}\ \text{mol L}^{-1}$

$\therefore$ molar solubility of NY_3 is more than MY in water.

88. **(a)** Among the given acids, $HClO_4$ is a very strong acid, completely dissociates

$\therefore [HA] \rightarrow 0$ in this case, hence cannot be used for acidic buffer.

89. **(a)** $CaCO_3 \longrightarrow \underset{x}{Ca^{2+}} + \underset{x}{CO_3^{2-}}$

$CaC_2O_4 \longrightarrow \underset{y}{Ca^{2+}} + \underset{y}{C_2O_4^{2-}}$

$\therefore [Ca^{2+}] = x + y$

Now, $K_{sp}(CaCO_3) = [Ca^{2+}]\,[CO_3^{2-}]$

or $\quad 4.7 \times 10^{-9} = (x + y)x$

similarly, $\quad K_{sp}(CaC_2O_4) = [Ca^{2+}]\,[C_2O_4^{2-}]$

or $\quad 1.3 \times 10^{-9} = (x + y)y$

On solving, we get

$[Ca^{2+}] = 7.746 \times 10^{-5}$ M

90. **(c)** Given, $K_a = 1 \times 10^{-4}$

$\therefore \quad pK_a = -\log(1 \times 10^{-4}) = 4$

Now from Handerson equation

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Putting the values

$$5 = 4 + \log\frac{[Salt]}{[Acid]}$$

$$\log\frac{[\text{Salt}]}{[\text{Acid}]} = 5 - 4 = 1$$

Taking antilog

[Salt]/[Acid] = 10 = 10 : 1

91. **(c)** Since, $(NH_4)_3PO_4$ is salt of weak acid (H_3PO_4) and weak base (NH_4OH).

$$\text{pH} = 7 + \frac{1}{2}(\text{pK}_a - \text{pK}_b)$$

$$= 7 + \frac{1}{2}(5.23 - 4.75)$$

$$= 7.24 \approx 7.0$$

92. **(c)** $K_{sp} = S^2$

$$S = \sqrt{K_{sp}} = \sqrt{8\times10^{-28}} = 2\sqrt{2}\times10^{-14}$$

$= 2.82 \times 10^{-14}$

$= 282 \times 10^{-16}$

93. **(a)** Solubility of $CaF_2 = 2.34 \times 10^{-3} \times 10$ g/L

$$s = \frac{2.34}{78}\times10^{-2}\,\text{mol / L}$$

$s = 3 \times 10^{-4}$ mol/L

$$\underset{}{CaF_2} \rightleftharpoons \underset{s}{Ca^{2+}} + \underset{2s}{2F^-}$$

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

$= 0.0108 \times 10^{-8}\,(\text{mol/L})^3$

94. **(a)** $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$

$$s\ (0.1 + 2s) \simeq 0.1$$

$K_{sp} = s(0.1)^2$

$2 \times 10^{-20} = s \times 10^{-2} \Rightarrow s = 2 \times 10^{-18}$

Therefore, x = 2

95. **(d)** $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$[NH_3] = 2 \times 0.0210 = 0.042$ m mol

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$

$[NH_4Cl] = 5 \times 0.0504 = 0.252$ m mol

By Henderson – Hasselbalch equation,

$$\text{pOH} = \text{pK}_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log\left(1.8\times10^{-5}\right) + \log\left(\frac{0.252}{0.042}\right) = 4.74 + 0.77$$

pOH = 5.51

$$\left[OH^-\right] = 10^{-5.51} = 3.09\times10^{-6} \simeq 3\times10^{-6}$$

96. **(c)** Henderson – Hasselbalch equation,

$$\text{pH} = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\Rightarrow\ 5.74 = 4.74 + \log\frac{[CH_3COONa]}{1}$$

$5.74 - 4.74 = \log[CH_3COONa] - \log 1$

$1 = \log[CH_3COONa] - 0$

$[CH_3COONa] = 10^1 \approx 10$ M

97. **(c)** $\text{pH} = \text{pK}_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$\text{pH} = 5 + \log\frac{0.2}{0.1} \qquad [\text{pK}_a = -\log K_a = -\log 10^{-5} = 5]$$

pH = 5 + log 2

pH = 5 + 0.3

pH = 5.3

98. **(c)** $Pb(NO_3)_2 \rightleftharpoons \underset{0.2}{Pb^{2+}} + \underset{0.2}{NO_3^-}$

$PbI_2\ Pb^{2+} + 2I^-$

$S + 0.2\ \ 2S$

Solubility of $Pb^{2+} = S + 0.2$

$K_{SP} = (S + 0.2) \times (2S)^2$

$K_{SP} = 4S^3 + 0.8S^2$

$4S^3 << 0.8S^2$

$\therefore\ 0.8S^2 = K_{SP}$

$$S = \sqrt{\frac{K_{sp}}{0.8}} = \left(\frac{K_{sp}}{0.8}\right)^{\frac{1}{2}}$$

99. **(d)** $pOH = pK_b + \log\dfrac{[\text{salt}]}{[\text{base}]}$

Mole of $NH_4OH = 30 \times 0.2 = 6$m mol $= 0.006$ mol

Mole of $NH_4Cl = 30 \times 2 = 60$ m mol $= 0.06$ mol

$pH + pOH = 14$

$pOH = 14 - pH = 14 - 8.2 = 5.8$

$$pOH = pK_b + \log\frac{0.06}{0.006}$$

$5.8 = pK_b + \log 10$

$5.8 = pK_b + 1 \Rightarrow pK_b = 5.8 - 1 = 4.8$

100. **(c)** $AgBr \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Br^-}$

$K_{sp} = 4 \times 10^{-13}$

In presence of strong electrolyte 0.1 M K Br

Br^- ion increases and dissociation of AgBr as

$[Ag^+] = 5$

$[Br^-] = 0.1 + 5$

$K_{sp} = 5 \times (0.1 + 5)$

$= 0.15 + s^2$

for very diluted $s^2 <<< 1$ thus s^2 ignored

$K_{sp} = 0.15$

$$S = \frac{4 \times 10^{-13}}{0.1}$$

$= 4 \times 10^{-12}$ M

101. **(c)** Solubility product (K_{sp}) of Ax = 10^{-10}

$[H^+] = [X^-] = 10^{-1}$ M

$[K_{sp}] = [H^+] [X^-]$

$10^{-10} = [10^{-1}] \times [S]$

$$\therefore \quad S = \frac{10^{-10}}{10^{-1}} = 10^{-9}$$

102. **(d)** Basic buffer solution is made by mixing a weak base with strong acid.

103. **(c)** A solution that has the concentration of Ag^+ or Cl^- greater than or equal to the solubility of Ag^+ or Cl^- from the value of K_{sp}, will precipitate out.

$K_{sp} = [Ag^+] [Cl^-] = (s) (s) = s^2 = 1 \times 10^{-10}\ M^2$

$\Rightarrow \quad s = 10^{-5}$ M

Thus, (iv) 1L of 10^{-3} M $AgNO_3$ and (v) 1L of 10^{-5} M NaCl will precipitate

104. **(c)** $K_{sp} = 1 \times 10^{-10}$

MCl ’! $M^{-+} + Cl^-$

In NaCl soln., total $[Cl^-] = (0.1 + s)M \quad \therefore \quad s(s + 0.1) = 10^{-10}$

or, $\quad 0.1s = 10^{-10} \qquad [\because s + 0.1 \because 0.1 \text{ as } s <<< 0.1]$

$$\text{or,} \quad s = \frac{10^{-10}}{0.1} = 10^{-9}\ M$$

105. **(b)** Smaller the value of K_{sp} of the salt, quicker is the formation of precipitate.

Sequence of precipitation : HgS, CdS, ZnS, NiS.

106. **(b)** Given, $[K_{sp}]$ of AgBr = 5×10^{-10}

[NaBr] = 0.2 M; $[Na^+] = [Br^-] = 0.2$ M

Now, $[K_{sp}] = [Ag^+] [Br^-]$

$s(0.2) = 5 \times 10^{-10}$ (s << 0.2)

$$s = \frac{5 \times 10^{-10}}{0.2} = 25 \times 10^{-10}\ M$$

107. **(c)** $\mathrm{Ni(OH)2} \rightleftharpoons \underset{s\,mol/L}{Ni^{2+}} + \underset{2s mol/L}{2OH^-}$

$\Rightarrow K_{sp} = [Ni^{2+}] [OH^-]^2 = s \times (2s)^2 = 4s^3$

$2 \times 10^{-15}\ (mol/L)^3 = 4s^3$

$$\Rightarrow s = \left(\frac{2}{4} \times 10^{-15}\right)^{1/3} = 7.9 \times 10^{-6} = 8 \times 10^{-6} \text{ mol/L}$$

$[OH^-] = 2s = 2 \times 8 \times 10^{-6}$ mol/L

pOH = 6 – log 16 = 4.983 5

$\therefore$ pH = 14 – pOH = 14 – 5 = 9 at 25°C.

108. **(b)** $A_2B \rightarrow \underset{2s}{2A^+} + \underset{s}{B^{2-}}$

$K_{sp} = [A^+] [B^{2-}] = (2s)^2 (s) = 4s^3$

Given, K_{sp} for $A_2B = 3.2 \times 10^{-11} \quad \therefore \quad 3.2 \times 10^{-11} = 4s^3$

$$s = \left(\frac{3.2}{4} \times 10^{-11}\right)^{1/3} = \left(8 \times 10^{-12}\right)^{1/3} = 2 \times 10^{-4}$$

Thus $s = 2 \times 10^{-4}$

109. **(c)** Dissolution $NH_4Cl \rightarrow NH_4^+ + Cl^-$

Cl^- will Cl^-(aq) and will not undergo hydrolysis.

Hydrolysis $NH_4^- + H_2O \rightleftharpoons NH_3 + H_3O^+$

110. **(a)** Let solubility of AgCl = x mole/L

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

i.e., $K_{sp(AgCl)} = x \times x$

$KCl \longrightarrow \underset{0.1}{K^+} + Cl^-$

$[Cl^-]$ from KCl = 0.1 m

Total $[Cl^-]$ in solution = $x + 0.1$

$K_{sp}(AgCl) = [Ag^+] [Cl^-] = x (x + 0.1)$

$1.0 \times 10^{-10} = x(x + 0.1)$

$1.0 \times 10^{-10} = x^2 + 0.1x$

$1.0 \times 10^{-10} = 0.1x \qquad (\text{as } x^2 << 1)$

$x = 1.0 \times 10^{-9}$ mol/L

Exercise 2 : ACCELERATOR
Topic-wise MCQs

1. **(b)** $pH = -\log [H^+] = \log\left[\frac{1}{H^+}\right]$

2. **(c)** Electron acceptors are Lewis acids

$AlCl_3$ is electron deficient compound (Al has 6 electrons in valence shell), so it is electron acceptor and Lewis acid.

3. **(b)**

4. **(d)** Conjugate acid of HF_2^- is H_2F_2.

$$\underset{\text{base}}{HF_2^- + H^+} \longrightarrow \underset{\text{conjugate acid}}{H_2F_2}$$

5. **(c)** BF_3 behaves as lewis acid.

6. **(d)** $H_2A \rightleftharpoons H^+ + HA^-$

$$\therefore K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]} \text{(Given)}$$

$$HA^- \longrightarrow H^+ + A^{--}$$

$$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[H^+][A^{--}]}{[HA^-]} \text{(Given)}$$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2$$

$$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$$

7. **(a)** $(HSO_4)^-$ can accept and donate a proton

$(HSO_4)^- + H^+ \rightleftharpoons H_2SO_4$ (acting as base)

$(HSO_4)^- - H^+ \rightleftharpoons SO_4^{2-}$. (acting as acid)

8. **(d)** Given concentration of NaOH = 10^{-10} M

$$\underset{10^{-10}\,M}{NaOH} \longrightarrow Na^+ + \underset{10^{-10}}{OH^-}$$

$\therefore$ $[OH^-]$ from NaOH = 10^{-10}

We have to consider dissociation of H_2O

$[OH^-]$ from $H_2O = 10^{-7}$

Total $[OH^-] = 10^{-7} + 10^{-10}$

$$= 10^{-7}(0.001+1) = 10^{-7}\left(\frac{1001}{1000}\right) = 10^{-10} \times 1001$$

$$\therefore pOH = -\log[OH^-]$$

$$= -(\log 1001 \times 10^{-10}) = -3.004 + 10 = 6.9996$$

pH = 14 – pOH = 14 – 6.996 = 7.004

$\therefore$ pH of 10^{-10} M NaOH solution is nearest to 7.

9. **(b)** (i) $\underset{0.1\,M}{HCl} \longrightarrow \underset{0.1\,M}{H^+} + Cl^-$

$\therefore [H^+] = 0.1$ M

$pH = -\log[H^+] = -\log 0.1 = 1$

(ii) NaCl is a salt of strong acid and strong base so it is not hydrolysed and hence its pH is 7.

(iii) $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

$\therefore$ The solution is acidic and pH is less than that of 0.1 M HCl.

(iv) $NaCN + H_2O \rightleftharpoons NaOH + HCN$

$\therefore$ The solution is basic and pH is more than that of 0.1 M HCl.

$\therefore$ Correct order for increase in pH is

$HCl < NH_4Cl < NaCl < NaCN$.

10. **(c)** $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

Given concentration of $H_2SO_4 = 0.005$ M

$\therefore$ $[H^+] = 0.005 \times 2 = 0.01 = 10^{-2}$

$pH = -\log[H^+] = -\log 10^{-2} = 2$

11. **(a)** $pOH = -\log[OH^-]$

pH + pOH = 14

For 10^{-4} KOH, $[OH^-] = 10^{-4}$

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

pH = 14 – pOH = 10

12. **(b)** According to Arrhenius, acids are those substances which give proton in aqueous solution, hence gaseous HCl is not an Arrhenius acid.

13. **(a)** $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x \times x}{0.1}$$

or $1.8 \times 10^{-5} = \dfrac{x^2}{0.1}$

$x^2 = 1.8 \times 10^{-6}$

$x = 1.35 \times 10^{-3}$

Thus at equilibrium, $[OH^-] = 1.35 \times 10^{-3}$

$pOH = -\log(1.35 \times 10^{-3}) = 2.87$

$\therefore$ pH = 14.00 – 2.87 = 11.13

14. **(d)** Lewis acids are electron pair acceptor whereas Bronsted acids are proton donor.

$$\underset{\text{Lewis acid}}{SO_3} + :\ddot{\underset{\cdot\cdot}{O}}:^{2-} \longrightarrow SO_4^{2-}$$

15. **(a)** The neutral water has $[OH^-] = 1 \times 10^{-7}$ M

By adding 10^{-8} M NaOH, a concentration of 10^{-8} M OH^- has increased in solution.

Thus, total $[OH^-] = 10^{-8} + 10^{-7} = 10^{-8} + 10 \times 10^{-8}$

$= 11 \times 10^{-8}$

$pOH = -\log 11 \times 10^{-8} = 6.9586$

pH = 14 – 6.9586 = 7.04

16. **(b)** Concentration $(C_1) = 0.5$ M, $V_1 = \dfrac{100}{1000}$

Concentration $(C_2) = 0.4$ M

$V_2 = 0.1$ L

$n_1(\text{mole}) = C_1 \times V_1$

$= 0.5 \times 0.1 = 0.05$

$n_2(\text{mole}) = C_2 \times V_2$

$= 0.4 \times 0.1 = 0.04$

$\therefore$ $n_3 = (n_2 - n_1)$ [for SA & SB]

= 0.05 – 0.04

$n_3 = 0.01$

$\therefore$ Final volume after adding water

= 200 + 800 = 1000 mL = 1 L

Final concentration $= \dfrac{0.01}{1} = 0.01$ mol / L

$\therefore$ $pH = -\log H^+$

$= -\log[10^{-2}]$

pH = 2.

17. **(c)** $O \underset{\leftarrow}{=} C \underset{\rightarrow}{=} O$ e^- deficiency due to attraction of more electronegative atom oxygen.
$AlCl_3$ electron deficient Al
Ag^+ electron deficient
$SnCl_4$, Sn electron deficient
Thus 4 species act as Lewis acid.

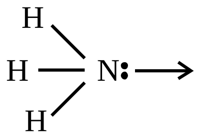
18. (a) $pH = pK_a + \log\frac{[salt]}{[Acid]}$

$[Acid] = [CH_3COOH] = \frac{10 \times 1}{100} = 0.1\text{ M}$

$[Salt] = [CH_3COO^-] = \frac{20 \times 0.5}{100} = 0.1\text{ M}$

$\Rightarrow \quad pH = 4.76 + \log\frac{0.1}{0.1} = 4.76$

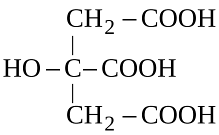
19. **(a)**



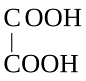
can donate this e^- pair.

20. **(c)**

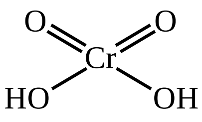
Citric acid:



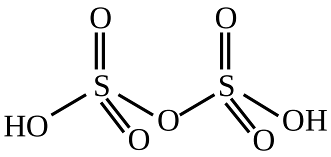
Oxalic acid



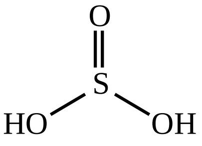
Chromic acid



Pyrosulfuric acid:



Sulfurous acid



21. **(a)** 118% oleum means 118 g f H_2SO_4 is obtained when we add 18 g of water in 100 g of oleum sample.

$2\,NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

2 moles of NaOH neutralise 1 mole of H_2SO_4

Moles of NaOH required to $= 2 \times \frac{118}{98}$

Complete neutralisation $= 2.4$ mol

22. **(d)** pH of water at 25°C is 7 as the dissociation of water generates 10^{-7}(M) of H^+ and OH^- each. As the temperature increases the dissociation of water increases. Therefore, the concentration of H^+ becomes more than 10^{-7} M. Hence, pH of the solution becomes < 7.0.

23. **(d)** The overall ionisation constants (K) will be product of ionisation constants of three steps, i.e.

$$K = K_1 \times K_2 \times K_3$$

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-; K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \quad \text{...(i)}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}; K_2 = \frac{[H^+][HPO_4^-]}{[H_2PO_4^-]} \quad \text{...(ii)}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}; K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \quad \text{...(iii)}$$

Adding Eqs. (i), (ii) and (iii), we get

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-} \quad \text{...(iv)}$$

$$K_1 \times K_2 \times K_3 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \times \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \times \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$K_1 \times K_2 \times K_3 = \frac{[H^+]^3[PO_4^{3-}]}{[H_3PO_4]}$$

The above expression is the ionisation constant for overall reaction (iv).

24. **(a)** Order of acidic strength is: $HClO_4 > HClO_3 > HClO_2$
Thus, order of basic strength is: $ClO^-_2 > ClO^-_3 > ClO^-_4$

25. **(c)** Ammonium chloride NH_4Cl is a salt of weak base (NH_3) and strong acid (HCl). Hence, it is acidic in nature, i.e., pH < 7.

26. **(d)** Given $K_b = 1.0 \times 10^{-12}$
$[BOH] = 0.01\text{ M}; \; [OH^-] = ?$

$$\begin{array}{cccccc} & BOH & \rightleftharpoons & B^+ & + & OH^- \\ t=0 & c & & 0 & & 0 \\ t_{eq} & C(1-x) & & Cx & & Cx \end{array}$$

$$K_b = \frac{C^2x^2}{C(1-x)} = \frac{Cx^2}{(1-x)} \Rightarrow 1.0 \times 10^{-12} = \frac{0.01x^2}{(1-x)}$$

On calculation, we get, $x = 1.0 \times 10^{-5}$
Now, $[OH^-] = Cx = 0.01 \times 10^{-5} = 1 \times 10^{-7}\text{mol L}^{-1}$

27. **(b)** $[H_3O]^+$ for a solution having pH = 3 is given by
$[H_3O]^+ = 1 \times 10^{-3}$ moles/litre $\quad [\because \; [H_3O]^+ = 10^{-pH}]$
Similarly for solution having pH = 4,
$[H_3O]^+ = 1 \times 10^{-4}$ moles/ litre and for pH = 5
$[H_3O^+] = 1 \times 10^{-5}$ moles/ litre
Let the volume of each solution in mixture be IL, then total volume of mixture solution L = (1 + 1 + 1) L = 3L
Total $[H_3O]^+$ ion present in mixture solution $= (10^{-3} + 10^{-4} + 10^{-5})$ moles

Then $[H_3O]^+$ ion concentration of mixture solution

$$= \frac{10^{-3}+10^{-4}+10^{-5}}{3}\,M = \frac{0.00111}{3}\,M$$

$= 0.00037\,M = 3.7 \times 10^{-4}\,M.$

28. **(a)** K_w at 25°C $= 1 \times 10^{-14}$

At 25°C

$K_w = [H^+][OH^-] = 10^{-14}$

At 100°C (given)

$K_w = [H^+][OH^-] = 55 \times 10^{-14}$

$\because$ for a neutral solution

$[H^+] = [OH^-]$

$\therefore$ $[H^+]^2 = 55 \times 10^{-14}$

or $[H^+] = (55 \times 10^{-14})^{1/2}$

$\because$ $pH = -\log[H^+]$

On taking log on both side

$-\log[H^+] = -\log(55 \times 10^{-14})^{1/2}$

$$pH = -\frac{1}{2}\log 55 + 7\log 10$$

$pH = -0.87 + 7 = 6.13$

29. **(c)** Higher the value of K_a lower will be the value of pK_a *i.e.*, higher will be the acidic nature. Further since, CN^-, F^- and NO_2^- are conjugate base of the acids HCN, HF and HNO_2 respectively hence, the correct order of base strength will be $F^- < NO_2^- < CN^-$

($\because$ stronger the acid weaker will be its conjugate base)

30. **(d)** As, molarity, $= \dfrac{\text{wt. of solute per litre of solution}}{\text{Mol. wt. of solute}}$

Molarity of $H_2O = \dfrac{1000}{18}$ mole/litre

$$\underset{c(1-\alpha)}{H_2O} \rightleftharpoons \underset{c\alpha}{H^+} + \underset{c\alpha}{OH^-}$$

Thus, $K_a = \dfrac{c\alpha^2}{1-\alpha} = c\alpha^2 = 1.8 \times 10^{-14}$

31. **(c)** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

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

Given that,

$[CH_3COO^-] = [H^+] = 3.4 \times 10^{-4}$ M

K_a for $CH_3COOH = 1.7 \times 10^{-5}$

CH_3COOH is weak acid, so in it $[CH_3COOH]$ is equal to initial concentration. Hence

$$1.7 \times 10^{-5} = \frac{(3.4\times10^{-4})(3.4\times10^{-4})}{[CH_3COOH]}$$

$$[CH_3COOH] = \frac{3.4\times10^{-4}\times3.4\times10^{-4}}{1.7\times10^{-5}} = 6.8\times10^{-3}M$$

32. **(c)** Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$;

$K_{a_1}, = 1.5 \times 10^{-5}$ ....(i)

$HCN \rightleftharpoons H^+ + CN^-$; $K_{a_2} = 4.5 \times 10^{-10}$

or $H^+ + CN^- \rightleftharpoons HCN$;

$$K'_{a_2} = \frac{1}{K_{a_2}} = \frac{1}{4.5\times10^{-10}} \quad \text{...(ii)}$$

$\therefore$ From (i) and (ii), we find that the equilibrium constant (K_a) for the reaction,

$CN^- + CH_3COOH \rightleftharpoons CH_3COO^- + HCN$, is

$$K_a = K_{a_1} \times K'_{a_2} = \frac{1.5\times10^{-5}}{4.5\times10^{-10}}$$

$$= \frac{1}{3}\times10^5 = 3.33\times10^4$$

33. **(c)** In aqueous solution BA(salt) hydrolyses to give

$$BA + H_2O \rightleftharpoons \underset{\text{Base}}{BOH} + \underset{\text{acid}}{HA}$$

Now pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pKa - \frac{1}{2}pK_b$$

substituting given values, we get

$$pH = \frac{1}{2}(14 + 4.80 - 4.78) = 7.01$$

34. **(b)** Given $[NH_3] = 0.3$ M, $[NH_4^+] = 0.2$ M,

$K_b = 1.8 \times 10^{-5}$.

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$[pK_b = -\log K_b;\ pK_b = -\log 1.8 \times 10^{-5}]$

$\therefore$ $pK_b = 4.74$

$$pOH = 4.74 + \log\frac{0.2}{0.3} = 4.74 + 0.3010 - 0.4771 = 4.56$$

$pH = 14 - 4.56 = 9.43$

35. **(d)** $pH = pK_a + \log\left[\dfrac{\text{Salt}}{\text{Acid}}\right]$

$$\log[H^+] = \log K_a - \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$$

$$\log[H^+] = \log K_a + \log\left[\frac{\text{Acid}}{\text{Salt}}\right]$$

$$[H^+] = K_a\left[\frac{\text{Acid}}{\text{Salt}}\right] = 1.8 \times 10^{-5} \times \frac{0.1}{0.2} = 9 \times 10^{-6}$$

36. **(b)** $$[H^+] = \frac{\left(n_{H^+}\right)_{HCl} + \left(n_{H^+}\right)_{H_2SO_4}}{\text{Total volume}}$$

$$= \frac{\left(M_{HCl} \times n_{factor,HCl} \times V_{HCl}\right) + M_{H_2SO_4} \times n_{f_{H_2SO_4}} \times V_{H_2SO_4}}{600}$$

$$[H^+] = \frac{(0.01 \times 1 \times 200) + (0.01 \times 2 \times 400)}{600}$$

$$= \frac{2+8}{600} = \frac{10}{600} = \frac{1}{60}$$

$$pH = -\log\left[\frac{1}{60}\right] = 1.78$$

37. **(a)** For an acid,

pH of an acid solution will be lower as the solution is more concentrated.

$pH = -\log[H^+]$

$$M_a = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

$$= \frac{2 \times 10^{-2} \times 10^{-2} + 2 \times 10^{-2} \times 2 \times 10^{-2}}{4 \times 10^{-2}} = 1.5 \times 10^{-2}$$

$$M_b = \frac{2 \times 10^{-2} \times 10^{-2} + 2 \times 10^{-2} \times 5 \times 10^{-3}}{4 \times 10^{-2}} = 0.75 \times 10^{-2}$$

$$M_c = \frac{2 \times 10^{-2} \times 10^{-2} + 2 \times 10^{-2} \times 1 \times 10^{-2}}{4 \times 10^{-2}}$$

$M_c = 1 \times 10^{-2}$

$$M_d = \frac{2 \times 10^{-2} \times 10^{-2} + 4 \times 10^{-2} \times 5 \times 10^{-3}}{6 \times 10^{-2}}$$

$$= \frac{4 \times 10^{-4}}{6 \times 10^{-2}}$$

$M_d = 0.66 \times 10^{-2}$

Order of concentration : $M_a > M_c > M_b > M_d$

Order of pH :- $M_d > M_b > M_c > M_a$

$\therefore$ Ma have the lowest pH.

38. **(c)** (a) NH_4Cl gives acidic solution in water due to cationic hydrolysis.

(b) CH_3COONa gives basic solution due to anionic hydrolysis.

(d) NH_4OH is a weak base.

39. **(c)** HCl + NH_4Cl. HCl is strong acid hence not used in buffer.

40. **(a)** $$\underset{}{Ag_2SO_4} \longrightarrow \underset{2x}{2Ag^+} + \underset{x}{SO_4^{2-}}$$

Moles after dissociation

$K_{sp} = [Ag^+]^2\,[SO_4^{2-}] = (2x)^2 \times x = 4x^3$

Given solubility $= x = 2.5 \times 10^{-2}$ mole/litre

$\therefore \quad K_{sp} = 4 \times (2.5 \times 10^{-2})^3$

$= 4 \times 15.6 \times 10^{-6} = 62.5 \times 10^{-6}$

41. **(c)** Let solubility of $PbCl_2 = x$ moles/L

$$\text{Moles} \quad \underset{x}{PbCl_2} \rightleftharpoons \underset{x}{Pb^{2+}} + \underset{2x}{2Cl^-}$$

$K_{sp} = [Pb^{2+}]\,[Cl^-]^2$

$\therefore \quad 1.7 \times 10^{-5} = (x)\,(2x)^2$

or $\quad 1.7 \times 10^{-5} = 4x^3$

$$\therefore \quad x = \sqrt[3]{\frac{1.7 \times 10^{-5}}{4}} = 1.62 \times 10^{-2}$$

42. **(b)** Let solubility of $BaCl_2 = x$ moles/L

$$\text{No. of mole} \quad \underset{x}{BaCl_2} \rightleftharpoons \underset{x}{Ba^{2+}} + \underset{2x}{2Cl^-}$$

$K_{sp} = [Ba^{2+}]\,[Cl^-]^2$

$= (x) \times (2x)^2 = 4x^3$

$\therefore \quad 4 \times 10^{-9} = 4x^3$

$$\text{or,} \quad x = \sqrt[3]{\frac{4 \times 10^{-9}}{4}} = 1 \times 10^{-3}$$

43. **(b)** Dissociation of CH_3COOH is suppressed by the addition of sodium acetate (CH_3COONa) due to common ion (CH_3COO^-) effect. The $[H^+]$ decreases raising the pH of the acid solution.

Note : After the addition of CH_3COONa to CH_3COOH, a buffer solution is formed which has reserved pH value.

44. **(d)** $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$\therefore \; K_{sp} = [Ba^{2+}]\,[SO_4^{2-}] = s \times s = s^2$

$\therefore \; s = \sqrt{K_{sp}} = \sqrt{1.5 \times 10^{-9}}$

or, $s = 3.9 \times 10^{-5}$

45. **(d)** $$CaF_2 \rightleftharpoons \underset{s}{Ca^{2+}} + \underset{2s}{2F^-}$$

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

$$K_{sp} = 4 \times (2.3 \times 10^{-4})^3$$

$$= 4.9 \times 10^{-11} (\text{mol dm}^{-3})^3$$

46. **(d)** $BA_2 \rightarrow \underset{x}{B} + \underset{2x}{2A}$

Solubility product = $[x]\ [2x]^2 = 4x^3$

$4 \times 10^{-12} = 4x^3$ or $x = \sqrt[3]{\frac{4\times10^{-12}}{4}}$

$\therefore\ x = 10^{-4}$

47. **(c)** Weak acid + its conjugate base $\longrightarrow$ acid buffer

Weak base + its conjugate acid $\longrightarrow$ basic buffer

A buffer solution resist the change in pH on adding a drop of acid or a base.

48. **(c)** Since for sparingly soluble salts, solubility (s) will be less than one. Therefore as the powers of s increases in K_{sp} expression, magnitude of K_{sp} will become smaller.

49. **(c)** $K_{sp}\ (AgBr) < K_{sp}\ (AgCl)$

Therefore, AgBr will precipitate first and at that time all Cl^- will be present.

50. **(c)** $K_a \times K_b = K_w$

$\therefore\ K_a$ for HX $= \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$

$pK_a = 9$

$pH = pK_a + \log \frac{[X^-]}{[HX]}$

$pH = 9 + \log \frac{0.1}{0.3} = 9 - \log 3$

51. **(d)** $PbCrO_4 \longrightarrow \underset{S}{Pb^{2+}} + \underset{S}{CrO_4^{2-}}$

Given $K_{sp} = 1 \times 10^{-16}$

$\therefore\ K_{sp} = [Pb^{2+}][CrO_4^{2-}]$

$1 \times 10^{-16} = (S) \times (S)$

$1 \times 10^{-16} = S^2 \Rightarrow S = 1 \times 10^{-8}$

52. **(d)** It is given that $pH + pK_b = 13$

We know,

$pOH = pK_b - \log \frac{[Base]}{[Salt]}$

$14 = pH + pK_b - \log \frac{[Base]}{[Salt]}$

$14 = 13 - \log \frac{[Base]}{[Salt]}$

$-1 = \log \frac{[Base]}{[Salt]}$

$\frac{[Base]}{[Salt]} = 0.1$

53. **(b)** For Bi_2S_3,

$K_{sp} = (2s)^2.(3s)^3 = 4s^2.\ 27s^3 = 108s^5$

where s = solubility

$\therefore\ s = \sqrt[5]{\frac{K_{sp}}{108}}$

For MnS, $K_{sp} = s^2$

$\therefore\ s = \sqrt{K_{sp}} = \sqrt{7\times10^{-16}}$

For CuS, $K_{sp} = s^2$

$\therefore\ s = \sqrt{K_{sp}} = \sqrt{8\times10^{-37}}$

For Ag_2S, $K_{sp} = 4s^3$

$\therefore\ s = \sqrt[3]{\frac{K_{sp}}{4}}$

Thus MnS has maximum solubility.

54. **(a)** Let solubility of AgCl = x moles/L

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

	$AgCl$	Ag^+	Cl^-
before dissociation	x	0	0
after dissociation		x	x

$NaCl \longrightarrow Na^+ + Cl^-$

Connection of $Cl^- = 0.2$

Total $[Cl^-] = x + 0.2$

$K_{sp}(AgCl) = [Ag^+][Cl^-] = (x)(x + 0.2) = x^2 + 0.2x$

$\therefore\ K_{sp} \simeq 0.2x \qquad (\because\ x^2 << 1)$

$\therefore\ 1.2 \times 10^{-10} = 0.2x$

$\therefore\ x = 6 \times 10^{-10}\ M$

55. **(d)** Total volume = 100 mL

$[acid] = 10\ mL \times \frac{1.0}{100} = 0.1$

$[salt] = 20\ mL \times \frac{0.5}{100} = 0.1$

pH of acidic buffer = $pK_a + \log \frac{[salt]}{[acid]}$

$= 4.76 + \log \frac{0.1}{0.1} = 4.76$

56. **(c)** Precipitation will occur when, ionic product > K_{sp}.

Among the given choices, the ionic product of 10^{-4} M $AgNO_3$ and 10^{-4} M KCl is 25×10^{-10} which exceeds the K_{sp} of AgCl which is shown below :

$AgNO_3$ ionizes completely in the solution as

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

$$[Ag^+] = [AgNO_3] = 10^{-4}\,M$$

KCl ionizes completely in the solution of

$$KCl \longrightarrow K^+ + Cl^-$$

$\therefore$ $[Cl^-] = [KCl] = 10^{-4}M$

Since equal volumes of two solutions are mixed together, therefore, the concentration of Ag^+ ions and Cl^- ions after mixing will be

$$[Ag^+] = \frac{10^{-4}}{2}M$$

and $[Cl^-] = \dfrac{10^{-4}}{2}M$

$\therefore$ Ionic product of AgCl $= \dfrac{10^{-4}}{2} \times \dfrac{10^{-4}}{2} = 25 \times 10^{-10}$

57. **(a)** The pH of mixture is due to the HCl only, because CH_3COOH is negligibly ionised due to common ion effect. Thus,

$[H^+] = 0.05\,M = 5 \times 10^{-2}\,M$

$pH = -\log(5 \times 10^{-2}) = -[\log 5 + \log 10^{-2}]$

$pH = 1.3$

58. **(d)** $Ba(OH)_2(s) \longrightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$

pH = 12 or pOH = 2

$[OH^-] = 10^{-2}\,M$

$$\underset{}{Ba(OH)_2} \longrightarrow \underset{0.5\times10^{-2}}{Ba^{2+}} + \underset{10^{-2}}{2\,OH^-}$$

[$\therefore$ Concentration of Ba^{2+} is half of OH^-]

$K_{sp} = [Ba^{2+}]\,[OH^-]^2$

$= [0.5 \times 10^{-2}]\,[1 \times 10^{-2}]^2$

$= 0.5 \times 10^{-6} = 5 \times 10^{-7}\ M^3$

59. **(d)** $K_b = 10^{-10}$; $K_a = 10^{-4}$ or $pK_a = 4$

For the buffer solution containing equal concentration of B^- and HB

$pH = pK_a + \log 1$

$pH = pK_a = 4$

60. **(a)** $\underset{1\times10^{-4}M}{Na_2CO_3} \longrightarrow \underset{1\times10^{-4}M}{2Na^+} + \underset{1\times10^{-4}M}{CO_3^{\,2-}}$

$K_{sp(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$

$$[Ba^{2+}] = \frac{5.1\times10^{-9}}{1\times10^{-4}} = 5.1\times10^{-5}M$$

61. **(b)** K_{sp} values determine solubility. Based on the K_{sp} values and salt analysis cation identification, the order of K_{sp} value is:

$HgS < PbS < AgBr < Ca(OH)_2$

K_{sp} values

$HgS \to 4 \times 10^{-53}$

$PbS \to 8 \times 10^{-28}$

$AgBr \to 5 \times 10^{-13}$

$Ca(OH)_2 \to 5.5 \times 10^{-6}$

Lower K_{sp} means lower solubility.

62. **(a)** At eq: $Cr(OH)_3(s) \rightleftharpoons \underset{s}{Cr^{+3}}(aq) + \underset{3s}{3OH^-}(aq)$

$K_{sp} = (s).(3s)^3 = 27s^4$

$27s^4 = 1.6 \times 10^{-30}$; $s = \left(\dfrac{1.6}{27}\times10^{-30}\right)^{1/4}$

63. **(a)** $Zr_3(PO_4)_4(s) \rightleftharpoons 3Zr^{+4}(aq) + 4PO_4^{-3}(aq)$

– 3s 4s

$K_{sp} = (3s)^3(4s)^4 = 27s^3 \times 256\,s^4 = 6912\,s^7$

$$s = \left(\frac{K_{sp}}{6912}\right)^{\frac{1}{7}}$$

64. **(b)** Let *s* be the solubility of $Ca(OH)_2$ in water

$$Ca(OH)_2 \rightleftharpoons \underset{s}{Ca^{2+}} + \underset{2s}{2OH^-}$$

$K_{sp} = [Ca^{2+}][OH^-]^2 = s \times (2s)^2$

$\Rightarrow 5.5\times10^{-6} = 4s^3 \Rightarrow s^3 = \dfrac{5.5}{4}\times10^{-6}$

$$s = \left[\frac{5.5}{4}\right]^{\frac{1}{3}} \times 10^{-2} = 1.11\times10^{-2}$$

65. **(c)** Let the solubility of $Al(OH)_3$ in 0.2M NaOH solution be s.

Then, $Al(OH)_3 \rightleftharpoons \underset{s}{Al^{3+}} + \underset{3s}{3OH^-}$

and $\underset{0.2M}{NaOH} \rightleftharpoons \underset{0.2M}{Na^+} + \underset{0.2M}{OH^-}$

$[Al^{3+}] = s$ and $[OH^-] = 3s + 0.2 \approx 0.2$

$K_{sp} = 2.4 \times 10^{-24} = [Al^{3+}]\,[OH]^3$

$2.4 \times 10^{-24} = s(0.2)^3$

$$s = \frac{2.4\times10^{-24}}{8\times10^3} = 3\times10^{-22}\,mol/L$$

66. **(a)** When ionic product, i.e., the product of the concentration of ions in the solution exceeds the value of solubility product, formation of precitpiate occurs.

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

Ionic product=$[Ca^{2+}]\,[F^-]^2=(1\times10^{-2})$

$(1\times10^{-6})=1\times10^{-8}$

In this case,

Ionic product (1×10^{-8}) > solubility product (1.7×10^{-10})

67. **(a)** $\underset{x}{Mg(OH)_2} \rightarrow \underset{2x}{[Mg^{2+}]} + 2[OH^-]$

$K_{sp} = [Mg]\,[OH]^2 = [x][2x]^2 = x.4x^2 = 4x^3.$

68. **(d)** $PbCl_2 \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2Cl^-}$

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

$4s^3 = 3.2 \times 10^{-8}$

$s = 2 \times 10^{-3}$

Molecular weight of $PbCl_2 = 278$

Weight of $PbCl_2 = 0.1$ g

Mole of $PbCl_2 = \dfrac{0.1}{278} = 3.6\times10^{-4}$

Let 'v' is the volume of water.

$\therefore$ Solubility $(s) = \dfrac{3.6\times10^{-4}}{v}$

$\therefore\ \dfrac{3.6\times10^{-4}}{v} = 2\times10^{-3}$

or, $v = \dfrac{3.6\times10^{-4}}{2\times10^{-3}}$

$v_{ml} = 1.8 \times 10^{-1} \times 10^3$ ml = 180 ml.

69. **(d)** CO_3^{2-} from $MgCO_3$

$K_{sp} = [CO_3^{2-}]\,[Mg^{2+}]$

$1.6\times 10^{-6} = [CO_3^{2-}]\,[3.2 \times 10^{-5}]$

$[CO_3^{2-}] = \dfrac{1.6\times10^{-6}}{3.2\times10^{-5}} = 5\times10^{-2}$

CO_3^{2-} from $MgCO_3$ suppress the dissociation of Ag_2CO_3. Applying common ion effect

$K_{sp\ Ag_2CO_3} = [CO_3^{2-}][Ag^+]^2$

$[Ag^+] = \sqrt{\dfrac{8\times10^{-12}}{5\times10^{-2}}} = \sqrt{1.6}\times10^{-5}.$

70. **(b)** Volume of HCl (V_1) = 200 ml = 0.2 L

Concentration of HCl = 10^{-2} M

Moles of HCl = 2×10^{-3}

Volume of NaOH (V_2) = 300 ml = 0.3 L

pH of NaOH = 12

pOH of NaOH = 14 – 12 = 2

Concentration of NaOH = 10^{-2} M

Moles of NaOH = 3×10^{-3}

Excess moles of NaOH = $3 \times 10^{-3} - 2 \times 10^{-3}$

= 1×10^{-3} moles

Concentration of excess $OH^- = \dfrac{10^{-3}}{1\,L} = 10^{-3}$ M

$pOH = -\log[OH^-] = 3$

pH = 14 – 3 = 11.

71. **(b)** $KOH \rightarrow \underset{0.1}{K^+} + \underset{0.1}{OH^-}$

$Cd(OH)_2 \rightleftharpoons \underset{S}{Cd^{2+}} + \underset{2S}{2\,OH^-}$

Solubility product $k_{sp} = [S]^1\,[2S + 0.1]^2$

$k_{sp} = [S]^1\,[0.1]^2\ (\because 0.1 >>> 2S)$

$2.5 \times 10^{-14} = [S] \times 0.01$

$[S] = 2.5 \times 10^{-12}$

$[S] = 25 \times 10^{-13} = x \times 10^{-y}$

So, x = 25, y = 13.

72. **(c)** A buffer solution is formed when we have a mixture of a weak acid or base and its corresponding salt with a strong base or acid.

A 1 : 1 mixture of NaOH and CH_3COOH will have unequal concentrations of CH_3COOH and CH_3COONa so it will not act as a buffer.

73. **(b)** For H_2SO_4

$100 \times 0.5 = 50$ m mol $= 50 \times 98 \times 10^{-3}$ g

$\underset{2\times40g}{2NaOH} + \underset{98g}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$

$98g \equiv 2 \times 40g$

$50 \times 98 \times 10^{-3} \equiv \dfrac{2\times40}{98} \times 50 \times 98 \times 10^{-3} = x = 4g$ NaOH

Mass of Na_2SO_4 = 100 – 4g = 96g.

74. **(a)** If [Conjugate acid] = [Base]

According to Henderson Hassel balch equation for buffer solution.

$pOH = pK_b + \log \dfrac{[\text{Conjugate acid}]}{[\text{Base}]}$

Then, $[pOH = pK_b]$

So, pOH of the buffer solution is same as pK_b of base.

75. **(c)** Concentration of salt (NH_4Cl) = 0.01 M

Concentration of base (NH_4OH) = 0.1 M

$pK_b = 5$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \Rightarrow pOH = 5 + \log \frac{0.01}{0.1} = 4$$

$= pH = 14 - pOH = 14 - 4 = 10$

76. **(a)** Given, K_b of $NH_4OH = 5.00 \times 10^{-10}$

$K_w = 10^{-14}$ at 298 K

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{5 \times 10^{-10}} = 2 \times 10^{-5}$$

77. **(c)** $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

Given; $K_{sp} = 1.6 \times 10^{-5}$

$$[Pb^{2+}] = \frac{300 \times 0.134}{400} = 0.1005;\ [Cl^-]$$

$$= \frac{100 \times 0.4}{400} = 0.1$$

$Q = [Pb^{2+}][Cl^-]^2 = 0.1005 \times (0.1)^2 = 1.005 \times 10^{-3}$

Therefore, $Q > K_{sp}$

78. **(b)** $Cr(OH)_3 \rightarrow \underset{s}{Cr^{3+}} + \underset{3s}{3OH^-}$

$K_{sp} = s \cdot (3s)^3$

$$\Rightarrow 6 \times 10^{-31} = 27 \cdot s^4;\ s = \left(\frac{6}{27} \times 10^{-31}\right)^{1/4}$$

$$[OH^-] = 3s = 3 \times \left(\frac{6}{27} \times 10^{-31}\right)^{1/4}$$

$= (18 \times 10^{-31})^{1/4}$ M

79. **(b)** From the given curve,

if [X] = 1 mM then [Y] = 2 mM $\therefore$ Salt is XY_2

$K_{sp} = [X][Y]^2 = (10^{-3})(2 \times 10^{-3})^2 = 4 \times 10^{-9}\ M^3$

80. **(d)** $Cd(OH)_2 \rightleftharpoons \underset{s}{Cd^{2+}} + \underset{2s}{2OH^-}$

At equilibrium, $K_{sp} = s(2s)^2 = 4s^3$

$\Rightarrow \quad K_{sp} = 4 \times (1.84 \times 10^{-5})^3$

Solubility in buffer solution having pH = 12

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

$$Cd(OH)_2 \rightleftharpoons \underset{s'}{Cd^{2+}} + \underset{2s+10^{-2} \approx 10^{-2}}{2OH^-}$$

$\therefore \quad K_{sp} = 4 \times (1.84 \times 10^{-5})^3 = s'(10^{-2})^2$

$$\Rightarrow s' = \frac{24.9 \times 10^{-15}}{10^{-4}} = 2.49 \times 10^{-10}\ M$$

81. **(d)** pH of acidic buffer $= -\log K_a + \log\left[\frac{salt}{acid}\right]$

$\therefore$ pH of acidic buffer depends upon value of K_a.

82. **(c)** For Ag_2CrO_4;

$K_{sp} = [Ag^+]^2\left[CrO_4^{-2}\right] = 1.1 \times 10^{-12}$

$$[Ag^+] = \sqrt{\frac{1.1 \times 10^{-12}}{\left[CrO_4^{-2}\right]}}$$

For AgCl;

$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{[Cl^-]}$$

For AgBr;

$K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13}$

$$[Ag^+] = \frac{5.3 \times 10^{-13}}{[Br^-]}$$

For AgI;

$K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$

$$[Ag^+] = \frac{8.3 \times 10^{-17}}{[I^-]}$$

If we take $\left[CrO_4^{-2}\right] = [Cl^-] = [Br^-] = [I^-] = 1$

then maximum $[Ag^+]$ will be required in case of Ag_2CrO_4.

83. **(a)** $AgCN \rightleftharpoons Ag^+ + CN^-$

Solubility of AgCN is x.

pH = 3 $\Rightarrow$ $[H^+] = 10^{-3}$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \Rightarrow \frac{[10^{-3}][CN^-]}{[HCN]} = 6.2 \times 10^{-10}$$

$$\Rightarrow \frac{[CN^-]}{[HCN]} = 6.2 \times 10^{-7}$$

Each CN– hydrolyses to give one HCN as:

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

HCN is a weak acid, thus, $[HCN] >> [CN^-]$

$x = [Ag^+] = [CN^-] + [HCN]$

$\Rightarrow \quad x = [Ag^+] \approx [HCN] \Rightarrow [CN^-] = x \times 6.2 \times 10^{-7}$

$K_{sp}(AgCN) = [Ag^+][CN^-]$

$\Rightarrow \quad 2.2 \times 10^{-16} = (x)(x \times 6.2 \times 10^{-7})$

$\Rightarrow \quad x^2 = 3.55 \times 10^{-10} \Rightarrow \quad x = 1.88 \times 10^{-5}$

84. **(a)** $K_{sp}\ MX_2 = 5 \times 10^{-13}$

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

$MX = 1.6 \times 10^{-11} \Rightarrow K_{sp} = s \times s = s^2$

Solubility $MX_2 = \sqrt[3]{\frac{K_{sp}}{4}}$

Solubility MX = $\sqrt{K_{sp}}$

$$\text{Ratio of solubility} = \frac{\frac{\sqrt[3]{5\times10^{-13}}}{4}}{\sqrt{1.6\times10^{-11}}}$$

$$= \frac{\sqrt[3]{1.25\times10^{-13}}}{4\times10^{-6}} = \frac{\sqrt[3]{125\times10^{-15}}}{4\times10^{-6}}$$

$$= \frac{5\times10^{-5}}{4\times10^{-6}} = 1.25\times10 = 12.5$$

85. **(b)** $AB_2(s) \rightleftharpoons A^{+2}(aq) + 2B^-(aq)$

$K_{sp} = [A^{+2}]\,[B^-]^2$

$= 1.2 \times 10^{-4} \times (2.4 \times 10^{-4})^2$

$= 6.91 \times 10^{-12}\ M^3$

86. **(b)** $K_{sp} = 3.2 \times 10^{-5}$

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$

$K_{sp} = (x^x)(y^y)(S^{x+y})\ \begin{matrix} x = 1 \\ y = 2 \end{matrix}$

$K_{sp} = (1)(2)^2(S^{2+1}) = 4S^3$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt{\frac{3.2\times10^{-5}}{4}} = \sqrt[3]{8\times10^{-6}}$$

$= 2 \times 10^{-2}$ mol/dm^3

87. **(a)** Basic buffer is mixture of weak base and its salt with strong acid.

$NH_4OH + NH_4Cl \rightarrow NH_4OH$ is weak base.

NH_4Cl is salt of strong acid and weak base.

88. **(c)** Using Henderson's equation for an acidic buffer,

$$pH = pK_a + \log_{10}\left[\frac{\text{Salt}}{\text{Acid}}\right]$$

$$= 4.56 + \log_{10}\left[\frac{0.70}{0.35}\right] = 4.56 + \log 2$$

$= 4.56 + 0.3010 = 4.861$

89. **(c)** $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

$$S = \left(\frac{W\times1000}{M\times100}\right) = \frac{W\times10}{M}$$

$\therefore K_{sp} = [Ca^{2+}]\,[PO_4^{3-}]$

$= (3S)^3\,(2S)^2 = 108S^5$

$$= 108\times\left(\frac{W\times10}{M}\right)^5 = 108\times10^5\left(\frac{W}{M}\right)$$

$$= 1.08\times10^7\left(\frac{W}{M}\right)$$

$$K_{sp} = 10^7\left(\frac{W}{M}\right)^5$$

90. **(b)** $AgCl(s) \rightarrow Ag^+(aq.) + Cl^-(aq.)$

$$K_{sp} = S^2 = \left(\frac{1.43}{143.4}\times10^{-3}\right)^2 = 10^{-10} \quad -\log K_{sp} = 10$$

Exercise 3 : PREVIOUS YEARS MCQs

1. **(d)** $HCl + NaOH \rightarrow NaCl + H_2O$

Excess NaOH = 0.02 – 0.01 = 0.01 mol

$$[\bar{O}H] = \frac{0.01}{0.2} = 0.05\ M$$

pOH = –log(0.05) = 1.3

pH = 14 – 1.3 = 12.7

2. **(c)** $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

$= \frac{1}{2}(14 + 4 - 5) = 6.5$

3. **(b)** $pH = -\log[H^+]$

$[H^+] = 1 \times 10^{-4}$

pH = 4

4. **(a)** $pOH = -\log[\bar{O}H]$

pOH = –log(0.1)

pOH = 1

pH + pOH = 14

pH = 13

5. **(a)** $K_b = C\alpha^2 = (4.24 \times 10^{-2})^2 \times 0.01$

$= 17.9 \times 10^{-6} = 1.79 \times 10^{-5}$

6. **(b)** $\Delta[H^+] = 1000$

$\Delta pH = -\log \Delta[H^+] = -\log 10^3$

= –3; (–ve) sign indicates decrease in pH.

7. **(b)** $A_3B_2 \rightleftharpoons \underset{3s}{3A^{2+}}(aq) + \underset{2s}{2B^{3-}}(aq)$

$K_{sp} = (3s)^3(2s)^2 = 108s^5$

$$K_{sp}108\left(\frac{x}{M}\right)^5 \quad \left(\because \frac{x}{M} = s\right)$$

$$\text{(Given) } K_{sp} = a\left(\frac{x}{M}\right)^5$$

On comparing, a = 108

8. **(a)** NH_4F is formed from a weak base, ammonium hydroxide and a strong acid, hydrogen fluoride.

On dissolving in water, NH_4F undergoes hydrolysis to form more H^+ ions than OH^- ions.

As the aqueous solution of the salt is acidic. So, it turns blue litmus red.

9. **(b)** $CaF_2(s) \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2F^-}$

Considering the solubility of CaF_2 to be S mol dm^{-3}.

$K_{sp} = [Ca^{2+}][F^-]^2 = S \times (2S)^2$

$1.08 \times 10^{-7} = 4S^3$

$$S^3 = \frac{1.08 \times 10^{-7}}{4} = 0.27 \times 10^{-7}$$

$$S = \left(2.7 \times 10^{-8}\right)^{\frac{1}{8}} = \left(2.7 \times 10^{-9}\right)^{\frac{1}{3}}$$

$S = 3 \times 10^{-3}$ mol dm^{-3}

10. **(a)** $K_a = \alpha^2 C$

Percent of dissociation = 3%

Degree of dissociation (α) = 0.03 (Given)

$K_a = 1.8 \times 10^{-5}$

$$C = \frac{K_a}{\alpha^2}$$

$$C = \frac{1.8 \times 10^{-5}}{0.03 \times 0.03} = 0.02 \text{ M}$$

11. **(a)** $\underset{\text{Base}}{ClO_4^-} + \underset{\text{Acid}}{HCO_3^-} \rightarrow \underset{\text{Acid}}{HClO_4} + \underset{\text{Base}}{CO_3^{2-}}$

12. **(a)** $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

$[OH^-] = C = 0.01$ M

Now, $K_w = [H_3O^+][OH^-] = 10^{-14}$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{0.01} = 10^{-12} \text{ M}$$

13. **(a)** $\alpha = \dfrac{\text{Percent dissociation}}{100} = \dfrac{5}{100} = 0.05$

Now, $K_a = C\alpha^2 = (0.05)(0.05)^2 = 1.25 \times 10^{-4}$

14. **(c)** KOH being a strong electrolyte so it is completely dissociate in water.

$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

$[OH^-] = C = 0.002 \text{ M} = 2 \times 10^{-3}$ M

$pOH = -\log_{10}[OH^-] = -\log_{10}[2 \times 10^{-3}]$

$= -\log_{10}2 - \log_{10}[10^{-3}] = -0.3010 - (-3)$

$pOH = 3 - 0.3010 = 2.669$

Now, $pH + pOH = 14$

$pH = 14 - 2.669 = 11.3$

15. **(a)** CH_3COONa it is salt of strong base and weak acid. hence, it is a basic in nature and it turns red litmus to blue litmus.

16. **(a)** For PbI_2,

$PbI_2(s) \rightleftharpoons Pb^+(aq) + 2I^-(aq)$

$x = 1, y = 2$

$K_{sp} = (1)^1(2)^2(S^{1+2}) = 4S^3$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{7.0 \times 10^{-9}}{4}} = 1.21 \times 10^{-3} \text{ mol/L}$$

17. **(b)** 0.5 M sodium acetate and 5 M acetic acid form acidic buffer.

$$pH = pK_a + \log_{10}\left[\frac{\text{Salt}}{\text{Acid}}\right]$$

$$= 4.74 + \log\left[\frac{0.5}{5}\right] = 4.74 + \log\left[\frac{1}{10}\right]$$

$= 4.74 + (-1) = 3.74$

$pH = 3.74$

18. **(a)** $K_a = 1.8 \times 10^{-5}$, C = 0.045 M.

For monobasic acid,

$$K_a = C\alpha^2; \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.045}}$$

$$\alpha = \sqrt{4 \times 10^{-4}}$$

$$\alpha = 2 \times 10^{-2}$$

19. **(b)** Conjugate base is formed when a Bronsted-Lowry acid donates a proton.

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

Therefore, conjugate base of HCO_3^- is CO_3^{2-} and conjugate base of HSO_4^- is SO_4^{2-}.

20. **(c)** KNO_3 (Potassium nitrate) is a salt of strong base and strong acid. When KNO_3 is dissolved in water, it gives neutral solution. i.e., The pH of the solution is equal to 7.

21. **(a)** For a basic buffer solution,

$$pOH = pK_b + \log_{10}\left[\frac{\text{Salt}}{\text{Base}}\right]$$

$$6 = pK_b + \log_{10}\left[\frac{0.25}{0.1}\right] = 6 - [\log 5 - \log 2]$$

$= 6 - [0.699 - 0.301]$

$pK_b = 5.602$

22. **(b)** Strong acid have weak conjugate base.

Acidic strength :

$H{-}Cl > CH_3COOH > H_2O > R{-}OH$

Conjugate base strength :

$Cl^- < CH_3COO^- < \bar{O}H < RO^-$

23. **(b)** $K_a = 1.8 \times 10^{-5}$

$\alpha = 0.02$

For a weak mono basic acid, $K_a = C\alpha^2$

$$C = \frac{K_a}{\alpha^2} = \frac{1.8 \times 10^{-5}}{(0.02)^2}$$

$$= \frac{1.8 \times 10^{-5}}{4 \times 10^{-4}} = 4.5 \times 10^{-2} \text{ M}$$

24. **(d)** The equilibrium is established between ions and unionised molecules involves ions in aqueous solution.

25. **(b)** $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}} = \sqrt{\dfrac{3.14 \times 10^{-4}}{1.96 \times 10^{-5}}} = 4:1$

26. **(a)** $(M_1 \times V_1) = (M_2 \times V_2)$

$10^{-1} \times 1 = 10^{-2} \times V_2$

$V_2 = 10L$

Water added = 10 – 1 = 9 Litre = 9000 mL

4 Chemical Thermodynamics

Exercise 1 : WARM-UP
Topic-wise MCQs

1. **(b)** The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.

2. **(c)** Closed system can exchange energy but not matter with surroundings. Pressure cooker provides closed system.

3. **(b)** We can describe the state of a gas by quoting its pressure (*P*), volume (*V*), temperature (*T*), amount (*n*) etc.

4. **(c)** Enthalpy is a state function which depends on the initial and final state.

5. **(d)** The factor which affects the internal energy is:
   (i) Heat passes into or out.
   (ii) Work is done on or by the system.
   (iii) Matter enters or leaves the system.

6. **(a)** $\Delta E = \Delta Q - W$

   For adiabatic expansion, $\Delta Q = 0$

   $\Rightarrow \Delta E = -W$

   The negative sign shows decrease in internal energy, which is equal to the work done by the system on the surroundings.

7. **(c)** State Variable is an independent variable of a state function.

   Internal energy, volume and enthalpy are state variable.

8. **(d)** Mathematical expression of first law of thermodynamics $\Delta E = q + w$, ΔE is a state function, where ΔE = Internal energy

9. **(a)** $W = -P_{ext}(V_2 - V_1)$

   (Irreversible isothermal expansion)

   $= -2\,(0.25 - 0.1) = -2\,(0.15) = -0.3$ L bar

   $= -0.3 \times 100$ J $= -30$ J.

10. **(b)** The system is in isolated state.

    $\because$ For an adiabatic process, $q = 0$

    $\Delta U = q + w$

    $\therefore$ $\Delta U = w$

    $= -P\Delta V$

    $= -2.5 \text{ atm} \times (4.5 - 2.5) \text{ L}$

    $= -2.5 \times 2$ L-atm

    $= -5 \times 101.3$ J

    $= -506.5 \text{ J} \approx -505\text{J}$

11. **(b)** $n = 5$ mol

    $T = 300$ K

    $V_1 = 10$ L

    $V_2 = 20$ L

    Work done in isothermal condition.

    $$w_{rev} = -nRT\ln\frac{V_2}{V_1} = -5\times 8.3\times 300\ln\frac{20}{10} = -8630.38\text{ J}$$

12. **(a)** For free expansion : $w = -P_{ext}dV$

    $P_{ext} = 0$

    $w = 0$

    isothermal expansion, $\Delta U = 0$

    $\Delta U = q + w = q = -w = 0$

13. **(d)** Given equation is

    $H_2O(l) \rightarrow H_2O(g) : \Delta H = 41$

    $\Rightarrow$ From the relation : $\Delta H = \Delta U + \Delta n_g RT$

    $$\Rightarrow\quad 41\frac{\text{kJ}}{\text{mol}} = \Delta U + (1)\times\frac{8.3}{1000}\times 373$$

    $\Delta U = 41 - 3.0959 = 38$ kJ/mol

14. **(a)** $Fe + 2HCl \longrightarrow FeCl_2 + H_2$

    $$\text{No. of moles of Fe} = \frac{50}{55.85}\text{ moles}$$

    $$\text{No. of moles of } H_2 \text{ produced} = \frac{50}{55.85}\text{ moles}$$

    $$\text{Word done} = -P_{ext}\cdot\Delta V = -\Delta n_g RT$$

    $$= \frac{50}{55.85}\times 8.314\times 298 \approx 2218\text{ J}$$

15. **(d)** The difference between ΔH and ΔU is not usually significant for systems consisting of only solids or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved.

16. **(a)** Volume of 0.5 mole of steam at 1 atm pressure

    $$= \frac{nRT}{P} = \frac{0.5\times 0.0821\times 373}{1.0} = 15.3\text{ L}$$

Change in volume = vol. of steam – vol. of water

= 15.3 –negligible = 15.3 L

Work done by the system,

w = P_{ext} × volume change

= 1 × 15.3 = 15.3 litre-atm

= 15.3 × 101.3 J = 1549.89 J

'w' should be negative as the work has been done by the system on the surroundings.

w = –1549.89 J = –1.54 kJ.

17. **(c)** $\Delta U = nC_v\Delta T$

$5000 = 4 \times C_v (500 - 300)$

$C_v = 6.25\ JK^{-1}\ mol^{-1}$

18. **(a)** H = U + PV (By definition)

$\Delta H = \Delta U + \Delta(PV)$ at constant pressure

$\Delta H = \Delta U + P\Delta V$

19. **(b)** $\Delta n = -\frac{1}{2}$; $\Delta H = \Delta E - \frac{1}{2}RT$; $\Rightarrow \Delta E > \Delta H$

20. **(a)** Volume depends upon mass. Hence, it is an extensive property.

21. **(b)** 1 Calorie = 4.184 Joule

22. **(d)** $\frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$

23. **(b)** $\Delta H = \Delta E + P\Delta V$, for solid and liquid,

$\Delta V = 0$ or $\Delta H = \Delta E + \Delta n\, RT$, for solids and liquids $\Delta n = 0$.

24. **(d)** The magnitude of the heat capacity depends on the size, composition and nature of the system.

25. **(a)** $-W_{\text{irreversible}} = P_{ext}(V_2 - V_1)$

$= 10\text{ atm }(2L - 1L) = 10\text{ atm} - L$

$-W_{\text{reversible}} = 2.303\, nRT \log \frac{V_2}{V_1}$

$= 1 \times 2.303 \times 0.0821 \times 298\text{ atm–L/K/mol} \times \log\frac{2}{1}$

= 16.96 atm–L

$\frac{W_{\text{reversible}}}{W_{\text{irreversible}}} = \frac{16.96}{10.00} = 1.69 \approx 1.7$

26. **(a)** For reactions involving gases, there is no work done as $\Delta V = 0$.

27. **(b)** q = 150 Joules

w = –200 Joules

$\Delta E = q + w$ (First law of thermodynamics)

$\Rightarrow$ $\Delta E = 150 + (-200) = -50$ Joules

28. **(d)** In expansion against vacuum,

$P_{ext} = 0$

$w = -P_{ext}\Delta V = 0$

29. **(c)** $w = -P\Delta V$

$= -(1\text{ bar}) \times (9\text{ L})$

$= -(10^5\text{ Pa}) \times (9 \times 10^{-3})\text{ m}^3$

$= -9 \times 10^2$ N.m [$\because$ 1 Pa = 1N/m^2]

= – 900 J = – 0.9 kJ

30. **(c)** w = 10 kJ

q = – 2 kJ

$\Delta U = q + w = -2 + 10 = 8$ kJ

31. **(d)** Free expansion of ideal gas

$P_{ex} = 0 \quad \therefore \quad w = -P_{ex}\Delta V = 0$

$\because$ Adiabatic process $\Rightarrow q = 0$

$\Delta E = q + w$ (first law of thermodynamics)

$\therefore$ $\Delta E = 0$

$\Delta E = nCvdT \Rightarrow \Delta E = 0$

So, $q = 0, \Delta T = 0, w = 0$.

32. **(c)** $W = -P_{ext}(V_f - V_i) = -10^5(10^{-2} - 10^{-3})$

= –900 J

33. **(a)** Since graph A to C represents adiabatic reversible expansion, so work is done on the expense of internal energy, therefore, there is decrease in internal energy. So the temperature decreases.

i.e., $T_C < T_A$

34. **(a)** Area under the p-V curve is maximum in the first option, which is equal to work done.

35. **(c)** $w = -2.303\, nRT \log \frac{V_2}{V_1}$

$P_1V_1 = P_2V_2 \quad \Rightarrow \quad \frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{6}{3} = 2$

$w = -2.303 \times 1 \times 8.3 \times 300 \times \log(2)$

w = – 1718.1 J

36. **(c)** Zeroth law of thermodynamics is called the law of thermal equilibrium.

37. **(d)** A process during which no heat enters or leaves the system during any step of the process is known as adiabatic process. i.e., dq = 0

Such reaction (processes) are often carried out in closed insulated containers such as thermos bottle.

38. **(b)** Internal energy is the sum of all type of energies present in the molecule, namely translational energy, rotational energy, vibrational energy, electronic energy and bonding energy.

39. **(a)** Thermodynamic is based on conservation of energy. According to Ist law of thermodynamics heat supplied to any system is used as work and change in internal energy (ΔE).

Supplied heat to the system, $\Delta Q = w + \Delta E$

$\Delta E = \Delta Q - w$

40. **(d)**

41. **(a)** Work done by the gas under isothermal and at reversible condition is (W) $= -2.303 nRT \log \frac{P_1}{P_2}$

$$= -2.303 \times 1 \times 8.3 \times 300 \log \frac{20}{2}$$

$= –5734\ Jmol^{-1} = –5.73\ kJmol^{-1}$

$\therefore –x = 5.73\ kJmol^{-1}$.

42. **(a)** $C_P = 10.314\ J\ mol^{-1}\ K^{-1}$

$\Delta T = 1.0\ K$

$$C_P = \left(\frac{\Delta H}{\Delta T}\right)_P$$

$$\Rightarrow 10.314 = \frac{\Delta H}{1}$$

$\Delta H = 10.314\ J\ mol^{-1}$

$q_P = n\Delta H$

$q_P = 1 \times 10.314 = 10.314\ J.$

43. **(a)** For ideal gas,

Mole = 3

Temp = 300K

Pressure = 3 atm

PV = nRT

$$V = \frac{nRT}{P} = \frac{3\ mole \times 0.082\ atm\ k^{-1}mol^{-1} \times 300K}{3\ atm}$$

$V_1 = 24.6\ L$

$$\therefore\ V_2 = \frac{V_1}{2} = \frac{24.6}{2} = 12.3$$

$\Delta V = V_2 – V_1$

$= 12.3 – 24.6$

$\Delta V = – 12.3\ L$

Pext = 6 atm

$W = – Pext\ (\Delta V)$

$= – 6 \times (–12.3)\ atm\ L$

$= 73.8\ atm\ L$

$$W / in\ kJ = \frac{73.8 \times 101.3\ kJ}{1000}$$

W = 7.476 kJ.

44. **(a)** 11.52 L atm

Given $\Rightarrow V_1 = 1.0\ L$ $\quad V_2 = 10.0L$

$T = 61K$ $\quad n = 1$ $\quad R = 0.0821\ L\ atm/mol\ K$

Work done for Isothermal and Reversible Expansion

$W = n\ RT \ln (V_1 / V_2)$ ...(1)

Substituting the value in the equation (1)

$$W = 1 \times 0.0821 \times 61 \ln\left(\frac{1}{10}\right)$$

$W = 5.0081 \times –2.302$

$W = –11.52\ L\ atm.$

45. **(d)** $W = – nRT \ln \frac{P_2}{P_1} = –2.303\ nRT \log \frac{P_2}{P_1}$

$$W = –2.303 \times 2 \times 8.314 \times T \log \frac{10}{1}$$

$W = 38.29\ T\ J \Rightarrow W = 3.82 \times 10^{-2}\ T\ kJ$

46. **(c)** Extensive properties = Internal energy, enthalpy, Mass, volume, Heat capacity, Gibbs energy

Intensive properties = Density, pressure

47. **(c)** Reversible isothermal work is given by :-

$$W = –2.303\ nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= – 2.303\ (2.5)\ (8.314)\ (T) \log\left(\frac{20}{2}\right)$$

$= – 47.87\ T = – 16500\ J$

$\Rightarrow T = 344.68 \cong 345K$

48. **(a)** $q_p = n \times C_p \times \Delta T$

$$\Rightarrow\ 500 = 0.5 \times \frac{5}{2} \times 8.3(T_f – 298)$$

$$\left[C_p \text{ for ideal manoatomic gas} = \frac{5}{2}R\right]$$

$\Rightarrow\ T_f \simeq 346.2\ K$

$$\frac{\Delta H}{\Delta U} = \frac{C_p \Delta T}{C_v \Delta T} = \frac{C_p}{C_v} = \left(\frac{5}{3}\right)$$

$$\left[C_v \text{ for ideal manoatomic gas} = \frac{3}{2}R\right]$$

$$\Rightarrow\ \Delta U = \frac{C_v}{C_p} \times \Delta H = \frac{3}{5} \times 500 = 300\ J$$

[q = ΔH at constant p]

49. **(d)** $(10L, 300K) \xrightarrow{n=1} (20L, 300K)$

$$–q = w = –nRT \ln \frac{V_2}{V_1} = –8.3 \times 300 \times \ln\left(\frac{20}{10}\right)$$

$= –1.718\ kJ \Rightarrow q = 1.718\ kJ$

$w = –1.718\ kJ$

$\Delta U = 0$ ($\therefore\ \Delta T = 0$; Isothermal process)

50. **(b)** Combustion of glucose takes place as :

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell)$

Moles of glucose in 900g of glucose $= \frac{900}{180} = 5$ mol

1 mole glucose requires 6 moles of O_2

5 moles of glucose require 30 moles of O_2

Mass of O_2 required = 30 × 32 = 960 g.

51. **(d)** For standard state pressure should be 1 bar and temperature is specified only.

$$\Rightarrow \left(\Delta H_f^o\right)_{O_{2(g)}} = 0$$

The enthalpy of formation of O_2 is zero even at high temperature.

52. **(a)** The hydrogenation of benzene forms cyclohexane.

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 \longrightarrow \underset{\text{Cyclohexane}}{C_6H_{12}}$$

Enthalpy of hydrogenation of cyclohexane = – 119.5 kJ/mol

∴ Calculated enthalpy of benzene

$= 3 \times (-119.5) = -358.5$ kJ/mol

Resonance energy of benzene = – 150.4 kJ/mol

As we know,

Actual value of enthalpy

= Calculated enthalpy – Resonance energy

∴ Actual value of enthalpy = (–358.5) – (– 150.4)

= – 208.1 kJ/mol

Hence, the enthalpy of hydrogenation of benzene is – 208.1 kJ/mol.

53. **(b)** Heat of combustion of a substance is always negative as it is the amount of heat evolved (i.e. decrease in enthalpy) when one mole of the substance is completely burnt in air or oxygen.

54. **(a)** In endothermic reaction , the enthalpy of reactants is less than the enthalpy of products, since heat is absorbed in endothermic reaction.

Therefore, in endothermic reaction change in enthalpy is always positive.

$$\underset{H_R}{A + B} \rightleftharpoons \underset{H_P}{C + D} \qquad \Delta H = +\text{ve}$$

$$\Delta H = H_P - H_R = +\text{ve} \qquad (\because H_P > H_R)$$

55. **(a)** In exorthermic reactions heat is always given out by the reaction. For exothermic reactions :

$$\sum H_R > \sum H_P$$

56. **(a)** Hess's law is used for calculating enthalpy of reaction.

57. **(b)** $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$

$\Delta H^\ominus = -890$ kJ ... (i)

$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H^\ominus = -394$ kJ ... (ii)

$CO_2(g) \longrightarrow C(s) + O_2(g);\ \Delta H^\ominus = 394$ kJ

$CH_4 + O_2 \longrightarrow C(s) + 2H_2O;$

$(\Delta H^\ominus = -890 + 394 = -496$ kJ)

58. **(c)** $ABO_3(s) \longrightarrow AO(s) + BO_2(g)\ \Delta_r H^o = 175$

∴ $\Delta_r H^o = \Delta_f H^o(AO + BO_2) - \Delta_f H^o(ABO_3)$

$$\Delta_r H^o = \Delta_f H^o_{AO} + \Delta_f H^o_{BO_2} - \Delta_f H^o_{ABO_3}$$

$175 = -635 + x - (-1210)$

$175 + 635 = x + 1210$

∴ $x + 1210 = 175 + 635$

or, $x = -400.$

59. **(b)** $C + O_2 \rightarrow CO_2\ \Delta H = -393\ \text{kJ mol}^{-1}$

$2H_2 + O_2 \rightarrow 2H_2O\ \ \Delta H = -2 \times 286 = -572\ \text{kJ mol}^{-1}$

$CO_2 + 2H_2O \rightarrow CH_3OH + O_2 \Delta H = +726$

$C + 2H_2 + 2O_2 \rightarrow CH_3OH + O_2\ \Delta H = -239\ \text{kJ mol}^{-1}$

60. **(c)** $\Delta_r H^o = \sum_i a_i\ \Delta_f H^o\ (\text{products}) - \sum_i b_i\ \Delta_f H^o\ (\text{Reactants})$

$= [2 \times \Delta_f H^o(NH_3)] - [\Delta_f H^o(N_2) + 3\Delta_f H^o(H_2)]$

$= [2 \times (-46.2)] - [(0.0) + 3(0.0)]$

$= -92.4$ kJ.

61. **(a)** For the combustion of CO :-

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

For $O_2(g)$, $\Delta H_f^\circ = 0.0$ kJ/mol.

$$\Rightarrow \Delta H^\circ_{comb.(CO)} = \Delta H_r^\circ$$

$$= \Delta H^\circ_{f(CO_2)} - \left[\Delta H^\circ_{f(CO)} + \Delta H^\circ_{f(O_2)}\right]$$

$= -393 - [-110 + 0] = -283\ \text{kJ mol}^{-1}.$

62. **(b)** $\Delta H^\circ_r = [2\Delta H^\circ_f(NO)] - [\Delta H^\circ_f(N_2O) + \frac{1}{2}\ \Delta H_f^\circ(O_2)]$

$\Delta H^\circ_f(O_2) = 0$ (standard state of an element)

$\Rightarrow \Delta H_r^\circ = [2 \times 90.0] - [82.0 + 0.0]$

$= 180.0 - 82.0 = +98.0$ kJ.

63. **(b)** $D_2 + \frac{1}{2}O_2 \rightarrow D_2O$

$\Delta_r H^\circ$ = Bond enthalpies of

$$\left[\left[D - D + \frac{1}{2}(O - O)\right] - 2(D - O)\right]$$

$$= 400 + \left(\frac{1}{2} \times 498\right) - (2 \times 490) = -331\ \text{kJ / mol}$$

64. **(d)** As we know that, $q = -C_V \times \Delta T$

$= -20.7 \times (300 - 298) = -41.4$ kJ

For combustion of 1 mol of graphite

$$= \frac{12.0\ \text{g/mol} \times (-41.4)}{1}$$

$= -4.96 \times 10^2$ kJ/mol, since $\Delta n_g = 0$

$\Delta H = \Delta E = -4.96 \times 10^2$ kJ/mol

65. **(b)** Molar mass of NH_3 = 17 g/mol

moles of NH_3 given $= \frac{17}{17} = 1\text{mole}.$

For 1 mole enthalpy change = 23.4 kJ

5 moles enthalpy change = 23.4 × 5 = 117 kJ

66. **(b)** The coefficients in a balanced thermo-chemical equation refer to the number of moles (not to molecules) of reactants and products involved in the reaction.

67. **(b)** Enthalpy of formation of C_2H_4, CO_2 and H_2O are 52, – 394 and – 286 kJ/ mol respectively. (Given)

The reaction is

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O.$$

change in enthalpy,

$(\Delta H) = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

$= 2 \times (-394) + 2 \times (-286) - (52 + 0) = -1412$ kJ/ mol.

68. **(b)** Heat of combustion per mol (for 12 g) $= -2.48 \times 10^2$ kJ

$$\text{Heat generated for 1 g of graphite} = \frac{-2.48 \times 10^2}{12}$$

$$= -20.66 \text{ kJ} \approx 21 \text{ kJ}$$

69. **(a)** $H_2O\ (l) \rightarrow H_2O\ (g);\ \Delta H_{vap} = 40.79$ kJ/mol

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

$\Rightarrow 40.79 \text{ kJ/mol} = \Delta U + (1)\ (8.314 \text{ JK}^{-1} \text{ mol}^{-1})\ (373 \text{ K})$

$$\Rightarrow \Delta U^o = \left(40.79 \text{ kJ/mol} - \frac{8.314 \times 373}{1000} \text{kJ / mol}\right)$$

$$= (40.79 - 3.10) \text{ kJ/mol} = 37.69 \frac{\text{kJ}}{\text{mol}}$$

Internal energy change for 36 g of water

$$= 37.69 \frac{\text{kJ}}{\text{mol}} \times \frac{36\text{g}}{18 \text{g / mol}}$$

$\Delta U = 75.98$ kJ

70. **(d)**

$$\begin{tikzcd}
4NO_2(g) + O_2(g) \arrow[r] \arrow[dr, "\Delta H'"'] & 2N_2O_5(g),\ \Delta_r H = -111 \text{ kJ} \arrow[d, "-54 \text{ kJ}"] \\
& 2N_2O_5(s)
\end{tikzcd}$$

$\Delta H' - 111 - 54 =$

$\Delta H' = -165$ kJ

71. **(a)** $H_2O\ (l) \rightleftharpoons H_2O\ (g) + Q\ ;\ \Delta n_g = 1$

$\Delta H = \Delta E + \Delta n_g RT \Rightarrow 40660 = \Delta E + 8.314 \times 373$

$\Delta E = 37558 \text{ J / mol} = 37.56 \text{ kJ mol}^{-1}$

72. **(b)** $\underset{[H-H]}{H_2(g)} + \underset{[Br-Br]}{Br_2(g)} \longrightarrow \underset{[H-Br]}{2HBr(g)}$

$\Rightarrow \Delta_r H = \Sigma(BE)_{\text{Reactants}} - \Sigma(BE)_{\text{Products}}$

[∵ BE = bond energy]

$\Rightarrow\ = [(BE)_{H_2} + (BE)_{Br_2}] - (BE)_{HBr} \times 2$

$\Rightarrow -109 = (435 + 192) - (BE)_{HBr} \times 2$

$\Rightarrow [(BE)_{HBr} = 368 \text{ kJ mol}^{-1}$

73. **(c)** We know that, $Cl_2(g) \longrightarrow 2Cl(g)$ is endothermic reaction because it required energy to break bond.

So reverse reaction, $2Cl(g) \longrightarrow 2Cl_2(g)$ will be exothermic, $\Delta_r H < 0$.

Also, two gaseous atom combine together to form 1 gaseous molecule.

74. **(d)** Let B.E of X_2, Y_2 and XY are x kJ mol^{-1}, 0.5 x kJ mol^{-1} and x kJ mol^{-1} respectively

$\Delta H = -200 = \Sigma\ (B.E)_{\text{Reactants}} - \Sigma(B.E)_{\text{Product}}$

$$= \frac{1}{2} X_2 + \frac{1}{2} Y_2 \rightarrow XY;\ \Delta H = -200 \text{ kJ mol}^{-1}$$

On solving, $x = 800$ kJ mol^{-1}

75. **(a)** $\underset{12\text{ g}}{C} + O_2 \rightarrow \underset{44\text{ g}}{CO_2} + 393.5$ kJ/mol

44 g CO_2 is formed from 12g of carbon

$$35.2\text{g is formed from } \frac{12 \times 35.2}{44} \text{g of C}$$

= 9.6 g of C = 9.6/12 = 0.8 mole

1 mole release heat 393.5 kJ

0.8 mole release heat = 393.5 × 0.8

= 314.8 kJ ≈ 315 kJ.

76. **(c)** $\underset{x}{CH_4} + \underset{2x}{2O_2} \longrightarrow CO_2 + 2H_2O$

$\underset{(5-x)}{C_3H_8} + \underset{5(5-x)}{5O_2} \longrightarrow 3CO_2 + 4H_2O$

$\Rightarrow\ 2x + 5(5 - x) = 16 \qquad \Rightarrow x = 3L$

∴ The amount of heat released = Heat released during CH_4 combustion + Heat released during C_3H_8 combustion.

$$= \frac{3}{22.4} \times 890 + \frac{2}{22.4} \times 2220 = 317 \text{ kJ.}$$

77. **(b)** $C_{m,p} - C_{m,v} = R \Rightarrow 20.785 - C_{m,v} = 8.314$

$\Rightarrow\ C_{m,v} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta U = n\, C_{m,v}\, \Delta T$

$$\Rightarrow n = \frac{5000}{12.471 \times (500 - 300)} \Rightarrow n = 2$$

78. **(c)** Let x g of gas is burnt

moles of gas = $\frac{x}{280}$

Heat released by $\frac{x}{280}$ mole = 2.5 × 0.45 kJ

Heat released by 1 mole = $\frac{2.5\times0.45\times280}{x}$ kJ

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

$\Delta H \simeq \Delta U$

$$9 = \frac{2.5\times280\times0.45}{x} \Rightarrow x = 35g$$

79. **(a)** $\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = n_R(g) - n_p(g) = 2 - 1 = 1$

$\Delta H = -59.6 + 1 \times 8.314 \times 300 \times 10^{-3} = -\ 57.10$

80. **(d)**

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

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

$$\Delta n_g = 2 - \frac{3}{2} = 0.5$$

$$\Delta H_{298} = -742.24 + \frac{0.5\times8.314\times298}{1000}$$

$= -742.24 + 1.24 = -741$ kJ.

81. **(a)**

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ ....(1)

$\Delta H_1 = -2220.0$ kJ/mol

$C + O_2 \rightarrow CO_2$ ...(2)

$\Delta H_2 = -393.5$ kJ/mol

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ ...(3)

$\Delta H_3 = -285.8$ kJ/mol

Formation of C_3H_8 (1 mole):

$3C + 4H_2 \rightarrow C_3H_8$ ...(4)

Eq. (4) obtained by

3 × Eq (2) + 4 × Eq. (3) – Eq. (1)

$= 3 \times (-393.5) + 4 \times (-285.8) - (-2220.0)$

$= -1180.5 - 1143.2 + 2220.0 = -103.7$ kJ/mol

82. **(c)** $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$

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

$$\Delta n_g = \Sigma n_P - \Sigma n_R = 0 - \frac{1}{2} = -\frac{1}{2}$$

$$-601.70\times10^3 = \Delta U - \frac{1}{2}\times8.3\times300$$

$-601.70 \text{ kJ} = \Delta U - 1.245 \text{ kJ}$

$\Delta U = -600.455 \text{ kJ} \approx -600 \text{ kJ}$

83. **(b)** $\Delta U = -726$ kJ/mol

$\Delta n_g = 1 - 3/2 = -1/2$

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

$$= -726 - \frac{1}{2}\times\frac{8.3\times300}{1000} = -727.245$$

84. **(c)** $\Delta_r H = \Sigma\Delta_c H\,(\text{Reactant}) - \Sigma\Delta_c H\,(\text{Product})$

$= 3 \times (-1300) - (-3268) = -632 \text{ kJ mol}^{-1}$

85. **(a)** $\Delta H_{sub} = \Delta H_{fus.} + \Delta H_{vap.} = 2.8 + 98.2 = 101$ kJ/mol

86. **(a)**

$$C_2H_5OH\ (l) + O_2(g) \longrightarrow 2O_2(g) + 3H_2O(l);$$

$\Delta H_C = -327$ kcal

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

$\Rightarrow -327\times10^3 = \Delta U + (-1)\times2\times300$

$\Rightarrow \Delta U = -327\times10^3 + 600$

$\therefore \Delta U = -326400$ cal

87. **(a)** Given chemical reaction:

$$A \xrightarrow[T=300K]{} B \quad \Delta G = -49.4 \text{ kJ / mol}$$

$\Delta H = 51.4$ kJ/mol

$\Delta S = ?$

$\Rightarrow$ From the relation $\Delta G = \Delta H - T\Delta S$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{[51.4 - (-49.4)]\times1000}{300}\frac{J}{\text{mol K}}$$

$\Rightarrow$ $\Delta S = 336 \text{ JK}^{-1}\text{ mol}^{-1}$.

88. **(d)** Bi (s) $\longrightarrow$ Bi (g) ; $\Delta H = 207$ kJ

2Bi (s) $\longrightarrow$ Bi_2(g) ; $\Delta H = 125$ kJ per mole of Bi(s)

Reversing the first reaction and multiplying by 2,

2Bi (g) $\longrightarrow$ 2Bi(s) ; $\Delta H = -2 \times 207$ kJ

2Bi (s) $\longrightarrow$ Bi_2 (g) ; $\Delta H = 2 \times 125$ kJ

Adding, 2Bi(g) $\longrightarrow$ Bi_2(g) ;

$\Delta H = -414 + 250$

$= -164$ kJ per mole of Bi_2(g)

The bond energy of Bi – Bi bond = 164 kJ mol^{-1}

89. **(a)** Crystallization of sucrose solution. Entropy is a measure of randomness during the crystallisation of sucrose solution liquid state is changing into solid state hence entropy decreases.

90. **(d)** In $2H(g) \longrightarrow H_2(g)$, number of moles decreases, therefore entropy decreases.

91. **(a)** A system at higher temperature has greater entropy (randomness). S and ΔS are related with T as:

$$S_T = \int_0^T \frac{nC \cdot dT}{T} \text{ and } \Delta S = \int \frac{dq}{T}$$

Thus, both S and ΔS are function of temperature.

92. **(d)** In the process of synthesis of ammonia from N_2 and H_2, number of moles decreases which implies that the change in entropy will be negative.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

93. **(b)**

(a) When diamond is converted into graphite (it is heated to 1500 °C) entropy is increased, $\Delta S > 0$

(b) When pressure increases then molecules of gas will come closer and intermolecular distance decreases, so entropy will also decrease, $\Delta S < 0$

(c) When we increase the temperature of a gas then randomness is increased as the kinetic energy is gained by molecules. So, $\Delta S > 0$

(d) H_2 molecule is converted into atoms, the no. of particles increases. Thus entropy will increase, $\Delta S > 0$

94. **(b)** Given, $C_p = 10$ cals at 1000 K

$T_1 = 1000$ K. $T_2 = 100$ K

$m = 32$ g, $\Delta S = ?$

at constant pressure

$$\Delta S = C_p \ln \frac{T_2}{T_1} = 2.303 \times C_p \log \frac{T_2}{T_1}$$

$$= 2.303 \times 10 \log \frac{100}{1000} = -23.03 \text{ cal deg}^{-1}$$

95. **(a)** $\Delta S = \dfrac{q}{T}$

q → required heat per mole

T → constant absolute temperature

Unit of entropy is $JK^{-1}\ mol^{-1}$

96. **(d)** Entropy is measurement of randomness. When ice (solid) melts into water (liquid) randomness and thus entropy increases.

97. **(b)** Follow II law of thermodynamics.

98. **(b)** Given,

Heat = 1 kJ = 1000 J

Temperature = 3 K

$$\text{Entropy} = \frac{\text{Absorb heat}}{\text{Temperature}} = \frac{1000 \text{ J}}{3 \text{ K}}$$

Entropy = 333.3 J/K

99. **(b)** $\Delta G = \Delta H - T\Delta S$

$\Delta G = -T\Delta S$ (when $\Delta H = 0$ and $\Delta S = +ve$)

$\Rightarrow \Delta G = -ve$

100. **(d)** Since the process is at equilibrium $\Delta G = 0$, for $\Delta G = 0$, there should be $\Delta H > 0$, $\Delta S > 0$.

101. **(a)** For spontaneous reaction, $dS > 0$ and dG should be negative *i.e.* < 0.

102. **(c)** $\Delta H = 200\ J\ mol^{-1}$, $\Delta S = 40\ JK^{-1}\ mol^{-1}$

For spontaneous reaction,

$\Delta G < 0$

$\Delta H - T\Delta S < 0$; $\Delta H < T\Delta S$

$$\frac{\Delta H}{\Delta S} < T;\ \frac{200}{40} < T \Rightarrow 5 < T$$

So, minimum temperature is 5 K

103. **(a)** Given ΔH 35.5 kJ mol^{-1}

$\Delta S = 83.6\ JK^{-1}\ mol^{-1}$

$\because \quad \Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous, $\Delta G = -ve$

i.e., $\Delta H < T\Delta S$

$$\therefore \quad T > \frac{\Delta H}{\Delta S} = \frac{35.5 \times 10^3 \text{ Jmol}^{-1}}{83.6 \text{ JK}^{-1}}$$

So, the given reaction will be spontaneous at $T > 425$ K.

104. **(c)** $\Delta G = \Delta H - T \cdot \Delta S$

For a spontaneous reaction $\Delta G = -ve$ (always)

which is possible only if

$\Delta H < 0$ and $\Delta S > 0$

∴ spontaneous at all temperatures.

105. **(b)** Given $\Delta U = 2.1$ k cal, $\Delta S = 20$ cal. K^{-1}

$T = 300$ K

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

Putting the values given in the equation

$$\Delta H = 2.1 + 2 \times \frac{2}{1000} \times 300$$

$= 2.1 + 1.2 = 3.3$ k cal.

Now, $\Delta G = \Delta H - T\Delta S$

$$= 3.3 - 300 \times \frac{20}{1000} = -2.7 \text{ k cal}$$

106. **(b)** $\Delta G^\circ = RT \ln K_p$

$= -R(300)\ln(10)^2 \;\; = -R(300\times 2\times 2.3)$

$\Delta G^\circ = -1380R.$

107. **(b)** $\Delta G = \Delta H - T\Delta S = 0$ at equilibrium

$\Rightarrow \;\; -165\times 10^3 - T\times(-505) = 0 \Rightarrow T = 300K.$

108. **(c)** $\Delta G = \Delta H - T\Delta S$

$\Delta G = -57.8 - 298\times(-176\times 10^{-3}) = -5 \text{ kJ mol}^{-1}$

109. **(c)** A reaction is spontaneous if ΔG_{sys} is negative.

$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$

A reaction will be spontaneous at all temperatures if ΔH_{sys} is negative and ΔS_{sys} is positive.

110. **(c)** MgO (s) + C(s) $\rightarrow$ Mg (s) + CO (g)

For a reaction to be spontaneous,

$\Delta G < 0$

$\Delta H^\circ - T\Delta S^\circ < 0 \;\Rightarrow T > \dfrac{\Delta H^\circ}{\Delta S^\circ}$

$T > \dfrac{491.1\times 1000}{198}$

$T > 2480.3\text{ K}$

111. **(d)** Δ G is negative for a spontaneous process.

112. **(a)** The relation between free energy change and equilibrium constant is given by Nernst equation

$E = E^o - \dfrac{RT}{nF} lnQ$

At equilibrium, E = 0 and $Q = K_c$

$\therefore \;\; E^o = \dfrac{RT}{nF} ln\, K \qquad$ ...(i)

Again $-\Delta G^o = nFE^o$

$E^\circ = \dfrac{-\Delta G^\circ}{nF}$

By substituting value of E° in equation (i) we get,

$\dfrac{-\Delta G^o}{nF} = \dfrac{RT}{nF} lnK \;\; ; \;\; \Delta G^o = -RT\, lnK$

113. **(a)** The Gibb's free energy is zero at equilibrium because the rate of backward reaction is equal to the rate of forward reaction.

Hence, option (a) is correct.

114. **(d)** For a cyclic process

$\Delta E = 0, \Delta H = 0$ and $\Delta G = 0$. As all depend upon final state and initial state, w doesn't depend on path followed.

115. **(c)** For a spontaneous reaction

ΔG should be – ve, which is possible if ΔS = +ve, ΔH = +ve

and $T\Delta S > \Delta H \qquad [\therefore \Delta G = \Delta H - T\Delta S]$

116. **(a)** $\Delta G = \Delta H - T\Delta S$ is negative for spontaneity.

117. **(b)** Entropy is a measure of randomness or disorderness of the system. At absolute zero, the movement of molecules of the system or randomenss of the system is zero, hence entropy is also zero.

118. **(d)** For an exothermic reaction all three enthalpy, entropy and Gibb's free energy change have negative values.

119. **(c)** For reaction to be spontaneous according to IInd law: $\Delta G < 0$

$\Rightarrow \;\; \Delta H - T\Delta S < 0$ (ΔH or ΔS are + ve)

$\Rightarrow \;\; T > \left(\dfrac{\Delta H}{\Delta S}\right) = T_e$ (ΔG = – ve at high temperature)

$\Rightarrow \;\; T > T_e$

120. **(a)** If $\Delta G_{system} = 0$, the system has attained equilibrium, is right choice.

In it, alternative (d) is most confusing as when $\Delta G > 0$, the process may be spontaneous when it is coupled with a reaction which has $\Delta G < 0$ and total ΔG is negative, so right answer is (a).

Exercise 2 : ACCELERATOR

Topic-wise MCQs

1. **(d)** $\Delta U = q + w$, where ΔU is internal energy and ΔU is a state function.

2. **(c)** Given $\Delta H = 176$ kJ,

$T = 975°C = 975 + 273 = 1248\text{ K}$

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$\Delta n_g = n_p - n_r = 1 - 0 = 1$

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

$= 176 - 1\times\dfrac{8.314}{1000}\times 1248$

$= 176 - 10.375 = 165.63\text{ kJ}$

3. **(c)** $\Delta H = \Delta E - \Delta n_g RT$

For the reaction,

$H_2 + I_2 \rightleftharpoons 2HI$

$\Delta n_g = 0$ (at equilibrium)

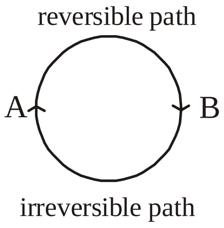
$\therefore \;\; \Delta H = \Delta E$

4. **(d)** $\Delta H = \Delta E + P\Delta V$

For isochoric process, $\Delta V = 0$

$\therefore \;\; \Delta H = \Delta E$

5. **(c)**



For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.

6. **(d)** Temperature remains constant during isothermal reaction.

7. **(b)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

According to thermodynamics's Ist law

$\Delta H = \Delta E + nRT$

Where ΔH = enthalpy of reaction at constant pressure

ΔE = Heat of reaction at constant volume

R = molar gas constant

T = temperature of the reaction

n = (no. of moles of product) – (no. of moles of reactant.)

From reaction,

$\Delta n = n_P - n_R = 2 - 4 = -2$

Hence, $\Delta H = \Delta E - 2RT$.

8. **(d)** Heat energy is absorbed during endothermic reaction. In all the given reactions, heat is absorbed during reaction.

$\therefore$ All of them are endothermic reactions.

9. **(b)** For an isothermal process $\Delta E = 0$

10. **(c)** $\Delta H = \Delta E + nRT$

$\Delta n = 3 - (1 + 5) = 3 - 6 = -3$

$\Delta H - \Delta E = (-3RT)$

11. **(b)** $W = -\ p\Delta V = -3(6-4) = -6$ litre atmosphere

$= -6 \times 101.32 = -608\,J$

12. **(d)** We know that $\Delta H = \Delta E + \Delta n_g RT$

In the reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$\Delta n = n_p - n_r = 2 - 2 = 0$

So, $\Delta H = \Delta E$ for this reaction

13. **(c)** $W = -P\Delta V = -10^5(1\times10^{-2} - 1\times10^{-3}) = -900J$

14. **(b)** $\Delta H = \Delta U + \Delta nRT$ for $N_2 + 3H_2 \longrightarrow 2NH_3$

$\Delta n_g = 2 - 4 = -2$

$\therefore \Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT$ $\therefore \Delta U > \Delta H$

15. **(a)** Internal energy is dependent upon temperature and according to first law of thermodynamics total energy of an isolated system remains same, i.e., in a system of constant mass, energy can neither be created nor destroyed by any physical or chemical change but can be transformed from one form to another

$\Delta E = q + w$

For closed insulated container, $q = 0$, so, $\Delta E = +w$, as work is done by the system

16. **(b)** $A(g) + 2B(g) \longrightarrow 2C(g) + 3D(g)$

$\Delta n = 5 - 3 = 2$

$\Delta H = \Delta E + nRT$ or $\Delta E = \Delta H - nRT$

$= 19 - 2 \times 2 \times 10^{-3} \times 300 = 17.8$ kcal

17. **(a)** $q = +10$ kJ, $W = -4$ kJ

$\because$ $\Delta E = q + W$

$= 10 - 4 = 6$ kJ

So, energy increases by 6 kJ

18. **(c)** In isolated system neither exchange of matter nor exchange of energy is possible with surroundings.

19. **(a)** Ideal gas during spontaneous expansion into vacuum does not do any external work.

20. **(b)** As volume is constant hence work done in this process is zero therefore heat supplied is equal to change in internal energy.

21. **(d)** $\Delta H = \Delta U + \Delta n_{(g)}RT$; $\Delta n_{(g)} = 1$ in (d); $\Delta n_{(g)} = 0$ in other cases.

22. **(c)** During isothermal expansion of ideal gas,

$\Delta T = 0$. Now $H = E + PV$

$\because$ $\Delta H = \Delta E + \Delta(PV)$

$\therefore$ $\Delta H = \Delta E + \Delta(nRT)$;

Thus if $\Delta T = 0.$, $\Delta H = \Delta E$

i.e., remain unaffected

23. **(d)** We know that heat (q) and work (w) are not state functions but (q + w) is a state function. H – TS (i.e. G) is also a state function. Thus II and III are not state functions so the correct answer is option (d).

24. **(d)** As $\Delta H = \Delta E + \Delta n_g RT$

if $n_p < n_r$; $\Delta n_g = n_p - n_r = -$ ve

Hence $\Delta H < \Delta E$

25. **(d)** The positive sign expresses when work is done on the system. Similarly, negative sign expresses when work is done by the system.

26. **(d)** When work is done by the system, $\Delta U = q - W$

27. **(a)** It is fact that absolute values of internal energy of substances cannot be determined. It is also true that it is not possible to determine exact values of constitutent energies of a substance.

28. **(d)** As $\Delta H = \Delta E + \Delta n_g RT$

if $n_p < n_r$; $\Delta n_g = n_p - n_r = -$ ve.

Hence $\Delta H < \Delta E$.

29. **(a)** Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.

30. **(c)** It may involve increase or decrease in temperature of the system. Systems in which such processes occur, are thermally insulated from the surroundings.

31. **(b)** In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).

$\therefore$ According to first law of thermodynamics

$\because$ $Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)

If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.

32. **(c)** Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.

33. **(c)** For isothermal reversible expansion

$$W = -nRT \ln \frac{V_2}{V_1}$$

34. **(a)** A – (p), B – (s), C – (r), D – (q)

35. **(a)** The shaded area shows work done on an ideal gas in a cylinder when it is compressed by a constant external pressure.

36. **(b)** Given $C + O_2 \rightarrow CO_2$, $\Delta H^o = -x\ kJ$ ....(i)

$2CO_2 \rightarrow 2CO + O_2 \quad \Delta H^o = +y\ kJ$ … (ii)

or $CO_2 \rightarrow CO + 1/2\,O_2, \quad \Delta H^o = +y/2\ kJ$ ...(iii)

By adding no. (i) and (iii) eq.

$$C + O_2 + CO_2 \longrightarrow CO_2 + CO + \frac{1}{2}O_2$$

$$C + \frac{1}{2}O_2 \longrightarrow CO, \ \Delta H^o = y/2 - x = \frac{y-2x}{2} kJ$$

37. **(c)** $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$

$$\Delta H = \Delta H^o_{f\,(SO_3)} - \Delta H^o_{f\,(SO_2)}$$

$$= -98.2 + 298.2 = 200\ kJ/mole$$

38. **(d)** Heat of reaction

39. **(a)** $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)\ \Delta H = ?$

$$\Delta H = [2 \times \Delta H_f \text{ of } H_2O(l) + (\Delta H_f \text{ of } O_2) - (2 \times \Delta H_f \text{ of } H_2O_2(l))]$$

$$= [(2 \times -286) + (0) - (2 \times -188)]$$

$$= [-572 + 376] = -196\ \ kJ/mole$$

40. **(d)** $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$$\Delta H^o = (BE)_{reactant} - (BE)_{product}$$

$$= (433 + 192) - (2 \times 364) = 625 - 728 = -103\ kJ$$

41. **(a)** Dissolution of NaOH in water is an exothermic reaction as indicated by negative value of enthalpy leading to increase in temperature.

42. **(b)** $\Delta H = \Sigma\left[\Delta H_f^\circ \text{ products}\right] - \Sigma\left[\Delta H_f^\circ \text{ reactants}\right]$

$$\Delta H^\circ = [\Delta H_f^\circ(CO)(g) + \Delta H_f^\circ(H_2O)(g)] - [\Delta H_f^\circ(CO_2)(g) + \Delta H_f^\circ(H_2)(g)]$$

$$= [-110.5 + (-241.8)] - [-393.5 + 0] = 41.2$$

43. **(b)** $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O.$

Change in enthalpy,

$$\Delta H = \Delta H_{products} - \Delta H_{reactants}$$

$$= 2 \times (-394) + 2 \times (-286) - (52 + 0)$$

$$= -1412\ kJ/\ mol.$$

44. **(c)** $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$$\Delta H \text{ of reaction} = [\Delta_f H\, CO_2 + 2\Delta_f H\, H_2O] - [\Delta_f H\, CH_4 - 2\Delta_f H O_2]$$

$$= -400 + 2 \times (-280) - (-70) - (0)$$

$$= -890\ kJ\ mol^{-1}$$

45. **(d)** eq. (i) + eq. (ii) find the required result and divide by 2.

46. **(c)** The reaction for formation of HCl can be written as

$H_2 + Cl_2 \rightarrow 2HCI$

$H-H + Cl-Cl \rightarrow 2\,(H-Cl)$

Substituting the given values, we get enthalpy of formation of

$2HCl = (676 - 862) = -186\ kJ.$

$\therefore$ Enthalpy of formation of HCl $= \frac{-186}{2} kJ = -93\ kJ.$

47. **(a)** $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$; $\Delta H = -26.8\ KJ$ ...(i)

$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$; $\Delta H = -16.5\ KJ$ ...(ii)

eq. (i) – 2 × eq. (ii), we get

$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$

$\Delta H = -26.8 + 33.0 = +6.2\ kJ$

48. **(d)** Combustion is heating of substance in excess of oxygen so as to form carbon bioxide and water. Sometimes water is not formed during combustion.

49. **(b)** $A \longrightarrow B, \Delta H = +24\ kJ/mol$

$\Rightarrow \quad H_B - H_A = +24$ ...(i)

$B \longrightarrow C, \Delta H = -18\ kJ/mol$

$\Rightarrow \quad H_C - H_B = -18$

or $H_B - H_C = +18$

From Eqs. (i) and (ii), we have

$H_C - H_A = 6$ ...(ii)

∴ $H_B > H_C > H_A$

50. **(d)** $X_2 + Y_2 \longrightarrow 2XY$, $\Delta H = 2(-200)\,\text{kJmol}^{-1}$

Let x be the bond dissociation energy of X_2. Then

$$\Delta H = -400 = \Sigma_{x-x} + \Sigma_{y-y} - 2\Sigma_{x-y}$$

$$= x + 0.5x - 2x = -0.5x$$

or $x = \frac{400}{0.5} = 800\ \text{kJ mol}^{-1}$

51. **(a)** $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$

$\Delta_r H = [\Delta H(I_2(s) \to I_2(g)) + \Delta H_{I-I} + \Delta H_{Cl-Cl}] - [\Delta H_{I-Cl}]$

$= 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46$

$$\Delta_f H^\circ(ICl) = \frac{33.46}{2} = 16.73\ \text{kJ/mol}$$

52. **(d)** This reaction shows the formation of H_2O, and the $-X_2$ represents the enthalpy of formation of H_2O because as the definition suggests that the enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent elements.

53. **(b)** $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$

$$\Delta_f H_{HCl} = \sum \text{B.E. of reactants} - \sum \text{B.E. of products}$$

$$-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \text{B.E. of HCl}$$

∴ B.E. of HCl $= 215 + 120 + 90$

$= 425\ \text{kJ mol}^{-1}$

54. **(b)** Enthalpy of reaction

$= \text{B.E}_{(\text{Reactant})} - \text{B.E}_{(\text{Product})}$

$$= \left[\text{B.E}_{(C=C)} + 4\,\text{B.E.}_{(C-H)} + \text{B.E.}_{(H-H)}\right]$$

$$-\left[\text{B.E.}_{(C-C)} + 6\,\text{B.E.}_{(C-H)}\right]$$

$= [606.1 + (4 \times 410.5) + 431.37)] - [336.49 + (6 \times 410.5)]$

$= -120.0\ \text{kJ mol}^{-1}$

55. **(c)** Given

$4H(g) \longrightarrow 2H_2(g);\ \Delta H = -869.6\ \text{kJ}$

or $2H_2(g) \longrightarrow 4H(g);\ \Delta H = 869.6\ \text{kJ}$

$$H_2(g) \longrightarrow 2H(g);\ \Delta H = \frac{869.6}{2} = 434.8\ \text{kJ}$$

56. **(b)** Given ΔH

$\frac{1}{2}A \longrightarrow B$ $+150$ ...(1)

$3B \longrightarrow 2C + D$ -125 ...(2)

$E + A \longrightarrow 2D$ $+350$ ...(3)

To calculate ΔH operate

$2 \times$ eq. (1) + eq. (2) – eq. (3)

$\Delta H = 300 - 125 - 350 = -175$

57. **(b)** The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^{-1}(aq)$ is given by

$$\Delta H = \frac{1}{2}\Delta_{diss}H^{\ominus}_{Cl_2} + \Delta_{eg}H^{\ominus}_{Cl} + \Delta_{hyd}H^{\ominus}_{Cl}$$

Substituting various values from given data, we get

$$\Delta H = \left(\frac{1}{2} \times 240\right) + (-349) + (-381)\,\text{kJmol}^{-1}$$

$= (120 - 349 - 381)\ \text{kJ mol}^{-1} = -610\ \text{kJ mol}^{-1}$

i.e., the correct answer is (b)

58. **(a)** $\Delta S = \frac{\text{Latent heat of fusion}}{\text{Melting point}} = \frac{\Delta H}{T}$

$$= \frac{2930}{300}\ \text{J K}^{-1}\text{mol}^{-1} = 9.77\ \text{J K}^{-1}\text{mol}^{-1}$$

59. **(b)** $2Al + \frac{3}{2}O_2 \to Al_2O_3,\ \Delta H = -1596\ \text{kJ}$ .....(i)

$2Cr + \frac{3}{2}O_2 \to Cr_2O_3,\ \Delta H = -1134\ \text{kJ}$ ....(ii)

By (i) –(ii)

$2Al + Cr_2O_3 \to 2Cr + Al_2O_3,\ \Delta H = -462\ \text{kJ}.$

60. **(d)** $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

$[\Delta n = 1 - \frac{1}{2} = \frac{1}{2}]$

$$\Delta H - \Delta U = \Delta nRT = \frac{1}{2} \times 8.314 \times 298 = 1238.78\ \text{J mol}^{-1}$$

61. **(d)**

(i) $2C(s) + H_2(g) \longrightarrow H-C \equiv C-H(g)$

$\Delta H = 225\ \text{kJ mol}^{-1}$

(ii) $2C(s) \longrightarrow 2C(g)$ $\Delta H = 1410\ \text{kJ mol}^{-1}$

$$C(s) \longrightarrow C(g)\,\Delta H = \frac{1410}{2} = 705\text{kJmol}^{-1}$$

(iii) $H_2(g) \longrightarrow 2H(g)$ $\Delta H = 330\ \text{kJ mol}^{-1}$

From equation (i) :

$$225 = \left[2 \times \Delta H_{C(s) \longrightarrow C(g)} + 1 \times BE_{H-H}\right]$$

$$-[2 \times BE_{C-H} + 1 \times BE_{C \equiv C}]$$

$$225 = [1410 + 1 \times 330] - [2 \times 350 + 1 \times BE_{C \equiv C}]$$

$$225 = [1410 + 330] - [700 + BE_{C \equiv C}]$$

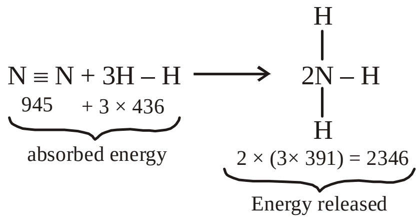
$$225 = 1740 - 700 - BE_{C \equiv C}$$

$$BE_{C \equiv C} = 815 \text{ kJ mol}^{-1}$$

62. **(c)** Standard heat of formation of a substance is amount of heat evolved or absorbed when one mole of substance is formed from its elements in their standard states. Since standard state of carbon and hydrogen are graphite and gaseous H_2 respectively. Hence standard heat of formation of methane is given by

$$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$$

63. **(a)**



$$\underbrace{\underset{945}{N \equiv N} + \underset{+3 \times 436}{3H-H}}_{\text{absorbed energy}} \longrightarrow \underbrace{\underset{2 \times (3 \times 391) = 2346}{2\overset{H}{\underset{H}{N}}-H}}_{\text{Energy released}}$$

$$\Delta H = 2253 - 2346 = -93 \text{ kJ}$$

64. **(b)** For the equation

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(g) + 3H_2O(g)$$

Eqs. (i) + 3 (ii) + 3 (iii) – (iv)

$$\Delta H = -1273 + 3(-286) + 3(44) - 36$$

$$= -1273 - 858 + 132 - 36$$

$$= -2035 \text{ kJ/mol}$$

65. **(d)** Entropy change

$$\Delta S = \Delta S_{product} - \Delta S_{reactant} = 2(186.7) - (223 + 130.6)$$

$$= 373.4 - 353.6 = 19.8 \text{ JK}^{-1} \text{ mol}^{-1}$$

66. **(c)** When gas is compressed its entropy decreases so, ΔS is negative.

67. **(a)** $\Delta S = \dfrac{\Delta H}{T}$

$$\Delta S(\text{per mole}) = \frac{\Delta H \text{ per mole}}{T} = \frac{6000}{273}$$

$$= 21.98 \text{ JK}^{-1}\text{mol}^{-1}$$

68. **(a)** For a spontaneous process, ΔS_{total} is always positive

69. **(a)** Because randomness is decreased.

70. **(d)** For isothermal reversible expansion

$$w = q = nRT \times 2.303 \log \frac{V_2}{V_1}$$

$$= 2RT \times 2.303 \log \frac{20}{2}$$

$$= 2 \times 2 \times T \times 2.303 \times 1 = 9.2\,T$$

Entropy change, $\Delta S = \dfrac{q}{T} = \dfrac{9.2T}{T} = 9.2$ cal.

71. **(c)** Conversion of graphite into diamond is an endothermic reaction. But ΔS would be negative for the conversion of graphite into diamond. Diamond has more compact structure so the volume is smaller. However, the atoms in graphite are able to move with in their lattice so the entropy is higher.

72. **(c)** For reverse reaction signs will be change.

73. **(d)** Entropy of a gas is greater than liquid and solid because gaseous particles are quite apart from each other and are in random motion.

74. **(d)** Given $\Delta H = 30 \text{ kJ mol}^{-1}$ $T = 273 + 27 = 300$ K

$$\Delta S_T = \frac{\Delta H_T}{T} = \frac{3 \times 10^4}{300} \text{ J mol}^{-1}$$

$$= 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

75. **(d)** Raking up leaves into a thrash bag results in decrease in randomness i.e. decrease in entropy.

76. **(c)** ΔS has negative value if number of gaseous moles decreases during a reaction, $\Delta n_g = -ve$

For the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$\Delta n_g = 2 - 3 = -1$$

77. **(b)** Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

78. **(b)** Eq. (b) shows largest phase change i.e., gas → solid

79. **(a)** Measure of disorder of a system is nothing but entropy. For a spontaneous reaction, $\Delta G < 0$. As per Gibbs Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

Thus ΔG is –ve only

When $\Delta H = -ve$ (exothermic)

and $\Delta S = +ve$ (increasing disorder)

80. **(d)** We know that, $\Delta G = \Delta H - T\Delta S$

When the reaction is in equilibrium, $\Delta G = 0$

$$0 = \Delta H - T\Delta S \Rightarrow T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30 \times 1000}{105} = 285.7 \text{ K}$$

81. **(a)** If $\Delta G_{system} = 0$ the system has attained equilibrium is right choice.

In it alternative (d) is most confusing as when $\Delta G > 0$, the process may be spontaneous when it is coupled with a reaction which has $\Delta G < 0$ and total ΔG is negative, so right answer is (a).

82. **(a)** $\Delta G = \Delta H - T\Delta S$

$= 177.9 - (298 \times 160.4/1000) = 177.9 - 47.79 = +130.1\text{kJ}$

83. **(a)** For a spontaneous process $\Delta G < 0$. Hence, for a spontaneous process ΔG must be –ve or we can say free energy is the quantity that decreases to a minimum in any chemical reaction.

84. **(d)** All are correct statements.

85. **(b)** For the reaction

$2\,ZnS \rightarrow 2\,Zn + S_2\,;\ \Delta G_1^o = 293\text{ kJ}$ ....(1)

$2\,Zn + O_2 \rightarrow 2\,ZnO\,;\ \Delta G_2^o = -480\text{ kJ}$ ....(2)

$S_2 + 2\,O_2 \rightarrow 2\,SO_2\,;\ \Delta G_3^o = -544\text{ kJ}$ ....(3)

ΔG^o for the reaction

$2\,ZnS + 3\,O_2 \rightarrow 2\,ZnO + 2\,SO_2$

can be obtained by adding eqn. (1), (2) and (3)

$\Rightarrow \Delta G^o = 293 - 480 - 544 = -731\text{ kJ}$

86. **(d)** A process is spontaneous only when there is decrease in the value of free energy, i.e., ΔG is –ve.

87. **(b)** For the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The reaction given is an example of decomposition reaction and we know that decomposition reactions are endothermic in nature, i.e., $\Delta H > 0$.

Further

$\Delta n = (1+1) - 1 = +1$

Hence more number of gaseous molecules are present in products which shows more randomness i.e., $\Delta S > 0$ (ΔS is positive)

88. **(b)** $\Delta G = \Delta H - T\,\Delta\,S$

At equilibrium, $\Delta G = 0$

$\Rightarrow\ 0 = (170 \times 10^3\,J) - T\,(170\,JK^{-1})$

$\Rightarrow\ T = 1000\,K$

For spontaneity, ΔG is – ve, which is possible only if $T > 1000\,K$.

89. **(a)** ΔS for the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$

$\Delta S = 50 - (30 + 60) = -40\text{ J}$

For equilibrium $\Delta G = 0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-40} = 750\text{ K}$$

90. **(a)** $\Delta G° = \Delta H° - T\Delta S°$

For a spontaneous reaction $\Delta G° < 0$

or $\Delta H° - T\Delta S° < 0 \Rightarrow T > \frac{\Delta H°}{\Delta S°}$

$$\Rightarrow\ T > \frac{179.1 \times 10^3}{160.2} > 1117.9\text{K} \approx 1118\text{K}$$

91. **(b)** $A \rightleftharpoons B$

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = -2.303\,RT\log_{10} K$

$-2.303\,RT\log_{10} K = \Delta H° - T\Delta S°$

$2.303\,RT\log_{10} K = T\Delta S° - \Delta H°$

$$\log_{10} K = \frac{T\Delta S° - \Delta H°}{2.303RT} = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 8.314 \times 298}$$

$= 9.998 \approx 10$

92. **(b)** For combustion reaction, ΔH is negative,

$\Delta n = (16+18) - (25+2) = +7$, so ΔS is + ve, reaction is spontaneous, hence ΔG is –ve.

93. **(a)** $\Delta G = -ve$ means the process is spontaneous.

94. **(c)** $\because\ \Delta G = \Delta H - T \cdot \Delta S$

For a spontaneous reaction ΔG should be negative

$\Delta H = -238\text{ kJ}, \Delta S = -87\text{ JK}^{-1}$

Hence, reaction will be spontaneous when $\Delta H > T \cdot \Delta S$. Therefore, at 1000, 1500 and 3000 K the reaction would be spontaneous.

95. **(d)** By $2\times$ (ii) – (i) + (iii)

$H_2(g) + 2C(s) \rightarrow C_2H_2(g),\ \Delta G° = 209\,kJ$

96. **(b)** A – (r), B – (p), C – (q), D – (s)

For spontaneity, $\Delta H - T\Delta S < 0$

97. **(a)** $\Delta G = \Delta H - T\Delta S$

$\because \Delta S_g > \Delta S_l > \Delta S_s$

$\therefore$ on melting the entropy increases and ΔG becomes more negative and hence it becomes easier to reduce metal

98. **(a)** $\Delta G = \Delta H - T\Delta S$ and $\Delta H = \Delta U + P\Delta V$

$= \Delta U + \Delta n_g RT$

$\Rightarrow \Delta H = (2100) + (2 \times 2 \times 298) = 3292\text{ cal}$

$\Rightarrow \Delta G = 3292 - 298\,(20) = -2668\text{ cal} = -2.67\text{ k cal}.$

99. **(d)** $\Delta G = \Delta H - T\,\Delta\,S$; ΔG is positive for a reaction to be non-spontaneous when ΔH is positive and ΔS is negative.

100. **(b)** (A) For a spontaneous process Gibb's free energy value is negative at constant temperature and pressure i.e. $\Delta G_{T,P} < 0$.

(B) In isobaric pressure, pressure remains constant i.e., $\Delta P = 0$ while in isothermal process, temperature remains constant i.e., $\Delta T = 0$.

(C) $\Delta H_{reaction}$ = (Σ bond energies of reactants) – (Σ bond energies of products)

(D) In exothermic process, energy is released.

So, the value of enthalpy is negative i.e., $\Delta H < 0$.

Exercise 3 : PREVIOUS YEARS MCQs

1. **(a)** $\Delta_r G^{\ominus} = -2.303\ RT \log K_p$

$T = 298$ K

$R = 8.314\ JK^{-1}mol^{-1}$

$\Delta_r G^{\ominus} = -115 \times 10^3$ J

$-115 \times 10^3\ J = -2.303 \times 8.314\ JK^{-1}mol^{-1} \times 298\ K \log_{10} K_P$

$\log_{10} K_P = 20.15$

2. **(d)** entropy $(\Delta S) = -42.4\ JK^{-1}$

enthalpy $(\Delta H) = -41.2 \times 10^3$ J

$$\Delta S = \frac{\Delta H}{T}$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-41.2 \times 10^3\ J}{-42.4\ JK^{-1}} = 971.7\ K.$$

3. **(b)** $\Delta G = \Delta H - T\Delta S$

$\Delta G = -57.8 - 298 \times (-176 \times 10^{-3}) = -5\ kJ\ mol^{-1}$

4. **(b)** Metallic bonding breaks in this reaction.

5. **(c)** The repulsion between two lone pair of electrons on oxygen atom decreases the bond angle whereas the –R groups at 'oxygen' atom shows repulsive interaction. As a result, there is a slight increase in the bond angle.

6. **(c)** Given $C_p = 75\ JK^{-1}\ mol^{-1}$

$n = \frac{100}{18}$ mole, $\quad Q = 1000$ J $\quad \Delta T = ?$

$$Q = nC_p\Delta T \Rightarrow \Delta T = \frac{1000 \times 18}{100 \times 75} = 2.4\ K$$

7. **(d)** We know that $\Delta G = \Delta H - T\Delta S$

When $\Delta H < 0$ and $\Delta S < 0$ then ΔG will be negative at low temperatures (positive at high temperature) and the reaction will be spontaneous.

8. **(b)** $\Delta U = q + w$

$= 10 \times 1000 - 2 \times (20) \times 101.3 = 5948$ J

9. **(b)** $PV = RT,\ PV = \frac{w}{M} RT,$

$$20P = \frac{120}{40} \times .0821 \times 400$$

or $\quad P = 4.92$ atm

10. **(b)** $\Delta G = \Delta H - T\Delta S$

$= -382.64 + (298 \times 145.6 \times 10^{-3})$

$= -339.3\ kJ\ mol^{-1}$

11. **(a)** Work done during adiabatic expansion

$= C_V(T_2 - T_1)$

or $\quad -3000 = 20(T_2 - 300) \Rightarrow T_2 = 150K$

12. **(a)** Given, n = 3 moles, $v_1 = 0.3L$, $v_2 = 2.5L$, $P_{ext} = 1.9$ atm

Workdone in isothermal process, $w = -P_{ex}dv$

$\therefore \quad w = -1.9 \times (2.5 - 0.3)$

$w = -4.18$L atm

$w = -4.18\text{L atm} \times 101.325\ JL^{-1}\ atm^{-1}$

$= -423.54$J

13. **(c)** $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

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

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

$\Delta n_g = 1 - 1 + \frac{1}{2} = -\frac{1}{2}$

$\therefore \quad \Delta H - \Delta U = -\frac{1}{2} \times 2 \times 300 = -300$cal

14. **(a)** $\Delta s = \frac{q_{rev}}{T}$

15. **(a)** $\Delta U = q + W$

According to first law of thermodynamics

$= q + (-P_{ex}.\Delta V) \quad (\because\ W = -P_{ex}.\Delta V)$

$\Delta U = q_p - P_{ex}.\Delta V$

16. **(a)** Work done is as :-

$W = -PdV$

$W = -P(V_2 - V_1)$

$V_1 = 10\ dm^3 = 10^{-2}\ m^3$

$V_2 = 2m^3$

$P = 101.325 \times 10^3$ pa

$W = -101.325 \times 10^3 (1.99) = -201.6$ kJ

17. **(b)** Combustion of ethanol is as :-

$$\begin{array}{cccc} C_2H_5OH\ + & 3O_2 \longrightarrow & 2CO_2\ + & 3H_2O \\ \downarrow & \downarrow & \downarrow & \downarrow \\ 1 & 3 & 2 & 3 \end{array}$$

0.138 kg = 138/46 = 3 mole

138 g

$3C_2H_5OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 9H_2O(l)$

$\Delta n = 6 - 9 = -3$

Work $= -\Delta nRT$

$= -(-3) \times 8.314 \times 300 = 7482$ J

18. **(c)** Work done in a chemical reaction,

$$W = -\Delta n_g RT$$

Where, Δn_g = number of moles of gaseous products – number of moles of gaseous reactants.

Reaction involved in combustion of ethane is,

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$\therefore \quad \Delta n_g = 2 - 4.5 = -2.5$

$W = (2.5\ \text{mol})\ (8.314\ JK^{-1}mol^{-1}) \times 300\ K$

$= 6235.5\ J = 6.2355\ KJ$

1 mole of C_2H_6 = 30g of C_2H_6

Work done during combustion of 30 g of

$C_2H_6 = 6.2355\ kJ$

$\therefore$ Work done during combustion of 90g of C_2H_6

$$= \frac{6.2355 \times 90}{30} = 18.7065\ kJ = 18.71\ kJ$$

19. **(b)** Work done during compression,

$W = p_{ext}\,\Delta V$

Given, $p_{ext} = 100\ KPa$, $T = 300\ K$

$\Delta V = V_2 - V_1$

$= (10 - 1)\ dm^3 = 9\ dm^3 = 0.99\ m^3$

$\therefore \quad W = 100\ KPa\ (0.99)\ m^3 = 99\ kJ.$

20. **(a)** According to first law of thermodynamics,

$\Delta U = q + W$

where, ΔU = Internal energy

q = Heat ; w = Work done

For isothermal process, $\Delta T = 0$, $\Delta U = 0$

$\therefore \quad q = -W$

21. **(c)** Relation between heat of reaction ($\Delta Hr°$) and bond enthalpies of reactants and products is

$\Delta H_r = \Sigma BE_{reactants} - \Sigma BE_{products}$

$\therefore \quad \Delta H°_{reaction} = \Sigma H°_{product\ bonds} - \Sigma H°_{reactant\ bonds}$

22. **(a)** For an isochoric process, $\Delta V = 0$

In this process, Acc to the first law of thermodynamics

$q = \Delta U - W$

$q = \Delta U - p\Delta V$

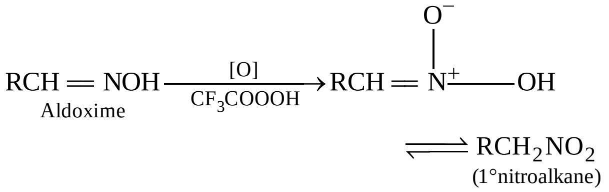
As $\Delta V = 0$

$q_V = \Delta U$

23. **(b)** The criterion for a spontaneous process is $\Delta G < 0$.

24. **(b)** Heat capacity is an extensive property.

25. **(a)** Primary nitroalkanes are obtained in good yield by oxidising aldoximes with the help of trifluoroperoxy acetic acid.



$$\underset{\text{Aldoxime}}{RCH = NOH} \xrightarrow[CF_3COOOH]{[O]} RCH = \overset{\overset{\displaystyle O^-}{|}}{N^+} - OH \rightleftharpoons \underset{(1°\text{nitroalkane})}{RCH_2NO_2}$$

5

Electrochemistry

Exercise 1 : WARM-UP

Topic-wise MCQs

1. **(d)** Charge on Mg and Ca ion is greater than that of Na and K, so Mg and Ca ions possess higher conductivity, also solvation of metal ion decreases as we move down the group, hence conductivity increases).

2. **(d)** Larger the size, lower the speed.

3. **(d)** ohm^{-1} cm^{-1}

4. **(d)** Conductance $G = \frac{KA}{l}$

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length.

Molar conductivity $\wedge_m = \frac{KA}{l}$

Since, $l = 1$ and $A = V$ (volume containing one mole of electrolyte) then $\wedge_m = K.V$

If the concentration is C mol/litre then $\wedge_m = K / C$

5. **(a)** $\kappa = \frac{1}{R} \times \frac{\ell}{A} \Rightarrow 1.3 = \frac{1}{50} \times \frac{\ell}{A} \Rightarrow \frac{\ell}{A} = 65 \text{m}^{-1}$

$$\Lambda = \frac{\kappa \times 1000}{\text{molarity}} = \frac{\left(\frac{1}{260} \times 65 \text{ m}^{-1}\right) \times 1000 \text{ cm}^3}{0.4 \text{ moles}}$$

$$= \frac{650 \text{ m}^{-1}}{260 \times 4 \text{ mol}} \times \frac{1}{1000} \text{ m}^3 = 6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

6. **(c)** [G (conductance) – siemens or ohm^{-1}(S).]

7. **(d)** $\kappa = \frac{1}{\text{R}} \times {}^{l}\!/_{\text{A}} = \left(\left(\frac{1}{1500}\right) \times 1.14\right) \text{S cm}^{-1}$

$$\Rightarrow \Lambda_\text{m} = \frac{1000 \times \kappa}{\text{C}} = 1000 \times \frac{\left(\frac{1.14}{1500}\right)}{0.001} \text{S cm}^2 \text{mol}^{-1}$$

$= 760 \text{ S cm}^2 \text{ mol}^{-1}$

8. **(d)** Cell constant $= l/a$ $\therefore$ Unit $= \text{m/m}^2 = \text{m}^{-1}$.

9. **(c)** $\Lambda_\text{m} = 1000 \times \frac{\kappa}{\text{M}}$

$$= 1000 \times \frac{2 \times 10^{-5}}{0.001} = 20 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Rightarrow \alpha = \frac{\Lambda_\text{m}}{\Lambda^\circ_\text{m}} = \frac{20}{190} = \left(\frac{2}{19}\right)$$

$$\underset{0.001(1-\alpha)}{\text{HA}} \rightleftharpoons \underset{0.001\,\alpha}{\text{H}^+} + \underset{0.001\alpha}{\text{A}^-}$$

$$K_\text{a} = 0.001\left(\frac{\alpha^2}{1-\alpha}\right) = \frac{0.001 \times \left(\frac{2}{19}\right)^2}{1 - \left(\frac{2}{19}\right)} = 12.3 \times 10^{-6}$$

10. **(b)** $\Lambda^\infty_{\text{AcOH}} = \Lambda^\infty_{\text{HCl}} + \Lambda^\infty_{\text{AcONa}} - {}^{\infty}_{\text{NaCl}}$

$= [426.2 + 91.0 - 126.5] = 390.7$

11. **(b)** Molar conductivity

$$\Lambda^\circ_{\text{Al}_2(\text{SO}_4)_3} = 2\Lambda^\circ_{\text{Al}^{3+}} + 3\Lambda^\circ_{\text{SO}_4^{2-}}$$

12. **(b)** $\Lambda^\circ_{\text{Ba(OH)}_2} = \Lambda^\circ_{\text{BaCl}_2} + 2\Lambda^\circ_{\text{NaOH}} - 2\Lambda^\circ_{\text{NaCl}}$

$$\Lambda^\circ_{\text{Ba(OH)}_2} = 280 \times 10^{-4} + 2 \times 248 \times 10^{-4} - 2 \times 126 \times 10^{-4}$$

$$\Lambda^\circ_{\text{Ba(OH)}_2} = 524 \times 10^{-4} \text{Sm}^2 \text{mol}^{-1}.$$

13. **(b)** Λ° for $\text{CH}_3\text{COOH} = \lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{H}^+}$

$$= \left(\lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{Na}^+}\right) + \left(\lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{Cl}^-}\right) - \left(\lambda^\circ_{\text{Na}^+} + \lambda^\circ_{\text{Cl}^-}\right)$$

$= 90 + 425 - 125 = 390 \text{ mho cm}^2 \text{ mol}^{-1}$.

Degree of dissociation $(\alpha) = \frac{\Lambda^\text{c}_\text{m}}{\Lambda^\circ_\text{m}} = \frac{7.8}{390} = 0.02$

14. **(a)** $xy \rightleftharpoons x^{2+} + y^{2-}$ $\Lambda^\infty_\text{m} = 57 + 73 = 130 \text{ S cm}^2 \text{mol}^{-1}$

15. **(d)** Molar conductivity $\wedge_\text{m} = \frac{\kappa \times 1000}{M}$

$$\kappa = \frac{1}{R} \times \text{cell constant}; = \frac{1}{R} \times \frac{\ell}{A}$$

$$= \frac{1}{5 \times 10^3 \Omega} \times \frac{1 \text{cm}}{100 \text{cm}^2}$$

$$= 2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1} \text{ or S cm}^{-1}$$

$$= \frac{2 \times 10^{-6} \times 1000}{0.1}; = \frac{2}{100} \text{ S cm}^2 \text{ mole}^{-1}$$

16. **(b)** Electronic conductance decreases with increase in temperature whereas electrolytic conductance increases with increase in temperature as no. of ions or charge carriers increases with increase in temperature.

17. **(c)** According to Kohlrausch law of independent migration of ions.

$$\Lambda^\text{o}_\text{m}(\text{CH}_3\text{COOH})$$

$= \Lambda^{o}_{m}(CH_3COONa) + \Lambda^{o}_{m}(HCl) - \Lambda^{o}_{m}(NaCl)$
$= 91.0\ S\,cm^2\,mol^{-1} + 426.16\ S\,cm^2\,mol^{-1} - 126.45\ S\,cm^2\,mol^{-1}$
$= 390.71\ S\,cm^2\,mol^{-1}$

18. **(d)** $\Lambda^{o}_{mCH_3COOH} = \Lambda^{o}_{mCH_3COO^-} + \Lambda^{o}_{mH^+}$

$= 50 + 350 = 400\ S\,cm^2\,mol^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda^{o}_{m}} = \frac{20}{400} = \frac{1}{20}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = C\alpha^2 = 7\times10^{-3}\times\left(\frac{1}{20}\right)^2$$

$= 1.7 \times 10^{-5}\ mol\ L^{-1}$

19. **(a)** According to Kohlrausch's law
$\lambda^{\circ}_{m}(AB) = \lambda^{\circ}_{m}(A^+) + \lambda^{\circ}_{m}(B^-)$
So, $\lambda^{\circ}_{m}(CH_3COOH) = \lambda^{\circ}_{m}(CH_3COO^-) + \lambda^{\circ}_{m}(H^+)$
So $\lambda^{\circ}_{m}(CH_3COOH)$

$$= \lambda^{\circ}_{m}(CH_3COOK) + \frac{1}{2}\lambda^{\circ}_{m}(H_2SO_4) - \frac{1}{2}\lambda^{\circ}_{m}(K_2SO_4)$$

$$= z + \frac{x}{2} - \frac{y}{2} = z + \left(\frac{x-y}{2}\right)$$

20. **(d)** Given:
$c_m = 0.5\ mol / dm^3$
$\kappa = 5.76 \times 10^{-3}\ S\ cm^{-1}$
$T = 298\ K$

$$\lambda_m = \frac{\kappa\times1000}{c_m} = \frac{5.76\times10^{-3}}{0.5} = 11.52\ Scm^2/mol$$

21. **(b)** HCl completely dissociates to give H^+ and Cl^- ions, hence it acts as very good electrolyte. While others are non-electrolytes.

22. **(b)** $\alpha = \dfrac{\Lambda_m}{\Lambda^{\infty}_{m}} = \dfrac{9.54}{238} = 0.04008 = 4.008\ \%.$

23. **(a)** Ratio of Molarity $= \dfrac{M_1}{M_2}$

$$= \frac{W_1 / mV}{W_2 / mV} = \frac{W_1}{W_2} = \frac{ppm_1}{ppm_2} = \frac{74.5}{149} = \frac{1}{2}$$

$$\frac{\Lambda_1}{\Lambda_2} = \frac{\kappa_1\times\frac{1000}{M_1}}{\kappa_2\times\frac{1000}{M_2}} = \frac{\kappa_1}{\kappa_2}\times\frac{M_2}{M_1} = \frac{50}{100}\times2 = 1$$

24. **(a)** $\Lambda_m = \dfrac{\kappa}{C} \Rightarrow \kappa = \Lambda_m \times C$

from question, $\kappa_1 = \kappa_2$

$\Lambda_{m_1}\times C_1 = \Lambda_{m_2}\times C_2$

$$\Lambda_{m_1}\times\frac{10\times10^3}{20} = \Lambda_{m_2}\times\frac{20\times10^3}{80}$$

$2\Lambda_{m_1} = \Lambda_{m_2}$

25. **(c)** $\lambda^{\infty}_{m}(AgI) = \lambda^{\infty}_{m}(NaI) + \lambda^{\infty}_{m}(AgNO_3) - \lambda^{\infty}_{m}(NaNO_3)$
$= 12.7 + 13.3 - 12.0 = 14.0$

26. **(a)** Given, $\kappa = 0.013\ cm^{-1}$, $R = 300\ \Omega$
Cell constant G* = conductivity(κ) × Resistance(R)
Cell constant $= 0.013 \times 300 = 3.9\ cm^{-1}$

27. **(b)** With the increase in concentration, conductivity of solution increases due to an increase in the number of ions. Thus, Z > X > Y.

28. **(d)**

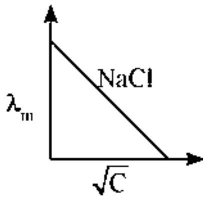
$$R_1 = 100\Omega;\ R_1 = \rho_1\frac{\ell}{A};\ \therefore\ \frac{\ell}{A} = R_1\lambda_1 = 1.29\times100\ cm^{-1}$$

$$R_2 = 258\Omega;\ Now,\ \frac{\ell}{A} = R_2\lambda_2;\ \lambda_2 = \frac{100\times1.29}{258} = \frac{1}{2}Scm^{-1}$$

$= 0.5\ Scm^{-1}$

29. **(b)** Acetic acid is a weak electrolyte. Gradual increase in dilution facilitates the dissociation of acetic acid. Therefore, molar conductivity increases.

30. **(c)**



31. **(a)** Given for 0.2 M solution,
$R = 50\ \Omega$
$k = 1.4\ S\ m^{-1} = 1.4 \times 10^{-2}\ S\ cm^{-1}$
Now, R =

$$\Rightarrow \frac{l}{A} = R\times\kappa = 50\times1.4\times10^{-2}\ cm^{-1}$$

For 0.5 M solution,
$R = 280\ \Omega$
$\kappa = ?$

$$\frac{l}{A} = 50\times1.4\times10^{-2}\ cm{-}1 \Rightarrow R = \rho\frac{l}{A} = \frac{1}{\kappa}\times\frac{l}{A}$$

$$\Rightarrow \kappa = \frac{1}{280}\times50\times1.4\times10^{-2} = \frac{1}{280}\times70\times10^{-2}$$

$= 2.5 \times 10^{-3}\ S\ cm^{-1}$

$$Now,\ \Lambda_m = \frac{\kappa\times1000}{M}$$

$$= \frac{2.5\times10^{-3}\ S\ cm^{-1}\times1000\ cm^3/L}{0.5\ mol/L}$$

$= 5\ S\ cm^2\ mol^{-1} = 5 \times 10^{-4}\ S\ m^2\ mol^{-1}$

32. **(c)** $ClCH_2COONa + HCl \rightarrow ClCH_2COOH + NaCl$

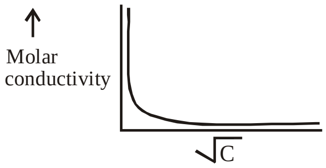
$\Lambda_{ClCH_2COONa} + \Lambda_{HCl} = \Lambda_{ClCH_2COOH} + \Lambda_{NaCl}$

$224 + 203 = \Lambda_{ClCH_2COOH} + 38.2$

$\Lambda_{ClCH_2COOH} = 427 - 38.2$

$= 388.8\ ohm^{-1}cm^2g\ eq^{-1}.$

33. **(d)**



Molar conductivity decreases sharply with the increase in concentration because the total volume V of solution containing 1 mol of electrolyte decreases

34. **(d)** Daniell cell is a type of galvanic cell.

35. **(b)** The cell in which Cu and Zn rods are dipped in its solution is called Daniell cell.

36. **(d)** In electrolytic cell, the flow of electrons is from anode to cathode through internal supply.

37. **(d)** When both the electrodes are kept in the same solution there will be no requirement of salt bridge.

38. **(c)** The magnitude of the electrode potential of a metal is a measure of its relative tendency to loose or gain electrons.

$$M \rightarrow M^{n+} + ne^- \quad \text{(oxidation potential)}$$

$$M^{n+} + ne^- \rightarrow M \quad \text{(reduction potential)}$$

39. **(c)** $2AgCl(s) + H_2(g) \rightarrow 2HCl(aq) + 2Ag(s)$

The activities of solids and liquids are taken as unity and at low concentrations, the activity of a solute is approximated to its molarity.

The cell reaction will be

$$Pt(s) \mid H_2(g), 1bar \mid H^+(aq)1M \mid AgCl(aq)1M \mid Ag(s)$$

40. **(a)** Salt bridge allows the flow of current by completing circuit. No current will flow and voltage will drop to zero, if salt bridge is removed.

41. **(b)** The oxidation state of Cr changes from +6 to +3.

$$\underset{1mol}{\overset{+6}{Cr_2}O_7^{-2}} + \underset{6\,mol}{6e^-} \longrightarrow 2Cr^{+3}$$

⇒ number of faradays = moles of electrons = 6

42. **(b)** Quantity of charge passed = 0.5 × 30 × 60 = 900 coulomb

900 coulomb will deposit = 0.2964g of copper

∴ 96500 coulomb will deposit

$$= \frac{0.2964}{900} \times 96500 = 31.75 \text{ g of copper}$$

Thus, 31.75 is the eq. mass of copper

At. mass = Eq. mass × Valency

$$63.56 = 31.75 \times x$$

$$x = +2.$$

43. **(a)** The charge carried by 1 mole of electrons is one faraday. Thus for a reaction

$$M^{n+} + ne^- \longrightarrow M$$

nF = 1 mole of M

$$\underset{\substack{3F \\ 1F}}{Al^{3+} + 3e^-} \longrightarrow \underset{\substack{1\text{ mol} \\ 1/3\text{ mol}}}{Al}$$

$$\underset{\substack{2F \\ 1F}}{Cu^{2+} + 2e^-} \longrightarrow \underset{\substack{1\text{ mol} \\ 1/2\text{ mol}}}{Cu}$$

$$\underset{1F}{Na^+ + e^-} \longrightarrow \underset{1\text{ mol}}{Na}$$

The mole ratio of Al, Cu and Na deposited at the respective cathode is $\frac{1}{3} : \frac{1}{2} : 1$ or 2 : 3 : 6.

44. **(b)** At Anode, $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

Equivalent wt. of chlorine $(E_{Cl_2}) = \frac{35.5 \times 2}{2} = 35.5$

$$W_{Cl_2} = \frac{E_{Cl_2} \times I \times t}{96500} = \frac{35.5 \times 2 \times 30 \times 60}{96500} = 1.32 \text{ g.}$$

45. **(b)** $H_2O \rightleftharpoons H^+ + OH^-$

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

∴ 0.5 mole of H_2 is liberated by 1 F = 96500 C

0.01 mole of H_2 will be liberated by

$$= \frac{96500}{0.5} \times 0.01 = 1930\,C$$

$$Q = I \times t$$

$$t = \frac{Q}{I} = \frac{1930\ C}{10 \times 10^{-3} A} = 19.3 \times 10^4 \text{ sec}$$

46. **(c)** Electrorefining and electroplating are done by electrolysis.

47. **(d)** $\frac{W_A}{E_A} = \frac{W_B}{E_B}; \ \frac{1.6}{8} = \frac{\text{Wt. of Ag}}{108}$

∴ Wt. of Ag = 21.6 g

48. **(b)** $Cu^{2+} + \underset{2 \times 96500\ C}{2e^-} \rightarrow \underset{63.6\ g}{Cu(s)}$

$$9650\ C \text{ will deposit} = \frac{63.6}{2 \times 96500} \times 9650 = 3.18\text{ g}$$

49. **(d)** $Ag^+ + e^- \longrightarrow Ag$

96500 coulombs deposit = 108 g of Ag

∴ 965 coulombs deposit $= \frac{108}{96500} \times 965 = 1.08$ g Ag

50. **(a)** According to Faraday law of electrolysis, amount of electricity required to deposit 1 mole of metal = 96500 C = 1 F

i.e., for deposition of 108g Ag, electricity required = 1 F

51. **(c)** $E = \frac{96500 \times w}{I \times t} \Rightarrow E = \frac{96500 \times m}{C \times t}$

52. **(d)** Charge (Coulombs) pass per second = 10^{-6}

Number of electrons passed per second

$$= \frac{10^{-6}}{1.602 \times 10^{-19}} = 6.24 \times 10^{12}$$

53. **(d)** Charge on one mole of electrons = 96500 C.

54. **(c)** According to the definition, 1 F or 96500 C is the charge carried by 1 mol of electrons. When water is electrolysed:

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$$

So, 4 Faraday of electricity liberate = 32 g of O_2.

Thus 1 Faraday of electricity liberate

$= \frac{32}{4}$ g of O_2 = 8 g of O_2

55. **(a)** When molten or fused NaCl is electrolysed, it yields metallic sodium and gaseous chlorine. Reactions involved are as follows:

$NaCl\,(s) \longrightarrow Na^+\,(l) + Cl^-\,(l)$

$Na^+\,(l) + e^- \longrightarrow Na\,(l)$ (at cathode) $Cl^-\,(l) \longrightarrow Cl\,(g) + e^-$ (at anode) $Cl\,(g) + Cl(g) \longrightarrow Cl_2\,(g)$

56. **(b)** $Pt^{4+} + 4e^- \longrightarrow Pt$

4F electricity is required to deposit 1 mole of Pt.

$\therefore$ 0.80 F of electricity will deposit

= 1/4 × 0.80 moles of Pt = 0.20 mol.

57. **(d)** 1 mole of e^- = 1F = 96500 C

27g of Al is deposited by 3 × 96500 C

5120 g of Al will be deposited by

$$= \frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7\,C$$

58. **(a)** $\overset{+4}{VO_3^{2-}} \longrightarrow \overset{+5}{VO_4^{3-}}$ This reaction involves transfer of one electrons.

Thus, for conversion of 1 mole, 1 F of electricity is required.

Charge = 0.2 × 1 Faraday = 0.2 × 96500 coulombs

= 19300 = 1.93×10^4 coulombs

59. **(d)** $C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

$$E_{C_6H_5NO_2}\,(\text{eq.wt}) = \frac{123}{6} = 20.5$$

Number of coulombs required

$$= \frac{w \times 96500}{\text{Eq. wt}} = \frac{12.3 \times 96500}{20.5} = 57900\text{ C}$$

60. **(d)** Oxidation reaction at anode, upon electrolysis of water:

$2H_2O\,(l) \longrightarrow O_2\,(g) + 4H^+\,(aq) + 4e^-;\ E^\circ_{cell} = +1.23$ V

Thus, 1 mole of oxygen is liberated by 4 moles of electrons.

4 × 96500 coulombs electricity liberates = 22.4 L. O_2 gas

9650 coulombs electricity liberates

$$= \frac{22.4}{4 \times 96500} \times 9650 = 0.56\text{ L. } O_2 \text{ gas}$$

61. **(b)** $Fe^{2+} + 2e^- \longrightarrow Fe;\ E_{Fe} = \frac{56}{2} = 28$

1 Faraday liberates = 28 g of Fe

3 Faraday liberates = 3 × 28 = 84 g

62. **(d)** Change in temperature, electrode or electrolyte compsoition does not effect faraday's law.

63. **(c)** $Fe^{3+} + 3e^- \longrightarrow Fe$

3F ≡ 1 mole Fe is deposited

For 56 g ≡ 3 × 96500 (required charge)

$$\text{For } 0.3482\text{ g} \equiv \frac{3 \times 96500}{56} \times 0.3482$$

= 1800 coulomb

$Q = it$

$\Rightarrow 1800 = 1.5\,t$

$\Rightarrow t = 1200$ s = 20 min

64. **(a)** Gold is an inert metal. Electrodes made up of inert metals does not participate in chemical reaction.

65. **(c)** Using Faraday's second law of electrolysis,

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equ. wt. of Cu}}{\text{Equ. wt. of Ag}}$$

$$\Rightarrow \frac{w_{Cu}}{0.18} = \frac{63.5}{2} \times \frac{1}{108}$$

$$\Rightarrow w_{Cu} = \frac{63.5 \times 18}{2 \times 108 \times 100} = 0.0529\text{ g.}$$

66. **(b)** Fe_3O_4 is a mixture of FeO and Fe_2O_3. The oxidation state of Fe in FeO and Fe_2O_3 are +2 and +3 respectively.

$\overset{(+2)}{FeO} \xrightarrow{2e^-} Fe$

$\overset{(+3)}{Fe_2\,O_3} \xrightarrow{6e^-} 2Fe$

$Fe_3O_4 \xrightarrow{8F} 3Fe$

3 mole Fe requires = 8F

1 mole Fe requires $\frac{8}{3}$ F = 2.6 F

67. **(a)** During the electrolysis of dil. sulphuric acid using Pt electrodes following reaction occurs.

At cathode : $4H^+\,(aq) + 4e^- \rightarrow 2H_2\,(g)$

At anode : $2H_2O\,(l) \rightarrow O_2\,(g) + 4H^+\,(aq) + 4e^-$

68. **(d)** 1 equivalent of any substance is deposited by 1 F of charge.

20 g calcium contains,

$$\text{Number of equivalents} = \frac{\text{Given mass}}{\text{Equivalent mass}}$$

$$\text{Equivalent mass of Ca} = \frac{\text{Atomic mass}}{\text{Valency}} = \frac{40}{2} = 20$$

$$\text{Number of equivalents} = \frac{20}{20} = 1$$

So, 1 Faraday of charge is required to deposit 1 equivalent of Ca.

69. **(c)** $\underset{0.1\text{ mole}}{\overset{(+6)}{MnO_4^{2-}}} \longrightarrow \overset{(+7)}{MnO_4^-} + e^-$

Quantity of electricity required = 0.1F

= 0.1 × 96500 = 9650 C

70. **(c)** Applying, $w = \frac{EIt}{96500}$

Equivalent weight of cobalt (II) = 59/2

$I = 10\,\text{A}$

Time (t) = 109 min = 109 × 60 sec

Substituting these values we get,

$$w = \frac{59 \times 10 \times 109 \times 60}{2 \times 96500} = 20.0$$

71. **(d)** Calomel electrode is used as reference electrode.

72. **(b)** Given $E_{Sn^{4+}/Sn^{2+}} = +0.15\,\text{V}$; $E_{Cr^{3+}/Cr} = -0.74\,\text{V}$

Sn^{4+} will reduce and Cr will oxidize, as the standard reduction potential value is positive for Sn^{4+}.

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (0.74 + 0.15)\,\text{V} = 0.89\,\text{V}$$

73. **(d)** As the reduction potential for second reaction is more than that of first reaction, Ag_2O will reduce and Zn will oxidize.

$$E^\circ_{Cell} = E^\circ_{OP} + E^\circ_{RP} = 0.76 + 0.34 = 1.10\,\text{V}$$

74. **(a)** $E = E^\circ - \frac{0.059}{n} \log \frac{1}{[H^+]}$

$$= 0 - \frac{0.059}{1} \log \frac{1}{10^{-4}} = -0.236\text{V}$$

75. **(d)** Here $n = 4$, and $[H^+] = 10^{-3}$ (as pH = 3)

Applying Nernst equation

$$E = E^\circ - \frac{0.059}{n} \log \frac{[Fe^{2+}]^2}{[H^+]^4 (p_{O_2})}$$

$$= 1.67 - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1}$$

$$= 1.67 - \frac{0.059}{4} \log 10^7 = 1.67 - 0.103 = 1.567\,\text{V}$$

76. **(b)** For $Zn^{2+} \rightarrow Zn$

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{2.303RT}{nF} \log \frac{[Zn]}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.06}{2} \log \frac{1}{[0.1]} = -0.76 - 0.03$$

$$E_{Zn^{2+}/Zn} = -0.79\text{V}$$

77. **(d)** When the concentration of all reacting and product species kept unity, then $E_{cell} = E^\circ_{cell}$ and the given relation will become $\Delta_r G = -nFE^\circ_{cell}$. *e.g.* redox reaction for Daniell cell :

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

solutions of $CuSO_4$ and $ZnSO_4$ are the reacting species.

The E_{cell} for this cell :

$$E_{cell} = E^\circ_{cell}$$

$$-\frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \Rightarrow E_{cell} = E_{cell}$$

if $[Zn^{2+}] = [Cu^{2+}] = 1$

78. **(c)** Using the relation,

$$E^\circ_{cell} = \frac{2.303\,RT}{nF} \log K_c = \frac{0.0591}{n} \log K_c$$

$$\therefore \quad 0.295\text{ V} = \frac{0.0591}{2} \log K_c \Rightarrow \log K_c = \frac{2 \times 0.295}{0.0591} = 10$$

or $K_c = 1 \times 10^{10}$

79. **(a)** The cell reaction is

$$H_2(g) + Cu^{2+}(aq.) \rightarrow 2H^+(aq.) + Cu(s)$$

$$n = 2$$

According to Nernst equation

$$0.31 = 0.34 - \frac{0.06}{2} \log \frac{[H^+]^2}{[Cu^{2+}]}$$

pH = 3–log[H⁺] = 3 $[H^+] = 10^{-3}$

$[Cu^{2+}] = 10^{-7}$ M

$x = 7$

80. **(d)** cell reaction → $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

According to Nernst equation

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$0.43 = E^\circ_{cell} - \frac{0.06}{2} \log \frac{(0.001)}{(0.01)^2}$$

$$E^\circ_{cell} = 0.46\text{V}$$

$$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} \Rightarrow 0.46 = 0.80 - E^\circ_{Cu^{2+}/Cu}$$

$$E^\circ_{Cu^{2+}/Cu} = 0.34\text{ volt} \Rightarrow 34 \times 10^{-2}$$

81. **(d)** $E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$

At equilibrium,

$E_{cell} = 0$ and $Q = K_c \Rightarrow E_{cell} \neq E^\circ_{cell}$

82. **(b)** For the given cell

$$E_{cell} = E^\circ_{cell} - \frac{0.059\text{V}}{2} \log \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

The cell potential decreases with increase in $[Zn^{2+}(aq)]$ and increases with increase in $[Cu^{2+}(aq)]$.

83. **(b)** $\frac{1}{2}H_2 + Ag^+ \rightarrow H^+ + Ag$; $n = 1$

$\Delta G^\circ = -nE^\circ F = -1 \times 0.5332 \times 96500$ J

= – 51.35 kJ/mol

84. **(c)** $Fe^{3+} + I^- \longrightarrow I_2 + Fe^{2+}$

The E° value for spontaneous reaction is positive.

$$E^\circ_{Cell} = E^\circ_{cathode} - E^\circ_{anode} = (0.77 - 0.54)\,\text{V} = 0.23\,\text{V}$$

$= 23 \times 10^{-2}$ V.

85. **(b)** From Nernst Eq.

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln Q$$

$$\text{or, } E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF}\log Q$$

$$\text{or, } 0.801 = (0.008 + 0.763) - \frac{0.06\times(-2)}{n} \quad \text{or, } n = 4$$

86. **(d)** $E_{red} = E^{o}_{red} + \frac{0.591}{n}\log[M^{n+}]$

Lower the concentration of M^{n+}, lower is the reduction potential.

Hence order of reduction potential is : $Q > R > S > P$

87. **(c)** $\Delta G = -nFE^{\circ}_{cell}$

$$Sn^{2+} + 2e^- \rightarrow Sn \quad \Delta G^{\circ}_1 = +2\times 0.140\times F \quad .....(i)$$
$$Sn^{4+} + 4e^- \rightarrow Sn \quad \Delta G^{\circ}_2 = -4\times 0.01\times F \quad .....(ii)$$

Subtracting (i) from (ii), we get

$$Sn^{4+} + 2e^- \rightarrow Sn^{2+} \quad \Delta G^{\circ}_3 = -2\times E^{\circ}_{Sn^{4+}/Sn^{2+}}\times F$$

$$\Delta G^{\circ}_3 = \Delta G^{\circ}_2 - \Delta G^{\circ}_1 \Rightarrow -2\times E^{\circ}\times F = -(0.04 + 0.28)\times F$$

$$E^{\circ} = 0.16 \text{ volt} = 16\times 10^{-2}\text{ V}$$

88. **(a)** The Half cell reaction is $Zn^{2+} + 2e^- \longrightarrow Zn$.

$[E°_{cell} = -E°_{ox}]$

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

$$= -0.763 - \frac{0.059}{2}\log\frac{1}{0.01} = -0.822\text{V}$$

$E_{oxi} = 0.822$ V

89. **(a)** Apply Nernst equation to the reaction

$Pb + Sn^{2+} \rightarrow Pb^{2+} + Sn$

$$E_{cell} = E^{\circ} - \frac{0.059}{2}\times\log\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

$$\text{or} \quad E° + \frac{0.059}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]} = E_{cell}$$

$$\text{or} \quad \log\frac{[Sn^{2+}]}{[Pb^{2+}]} = \frac{0.01\times 2}{0.059} = 0.3 \quad (\because E_{cell} = 0)$$

$$\text{or} \quad \frac{[Sn^{2+}]}{[Pb^{2+}]} = \text{antilog } (0.3)$$

90. **(d)** $E_{cell} = 0$; when cell is completely discharged.

$$E_{cell} = E°_{cell} - \frac{0.059}{2}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

$$\text{or } 0 = 1.1 - \frac{0.059}{2}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

$$\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = \frac{2\times 1.1}{0.059} = 37.3$$

$$\therefore \left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = 10^{37.3}$$

91. **(c)** $Mg \longrightarrow Mg^{2+}\, 2e^-$ (oxidation at anode)

$Ag^+ + e^- \longrightarrow Ag$ (reduction at cathode)

Anode is written on the left and cathode is written on the right side.

92. **(c)** $E^{\circ}_{cell} = \frac{2.303RT}{nF}\log K$

Given : $E^{\circ}_{cell} = 0.59$ V, n = 1

$$0.59 = \frac{0.059}{1}\log K$$

$$\frac{0.59}{0.059} = \log K$$

$10 = \log K$

$K = 10^{10}$

93. **(a)** $\Delta G = -nFE°$

$= -2\times 96500\times 0.24 = -46320$ J/mol

$= -46.32$ kJ/mol

94. **(b)** For cell,

$Zn|ZnSO_4(0.01\text{ M})\,||\,CuSO_4(1.0\text{ M})|Cu$

$$E_{cell} = E°_{cell} - \frac{2.303RT}{nF}\,\frac{\log[Zn^{2+}]}{[Cu^{2+}]}$$

$$\therefore \quad E_1 = E°_{cell} - \frac{2.303RT}{2\times F}\times\log\frac{(0.01)}{1}$$

When concentrations are changed for $ZnSO_4$ and $CuSO_4$, we can write

$$E_2 = E°_{cell} - \frac{2.303RT}{2F}\times\log\frac{1}{0.01}$$

$\therefore \quad E_1 > E_2$

95. **(a)** $2H^+(aq) + 2e^- \rightarrow H_2(g)$

$$\therefore \quad E \approx E^0 - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$$0 = 0 - 0.0295\log\frac{P_{H_2}}{(10^{-7})^2}$$

$$\frac{P_{H_2}}{(10^{-7})^2} = 1$$

$P_{H_2} = 10^{-14}$ atm

96. **(a)** $\Delta E° = E°_{red} + E°_{oxid} = -1.81 - 1.51 = -2.69$

Since $\Delta E°$ is negative

$\therefore \quad \Delta G = -nFE°$, ΔG will have positive value so, forward reaction is not possible.

97. **(a)** $\underset{1\text{ atm}}{H_2} \longrightarrow \underset{10^{-10}}{2H^+} + 2e^-$

$$E_{H_2/H^+} = 0 - \frac{0.059}{2}\log\frac{(10^{-10})^2}{1}$$

$$E_{H_2/H^+} = +\,0.59\text{V}$$

98. **(d)** We know that, $\ln K = \dfrac{nFE^{\circ}_{cell}}{RT}$

After putting the given values, we get

$\ln K = \dfrac{2 \times 96000 \times 2}{8 \times 300} = 160 \;\therefore\quad K = e^{160}$

99 **(b)** Cell reaction :

$$M(s) + 3Ag^+(aq) \longrightarrow M^{3+}(aq) + 3Ag(s)$$

$$E = E^0 - \frac{0.0591}{n}\log\frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

$$0.421 = E^0 - \frac{0.0591}{3}\log\frac{0.001}{(0.01)^3}$$

$E^0 = 0.48\text{ V}$

$$E^0 = E^0_{Ag^+/Ag} - E^0_{M^{3+}/M}$$

$$E^0_{M^{3+}/M} = 0.8\text{V} - 0.48\text{V} = 0.32\text{ Volt}$$

100. **(a)** pH of solution I = 3

$\therefore [H^+]_1 = 10^{-3}$ M

pH of solution II = 6

$\therefore [H^+]_2 = 10^{-6}$ M

Now, $E_{cell} = E^{\circ}_{cell} - \dfrac{0.059}{1}\log\dfrac{10^{-6}}{10^{-3}} = 0 + 0.059 \times 3$

$E_{cell} = 0.177$ V

101. **(d)**

102. **(d)**

103. **(b)** $H_2 - O_2$ fuel cell supply electrical power.

104. **(c)** Fuel cells produce electricity with an efficiency of about 100%.

105. **(b)** In $H_2 - O_2$ fuel cell, the combustion of H_2 occurs to create potential difference between the two electrodes.

106. **(b)** Oxidation takes place at zinc anode.

107. **(c)** $2NH_4Cl + Zn \rightarrow 2NH_3 + ZnCl_2 + H_2\uparrow$.

108. **(d)** Primary cells are those cells, in which the reaction occurs only once and after use over a period of time, it becomes dead and cannot be reused again. *e.g.*, Leclanche cell and mercury cell.

109. **(c)** The electrolyte used in Leclanche cell is moist paste of NH_4Cl and $ZnCl_2$.

110. **(c)** Mercury cell being primary in nature can be used only once.

111. **(b)** During charging, the lead storage battery behaves like an electrolytic cell. So, at anode the reaction is

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$$

112. **(c)** Ni – Cd cells have longer half-life than lead-storage battery.

113. **(d)** $Pb + PbO_2 + 2H_2SO_4 \xrightleftharpoons[\text{Recharge}]{\text{Discharge}} 2PbSO_4 + 2H_2O.$

Sulphuric acid is consumed on discharging.

114. **(c)** At cathode, reduction occurs according to following reaction.

$$\overset{+4}{Mn}O_2 + NH_4^+ + e^- \longrightarrow \overset{+3}{Mn}O(OH) + NH_3$$

115. **(a)** Batteries and fuel cells convert chemical energy into electrical energy.

116. **(c)** As the value of standard reduction potential decreases the reducing power increases *i.e.*, $\underset{(-3.0)}{Z} > \underset{(-1.2)}{X} > \underset{(+0.5)}{Y}$

117. **(a)** Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.

118. **(b)** Without losing its concentration, $ZnCl_2$ solution cannot kept in contact with Al because Al is more reactive than Zn due to its highly negative electrode reduction potential.

119. **(a)** According to standard electrode potential table, the order of electrode couple from top to bottom is :

$Cl_2/Cl^- > Ag^+/Ag > I_2/I^- > Na^+/Na > Li^+/Li$

120. **(d)** Higher the reduction potential, stronger is the oxidising agent.

121. **(a)** Since oxidation potential of Zn is highest hence strongest reducing agent.

122. **(c)** Fuel cell converts the chemical energy into electrical energy.

123. **(b)** The cell reactions during charging of lead storage battery are

At anode $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

At cathode $PbSO_4(s) + 2H_2O(l) \rightarrow$

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-.$$

124. **(b)** During the charging of lead storage battery, the following reaction takes place.

$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

At anode $PbSO_4$ reduced back to metallic Pb. At cathode $PbSO_4$ oxidised back to PbO_2.

From the balanced reacation.

$\because x_1 = +2, y_1 = 0$

$x_2 = +2, y_2 = 4$

125. **(b)** Reducing power $\propto \dfrac{1}{E_{RP}}$

Exercise 2 : ACCELERATOR

Topic-wise MCQs

1. **(d)** Molarity = 0.01 M ; Resistance = 40 ohm;

Cell constant $\frac{l}{A} = 0.4\,\text{cm}^{-1}$.

Specific conductivity (κ)

$$= \frac{\text{cell constant}}{\text{resistance}} = \frac{0.4}{40} = 0.01\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\text{Molar conductance } (\wedge_m) = \frac{1000\kappa}{\text{Molarity}}$$

$$= \frac{1000 \times 0.01}{.01} = 10^3\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

2. **(a)** Difluoroacetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity.

3. **(c)** $k = \frac{1}{R} \times \text{Cell constant} = \frac{0.47}{31.6} = 0.01487$

4. **(d)** $\Lambda^\circ_{m(NH_4Cl)} = \Lambda^\circ_{m NH_4^+} + \Lambda^\circ_{m Cl^-}$

$$\Lambda^\circ_{m(NaOH)} = \Lambda^\circ_{m Na^+} + \Lambda^\circ_{m OH^-}$$

$$\Lambda^\circ_{m(NaCl)} = \Lambda^\circ_{m Na^+} + \Lambda^\circ_{m Cl^-}$$

$$\therefore\ \Lambda^\circ_{m}\left(NH_4^+\right) + \Lambda^\circ_{m}\left(OH^-\right)$$

$$= \Lambda^\circ_{m}\left(NH_4^+\right) + \Lambda^\circ_{m}\left(Cl^-\right) + \Lambda^\circ_{m}\left(Na^+\right)$$

$$+ \Lambda^\circ_{m}\left(OH^-\right) - \left[\Lambda^\circ_{m}\left(Na^+\right) + \Lambda^\circ_{m}\left(Cl^-\right)\right]$$

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

5. **(c)**

6. **(b)** $\Lambda^\circ_{CH_3COOH}$ is given by the following equation

$$\Lambda^\circ_{CH_3COOH} = (\Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl}) - (\Lambda^\circ_{NaCl})$$

Hence Λ°_{NaCl} is required.

7. **(b)** Here, R = 31.6 ohm

$$\therefore\ \text{Conductance} = \frac{1}{R} = \frac{1}{31.6}\text{ohm}^{-1} = 0.0316\ \text{ohm}^{-1}$$

Specific conductance = conductance × cell constant.

$= 0.0316\ \text{ohm}^{-1} \times 0.367\ \text{cm}^{-1}$

$= 0.0116\ \text{ohm}^{-1}\ \text{cm}^{-1}$

Now, molar concentration = 0.5M (given)

$= 0.5 \times 10^{-3}$ mole cm^{-3}

$$\therefore\ \text{Molar conductance} = \frac{\kappa}{C} = \frac{0.0116}{0.5 \times 10^{-3}}$$

$$= 23.2\ \text{S cm}^2\ \text{mol}^{-1}$$

8. **(d)** $(\Lambda^0_m)_{NaBr} - (\Lambda^0_m)_{NaI}$

$$= \Lambda^\circ_m N\overset{+}{a} + \Lambda^\circ_m Br^- - (\Lambda^\circ_m N\overset{+}{a} + \Lambda^\circ_m I^-)$$

$$= \Lambda^\circ_m Br^- - \Lambda^\circ_m I^-$$

$(\Lambda^0_m)_{KBr} - (\Lambda^0_m)_{NaBr}$

$$= \Lambda^\circ_m K^+ + \Lambda^\circ_m Br^- - (\Lambda^\circ_m Na^+ + \Lambda^\circ_m Br^-)$$

$$= \Lambda^\circ_m K^+ - \Lambda^\circ_m N\overset{+}{a}$$

$$\therefore\ (\Lambda^0_m)_{NaBr} - (\Lambda^0_m)_{NaI} \neq (\Lambda^0_m)_{KBr} - (\Lambda^0_m)_{NaBr}$$

9. **(a)** Order of acidic strength is :

$HCOOH > C_6H_5COOH > CH_3COOH$

More the acidic strength, more will be the dissociation of acid into ions and more will be the conductivity.

Thus, order of conductivity will be,

$HCOOH > C_6H_5COOH > CH_3COOH$

(A) > (C) > (B)

10. **(a)** Since, KCl is more conducting than NaCl, therefore, graph (a) is correct.

11. **(c)** Given: $\Lambda^\circ_m(\text{NaCl}) = 126.4\ \text{S cm}^2\ \text{mol}^{-1}$, $\Lambda^\circ_m(\text{HCl}) = 425.9\ \text{S cm}^2\ \text{mol}^{-1}$ and $\Lambda^\circ_m(\text{NaA}) = 100.5\ \text{S cm}^2\ \text{mol}^{-1}$

$$\Lambda^\circ_m(\text{HA}) = \lambda^\circ_{H^+} + \lambda^\circ_{A^-}$$

$$= \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{A^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$$

$$= \Lambda^\circ_m(\text{HCl}) + \Lambda^\circ_m(\text{NaA}) - \Lambda^\circ_m(\text{NaCl})$$

$$\Lambda^\circ_m(\text{HA}) = 429.5 - 126.4 + 100.5 = 400\ \text{S cm}^2\ \text{mol}^{-1}$$

κ (HA) = 5×10^{-5} S cm^{-1}

$$\Lambda_m(\text{HA}) = \frac{\kappa(\text{HA}) \times 1000}{\text{Molarity of HA}} = \frac{5 \times 10^{-5} \times 1000}{0.001}$$

$$= 50\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m(\text{HA})}{\Lambda^\circ_m(\text{HA})} = \frac{50}{400} = 0.125$$

12. **(a)** $\lambda^\circ_m(NH_4Cl) = 185\ \text{Scm}^2\ \text{mol}^{-1}$

$$\Rightarrow\ \left(\lambda^\circ_m\right)_{NH_4^+} + \left(\lambda^\circ_m\right)_{Cl-} = 185$$

$$\left(\lambda^\circ_m\right)_{NH_4^+} = \left(\lambda^\circ_m\right)_{NH_4Cl} - \left(\lambda^\circ_m\right)_{Cl^-}$$

$$= 185 - 70 = 115\ \text{Scm}^2\ \text{mol}^{-1}$$

$$\left(\lambda^\circ_m\right)_{NH_4OH} = \left(\lambda^\circ_m\right)_{NH_4^+} + \left(\lambda^\circ_m\right)_{OH^-} = 115 + 170$$

$$= 285\ \text{Scm}^2\ \text{mol}^{-1}$$

$$\text{degree of dissociation} = \frac{(\lambda_m)NH_4OH}{\left(\lambda^\circ_m\right)_{NH_4OH}}$$

$$= \frac{85.5}{285} = 0.3 = 3 \times 10^{-1}$$

13. **(c)** We have 0.2 g of NaOH in 100 mL solution

$$M = \frac{0.2}{40 \times 100} \times 1000 = 0.0\,5\text{ M}$$

$$\kappa = \frac{1}{0.870} = 1.15\text{S m}^{-1} = 1.15 \times 10^{-2}\text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{m} = \frac{1.15 \times 10^{-2} \times 1000}{0.05} = 230\text{ S cm}^2\text{ mol}^{-1}$$

$= 23 \times 10^4$ m S cm^2 mol^{-1} = 23×10^2 m S dm^2 mol^{-1}

14. **(b)** Given : $\Lambda_+ = 57$ S cm^{2}mol^{-1} ; $\Lambda_- = 73$ S cm^{2}mol^{-1}

Apply Kohlrausch's law

$\Lambda_m = \lambda_+ + \lambda_- = 57 + 73 = 130$ S cm^{2}mol^{-1}

15. **(a)** $\Lambda_m = \Lambda_m^o - A\sqrt{C}$

Unit of $A\sqrt{C}$ = unit of Λ_m = S cm^2 mol^{-1}

Unit of A = S cm^2 mol$^{-3/2}$ L$^{1/2}$.

16. **(c)** Conductivity of electrolytic cell is affected by concentration of electrolyte, nature of electrolyte and nature of solvent.

17. **(b)** $G = \frac{1}{R}$

18. **(d)**

19. **(d)**

20. **(d)**

21. **(a)** On applying an external voltage greater than 1.1 V in a Daniell cell the current flows in the reverse direction i.e., from Zn to Cu (cathode to anode) and electrons flow from Cu to Zn.

22. **(d)** Electrolysis of H_2SO_4

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

23. **(c)** $Al^{3+} + 3e^- \longrightarrow Al(s)$

3F required for 27 gm

$$W = \frac{E \times i \times t}{96500} = \frac{M \times i \times t}{n \times 96500}$$

$$= \frac{27 \times 2 \times 30 \times 60}{3 \times 96500} = 0.336\text{ gm Al}$$

24. **(c)** At anode.

$$2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$$

25. **(b)** $Au^{3+} + 3e^- \longrightarrow Au\,(s)$

$$\Rightarrow \frac{W}{E} = \frac{Q}{1F}$$

$$\Rightarrow Q = \frac{W \times F}{E} = \frac{W}{E}F = \frac{1.314}{\frac{197}{3}}F = 0.02F = 2 \times 10^{-2}\text{ F}$$

26. **(c)** $Ag^+ + e^- \longrightarrow Ag$

1 F is required for 1 mole. So 3 F will produce 3 mole

$Ca^{2+} + 2e^- \longrightarrow Ca$

2F is required for 1 mole.

So 3 F will produce $\frac{1}{2} \times 3 = \frac{3}{2}$ mole.

$Al^{+3} + 3e^- \longrightarrow Al$

3F is required for 1 mole. So 3F will produce 1 mole.

Molar ratio $3 : \frac{3}{2} : 1 = 6 : 3 : 2$

27. **(a)** Charges passing through solution = 5 × 193 = 965C

Cu^{n+} + ne$^-$ ’! Cu

965C charge deposit 0.32g

or 96500n C charge deposit

$$= \frac{0.32 \times 96500n}{965} = 63.5 \therefore\ n \simeq \frac{64}{32} = 2$$

28. **(b)** Equivalent weight $= \frac{W \times F}{I \times t}$

$$= \frac{0.96 \times 96500}{1.2 \times 40 \times 60} = 32.1\text{g} \simeq 31.75\text{g}$$

29. **(d)** Charge on 1 mole of electron is required for electrode deposition of 1 equivalent of substance.

30. **(a)** Time, t = 1.608 min or 96.5 s

Formula, $W_{Al} = \frac{z \times i \times t}{96500} \Rightarrow W_{Al} = \frac{27}{3} \times \frac{10 \times 96.5}{96500}$

$\Rightarrow$ $W_{Al} = 0.09$ g

31. **(c)** Given,

Charge used = 19296 C

Molar mass of Cu = 63.5

2 × 96500 C of charge give = 63.5 g of Cu

Thus, 19296 C of charge give $= \frac{63.5 \times 19296}{2 \times 96500}$

= 6.35 g of copper (Cu).

Hence, option (c) is the correct answer.

32. **(b)** When same amount of electricity is passed through $AgNO_3$ and $CuSO_4$ aqueous solution.

Then 1 mole of Ag^+ will deposit and half mole of Cu^{2+} will deposit.

The relation between Ag^+ and Cu^{2+} ion is as follows

1 mol of Ag^+ = $\frac{1}{2}$ mol of Cu^{2+}

Thus for, $\frac{x\text{ mol of }Ag^+}{y\text{ mol of }Cu^{2+}} = \frac{1\text{ mol}}{1/2\text{ mole}}$

$\therefore$ $x = 2y$

33. **(a)**

34. **(a)** Anode has negative polarity.

35. **(b)** $E^o_{cell} = E^o_{Cu^{2+}|Cu} - E^o_{Zn^{2+}|Zn} = 1.1\text{V}$

So, if $E_{ext.}$ = 1.1 V, no electron will flow.

At, E_{ext} > 1.1 V, cell act as electrolytic cell and electron will flow from Cu to Zn.

At, E_{ext} < 1.1 V, cell act as electrochemical cells so Zn dissolves at anode and Cu deposits at cathode.

36. **(c)** Correct Nernst equation is

$$E = E^o + \frac{2.303\,RT}{nF}\log a_{M^{n+}}.$$

37. **(d)** In electrolytic purification cathode is of pure metal and anode impure metal.

38. **(a)** Total charge on one mole of monovalent metal ion = Charge on N_0 electrons

$1F = 96500$ coulombs $= 9.65 \times 10^4$ coulombs.

39. **(a)** For deposition of silver, reaction is

$$Ag^+ + e^- \longrightarrow Ag$$

1 mol of Ag will be deposited by

$= 1\ F = 96500\ C = 9.65 \times 10^4\ C$

Since 1 equivalent weight of Ag is also equal to the weight of its 1 mol, hence 1 equivalent weight of Ag will be deposited by $= 9.65 \times 10^4$ C

40. **(b)** Given I = 3.86 amp

t = 41 min 40 seconds = 2500 seconds

Mass deposited = ZIt

$$\text{Where } Z = \frac{\text{Equivalent weight}}{96500}$$

$$\text{Equivalent weight of Ca} = \frac{40}{2}\ (Ca^{2+} \rightarrow Ca) = 20$$

$$Z = \frac{20}{96500} \times 3.86 \times 2500 = 2$$

41. **(d)** $1F \rightarrow 11.2\ L\ Cl_2$ at STP

$$\therefore \text{ No. of Faradays} = \frac{9.65 \times 5 \times 60 \times 60}{96500} = 1.8$$

$\therefore$ Vol. of $Cl_2 = 1.8 \times 11.2\ L = 20.16$

42. **(a)** $\because Q = i \times t$

$\therefore Q = 4.0 \times 10^4 \times 6 \times 60 \times 60\ C$

$= 8.64 \times 10^8 C$

$$\underset{}{Al^{3+}} + \underset{3\times96500C}{3e^-} \longrightarrow \underset{27g}{Al}$$

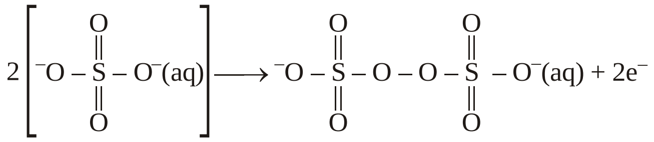
[3×96500 C liberates = 27 g of Al]

$\therefore$ 96500 C liberates 9 g of Al

$$8.64 \times 10^8\ C \text{ liberates} = \frac{9}{96500} \times 8.64 \times 10^8\ g\ Al$$

$= 8.1 \times 10^4$ g of Al

43. **(b)** At anode :



$$2\left[{}^-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-(aq)\right] \longrightarrow {}^-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-(aq) + 2e^-$$

At cathode :

$2H^+(aq) + 2e^- \longrightarrow H_2(g)$

Hence, the product will be

$HO_3S-O-O-SO_3H$.

44. **(a)** Millimoles of $Au^+ = 0.1 \times 250 = 25$

$$\text{Mole of } Au^+ = \frac{25}{1000} = \frac{1}{40} = 0.025$$

Similarly, moles of $Ag^+ = 0.025$

Charge passed = $I \times t = 1 \times 15 \times 60 = 900$ C

$$\text{Moles of } e^- \text{ passed} = \frac{900}{96500} = 0.0093 \text{ mol.}$$

Species with higher value of SRP will get deposited first at cathode.

$$\underset{0.025}{Au^+(aq)} + \underset{0.0093}{e^-} \longrightarrow Au(s)$$

So, only Au will get deposited.

45. **(c)** The anodic half cell reaction when the battery is recharged :

$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$

We require 2F for the electrolysis of 1 mol or 303 g of $PbSO_4$.

$\therefore$ Amount of $PbSO_4$ electrolysed by 0.05 F

$$= \frac{303}{2} \times 0.05 = 7.575\ g \approx 7.6\ g$$

46. **(c)** $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

27.66 g of B_2H_6 (1 mole) requires 3 moles of oxygen (O_2) for complete burning.

Now the oxygen is produced by the electrolysis of H_2O.

On electrolysis : $2H_2O \xrightarrow{4F} 2H_2 + O_2$

1 mole O_2 is produced by 4F charge

$\therefore$ 3 mole O_2 will be produced by 12F charge.

$\because$ Q = It

$12 \times 96500\ C = I \times t$

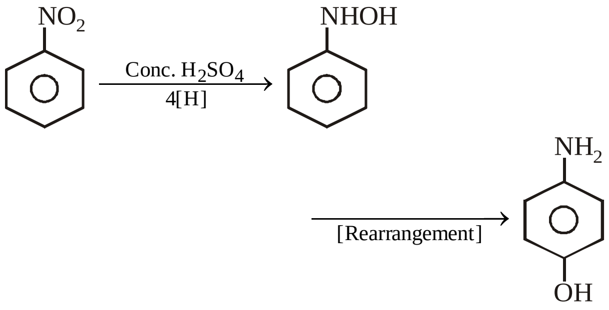
$12 \times 96500\ C = 100 \times t$

$$t = \frac{12 \times 96500}{100}\text{ second} = \frac{12 \times 96500}{100 \times 3600}\text{ hour} = 3.2 \text{ hours}$$

47. **(c)** 9.65 ampere current was passed for 1.0 hour (3600 seconds)

Number of moles of electrons passed

$$= \frac{I(A) \times t(s)}{96500} = \frac{9.65A \times 3600s}{96500} = 0.36 \text{ moles}$$



$C_6H_5NO_2 + 4e^- + 4H^+ \longrightarrow p$-Aminophenol + H_2O

$\because$ 4 moles of electrons reduces 1 mole of nitrobenzene to *p*-aminophenol.

∴ 0.36 moles of electrons will reduce $\frac{0.36}{4} = 0.09$ moles of nitrobenzene to *p*-aminophenol.

p-aminophenol molar mass = 109.14 g/mol

Mass of *p*-aminophenol obtained

= 109.14 g/mol × 0.09 mol = 9.81 g

48. **(d)** Reduction at cathode:

$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$ (valence factor) $H_2 = 2$

At NTP, 22400 mL of H_2 = 1 mole of H_2

$$112 \text{ mL of } H_2 = \frac{1}{22400}\times 112 = 0.005 \text{ mole of } H_2$$

$$\text{Mass of } H_2 \text{ produced} = \frac{I\times t}{96500}E_{H_2}$$

$$2\times 0.005 = \frac{I\times 965}{96500}\times\frac{2}{2}$$

I = 1.0 A

49. **(b)** $\Delta G = -RT\ln k = -nFE^\circ$

$\Rightarrow -RT\ln 1 = -nFE^\circ \Rightarrow nFE^\circ = 0 \Rightarrow E^\circ = 0$

50. **(b)**

Reduction

$$Fe^{3+} + Ce^{3+} \longrightarrow Fe^{2+} + Ce^{4+}$$

Oxidation

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = (-1.6 + 0.76) = -0.84 \text{ V}$$

51. **(c)** Reduction process: $2H^+ + 2e \rightarrow H_2$

$$E = E^\circ - \frac{0.059}{2}\log\frac{p_{H_2}}{[H^+]^2} \quad \begin{bmatrix}\text{neutral pH at 25°C,}\\ \log[H^+] = 7\\ \therefore [H^+] = 10^{-7}\end{bmatrix}$$

$$= 0.00 - \frac{0.059}{2}\log\frac{1}{(10^{-7})^2} = -\frac{0.059}{2}\times 14 = -0.413\text{V}$$

52. **(b)** $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Using Nernst equation,

$$E_{(Fe^{3+}/Fe^{2+})} = E^\circ_{(Fe^{3+}/Fe^{2+})}\ \frac{2.303RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Here, n = 1, $[Fe^{2+}]$ = 2M, $[Fe^{3+}]$ = 0.02 M,

$$\frac{2.303RT}{F} = 0.059,\ E^\circ = 0.771\text{V } (Fe^{3+}/Fe^{2+})$$

$$E\ (Fe^{3+}/Fe^{2+}) = 0.771 - 0.059\log\frac{2}{0.02}$$

$E\ (Fe^{3+}/Fe^{2+})$ = 0.653 V.

53. **(b)** $\Delta G^\circ = nFE^\circ_{cell}$

$\Delta G^\circ = -RT\ln K_c$

$$\therefore\ nFE^\circ_{cell} = -RT\ln K_c \boxed{= \frac{-2.303\ RT}{nF}\log K_c}$$

n = no. of electrons involved = 1

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode} = 0.5 - (-0.5) = 1.$

$$\therefore\ E^\circ_{cell} = \frac{-2.303RT\ \log K_c}{nF}$$

$1 = 0.06 \log K_c$. $\quad \therefore \log K_c = \frac{100}{6}$

54. **(a)** The nernst equation for reduction potential of an electrode is ;-

$$E = E^\circ - \frac{2.303RT}{nF}\log\frac{[Cl^-]}{P_{Cl_2}}$$

$$\text{or, } E = E^\circ - \frac{0.0591}{2}\log\frac{[Cl^-]}{P_{Cl_2}}$$

Thus the reduction/electrode potential will be highest for the lowest concentration of Cl^- ions.

The lowest concentration of Cl-$^-$ is 2.5 × 10^{-3} M.

Thus, x = 2.5 × 10^{-3}.

55. **(c)** $A + B^{2+} \rightleftharpoons A^{2+} + B$

$G^\circ = -RT\ln K_c$

$= -8.314 \times 298 \times 2.303 \times \log 10^{12} = 68.47$ kJ/mol

56. **(d)** Given $E^\circ_{Cu^{2+}/Cu} = 0.34$ V

So, $E^\circ_{Cu/Cu^{2+}} = -0.34$ V

At anode $Cu(s) \longrightarrow Cu^{2+}\ (aq) + 2e^-$

At anode $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

Overall reaction $Cu(s) + Cu^{2+} \longrightarrow Cu^{2+} + Cu(s)$

Using formula, $E^\circ_{cell} = E^\circ_{red.} - E^\circ_{oxi.}$

Using Nernst equation,

$$E_{cell} = E^\circ_{ceel} - \frac{0.0591}{n}\log\frac{C_1}{C_2}$$

$$E^\circ_{ceel} = (0.34 - 0.34) - \frac{0.059}{2}\log\left[\frac{0.1}{1}\right]$$

$= -0.029 \times \log 10^{-1}$ (∵ log 10 = 1)

$= -0.029 \times (-\log 10) = -0.029 \times (-1) = 0.029$ V

57. **(b)** Electrode with higher reduction potential will act as cathode.

Hence, silver electrode act as a cathode. Because reduction potential of silver electrode (E°) is +80 V. Which is more than given reduction potential of Cu (+34 V).

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = +0.80 - (+0.34) = +0.46 \text{ V}$$

58. **(a)** $E^\circ_{cell} = E^\circ_C - E^\circ_A = 0.34 - (-0.76)\text{V} = 1.1\text{V}$

$$E_{cell} = E^\circ_{Cell} - \frac{2.303RT}{nF}\log\left(\frac{Zn^{2+}}{Cu^{2+}}\right)$$

$$\Rightarrow\ E_{cell} = 1.1 - \frac{0.059}{n}\log\frac{C_2}{C_1} \quad \begin{pmatrix}Zn^{2+} = C_2\\ Cu^{2+} = C_1\end{pmatrix}$$

E_{Cell} value wil be maximum when, $\log\frac{C_2}{C_1}$ will be minimum.

From the given option $\log\frac{0.01}{0.1} = \log 10^{-1}$ will give the maximum value of E_{Cell}.

59. **(b)** According to Nernst equation:

$$E = E° - \frac{RT}{nF}\ln\frac{[\text{Product}]}{[\text{Reactant}]}$$

or $E = E° - \frac{RT}{nF}\ln\frac{[P]}{[R]}$ or $\ln\frac{[P]}{[A]} = \frac{-(E-E°)nF}{RT}$

or $\frac{[A]}{[P]} = \exp\left(\frac{nF}{RT}(E-E°)\right)$

60. **(c)** The Nernst equation is shown below:

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF}\log\frac{[P]}{[R]}$$

$$\Delta G = -nFE_{cell},\ \Delta G° = -nFE^{\circ}_{cell}$$

$$\Delta G° = \Delta G + 2.303RT\log\frac{[P]}{[R]}$$

$$\Delta G° = \Delta G + 2.303RT\log\frac{[R]}{[P]}$$

61. **(a)** $MCl + e^- \longrightarrow M + Cl^-$ cathode (reduction)

$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ anode (oxidation)

$MCl \longrightarrow M + \frac{1}{2}Cl_2$ (Cell reaction)

$$E_{cell} = E^0_{cell} - \frac{0.059}{n}\log K_c$$

$$\Rightarrow\ -1.140 = -0.55 - \frac{0.059}{1}\log K_c$$

$$\Rightarrow\ -0.59 = -0.059\log K_c \Rightarrow \log K_c = 10$$

$\therefore\ K_c = 10^{10}$

K_{sp} is for $M + \frac{1}{2}Cl_2 \longrightarrow MCl$

$$\therefore\ K_{sp} = \frac{1}{K_c} = \frac{1}{10^{10}} = 10^{-10}.$$

62. **(c)** $4H^+ + 4e^- \rightleftharpoons 2H_2$

$$E = E° - \frac{0.059}{n}\log\frac{(pH_2)^2}{[H^+]^4}$$

$$\Rightarrow\ -0.059 = 0 - \frac{0.059}{4}\log\frac{1}{[H^+]^4}$$

$$\Rightarrow\ [H^+] = 10^{-1} = 0.1\ M.$$

63. **(d)** Here Ni is anode and Au is cathode

Given $E^{\circ}_{Ni^{2+}/Ni} = -0.25V$ and

$E^{\circ}_{Au^{3+}/Au} = +1.5\,V$

$E^{\circ}_{cell} = E^{\circ}_C - E^{\circ}_A = 1.5 - (-0.25) = 1.5 + 0.25 = 1.75\,V$

64. **(b)** Reduction of MnO_4^- is pH dependent.

In acidic medium

$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$

In neutral medium

$MnO_4^- + 3e^- \longrightarrow Mn^{4+}$

In basic medium

$MnO_4^- + e^- \longrightarrow Mn^{6+}$

So, according to pH, the reaction and potential of cell changes.

65. **(b)** $Cu^{2+} + 2e^- \longrightarrow Cu,\ \Delta G_1^{\circ} = -2F(0.34)$ ...(i)

$Cu^+ + e^- \longrightarrow Cu,\ \Delta G_2^{\circ} = -F(0.522)$ ...(ii)

Subtract (ii) from (i)

$Cu^{2+} + e^- \longrightarrow Cu^+,\ \Delta G_3^{\circ} = -F(E^0)$

$\therefore\ \Delta G_1^{\circ} - \Delta G_2^{\circ} = \Delta G_3^{\circ}$

$\Rightarrow\ -FE° = -2F(0.34) + F(0.522)$

$\Rightarrow\ E° = 0.68 - 0.522 = 0.158\,V$

66. **(c)** $Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

$E^{\circ}_{cell} = E^{\circ}_{Ag^+/Ag} - E^{\circ}_{Fe^{3+}/Fe^{2+}}$

$$\begin{tikzcd} Fe^{3+} \arrow[r] \arrow[rr, bend right, "z"'] & Fe^{2+} \arrow[r] \arrow[r, bend left, "y"] & Fe \end{tikzcd}$$

$E^{\circ}_{Fe^{3+}/Fe^{2+}} = 3z - 2y$

$E^{\circ}_{Ag^+/Ag} = x$ (given)

$\therefore\ E^{\circ}_{cell} = x - 3z + 2y$

67. **(a)** $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}\ (n = 2e^-)$

$E^{\circ}_{cell} = (E^{\circ}_{R.P.})_{cathode} - (E^{\circ}_{R.P.})_{anode}$
$= 0.80 - (-0.76) = 1.56\,V$ for $2e^-$

$\therefore\ E^{\circ}_{cell}$ for $1e^- = \frac{1.56}{2} = 0.78\,V$

68. **(d)** $E° = \frac{0.0591}{n}\log K$

Here, $n = 2, E° = 0.295$

$\therefore \log K = \frac{2 \times 0.295}{0.0591} = 9.98 \approx 10$ or $K = 10^{10}$

69. **(c)** The $E°_{cell}$ is given by

$$E°_{cell} = \frac{0.0591}{n}\log K_{eq}$$

$$\therefore\ 0.591 = \frac{0.0591}{1}\log K_{eq}$$

or $\log K_{eq} = \dfrac{0.591}{0.0591} = 10$

or $K_{eq} = 1 \times 10^{10}$

70. **(b)** $Sn^{4+} 2e^- \longrightarrow Sn^{2+} \quad E° = 0.13V$

$Br_2 + 2e^- \longrightarrow 2Br^- \quad E° = 1.08V$

$E°$ value shows Br_2 has higher reduction potential.

Hence

$$E_{cell} = E_{Br_2/Br^-} - E_{Sn^{+4}/Sn^{+2}}$$

$$= 1.08 - 0.13 = 0.95 \text{ V}$$

Now $-\Delta G = nF\, E_{cell}$.

$n = 2, F = 96500.$

$-\Delta G = 2 \times 96500 \times 0.95 \text{ kJ/mol.}$

Also, $\Delta G = -2.303 RT \log K_{eq}$

$$\log K_{eq} = -\frac{\Delta G}{2.303 \times R \times T}$$

$$= \frac{-(-2 \times 96500 \times 0.95)}{2.303 \times 8.314 \times 298} = 32.13$$

K_{eq} = antilog 32.682 $\approx 10^{32}$

71. **(b)** (i) $A^{3+} + e^- \longrightarrow A^{2+}, \ \Delta G_1 = -1\, F\, y_2$

(ii) $A^{2+} + 2e^- \longrightarrow A, \ \Delta G_2 = -2F(-y_1) = 2Fy_1$

Add, (i) and (ii) we get

$A^{3+} + 3e^- \longrightarrow A$;

$\Delta G_3 = \Delta G_1 + \Delta G_2$

$-3FE° = -Fy_2 + 2Fy_1$

$-3FE° = -F(y_2 - 2y_1)$

$$E° = \frac{y_2 - 2y_1}{3}$$

72. **(d)** $Cu^{2+} + 2e^- \rightarrow Cu; \Delta G^o = -nE^oF$

$= -2 \times F \times 0.337$

$= -0.674\, F$ ....(i)

$Cu^+ \rightarrow Cu^{2+} + e^-; \Delta G^o = -nE^oF$

$= -1 \times F \times -0.153$

$= 0.153\, F$ ....(ii)

On adding eqn (i) & (ii)

$Cu^+ + e^- \rightarrow Cu$;

$\Delta G^o = -0.521\, F = -nE^oF;$

Here $n = 1 \quad \therefore E^o = +0.52$ V

73. **(a)** $Cu + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

Here, $n = 2$, $E^\circ_{cell} = +0.46$ V

$\Delta G° = -nE°F$

$$= \frac{-2 \times 0.46 \times 96500}{1000} \text{kJ} \simeq -89 \text{ kJ}$$

74. **(b)** $Cu^{2+} + 1e^- \rightarrow Cu^+ \quad E_1^o = 0.15V; \Delta G_1^o = -n_1E_1^oF$

$Cu^+ + 1e^- \rightarrow Cu \quad E_2^o = 0.50V; \Delta G_2^o = -n_2E_2^oF$

$Cu^{2+} + 2e^- \rightarrow Cu \quad \Delta G° = \Delta G°_1 + \Delta G°_2$

$-nE°F = -1\, n_1\, E_1{}^o\, F + (-1)\, n_2\, E_2^oF$

$-nE°F = -1\, (n_1\, E_1{}^o\, F + n_2\, E_2^oF)$

$$E° = \frac{n_1E_1{}^o + n_2E_2^o}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2}$$

$E° = 0.325$ V

75. **(d)** Standard Gibbs free energy is given as $\Delta G° = -nE°F$

If $E°_{cell} < 0$ i.e., – ve

$\Delta G° > 0$

Further $\Delta G° = -RT \ln K_{eq}$

$\therefore \quad \Delta G° > 0$ and $K_{eq} < 0$

76. **(d)** From the given representation of the cell, E_{cell} can be found as follows.

$$E_{cell} = \left(E^o_{Fe^{2+}/Fe} - E^o_{Cr^{3+}/Cr}\right) - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

[Nernst -Equ.]

$$= -0.42 - (-0.72) - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= -0.42 + 0.72 - \frac{0.059}{6} \log \frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}$$

$$= 0.3 - \frac{0.059}{6} \log \frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6} \times 4$$

$= 0.30 - 0.0393 = 0.26$ V

Hence option (d) is correct answer.

77. **(c)** $\Delta G = -nFE$

For 1 mol of Al, n = 3

For $\dfrac{4}{3}$ mol of Al, $n = \dfrac{4}{3} \times 3 = 4$

or $E = \dfrac{\Delta G}{-nF} = \dfrac{966 \times 10^3}{-4 \times 96500} = -2.5$ V

$\therefore$ The potential difference needed for the reduction = 2.5 V.

78. **(d)** For a spontaneous reaction ΔG must be –ve

Since $\Delta G = -nFE°$

Hence for ΔG to be -ve ΔE° has to be positive. Which is possible when X = Zn, Y = Ni

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

$E°_{Zn/Zn^{+2}} + E°_{Ni^{2+}/Ni} = 0.76 + (-0.23)$

$= +0.53$ (positive)

79. **(b)** Maximum work done = W_{max}

$$= -nFE^\circ_{cell} = -2\times 96500\times 1.10 = -212.30 \text{ KJ}$$

80. **(d)** For the concentration cell, $E^o_{cell} = 0$

Anode : $Cu(s) \longrightarrow Cu^{2+}\ (aq)_A$

Cathode : $Cu^{2+}(aq)_C \longrightarrow Cu\ (s)$

Overall : $\underset{(C_2M)}{Cu^{2+}(aq)_C} \longrightarrow \underset{(C_1M)}{Cu^{2+}\ (aq)_A}$

$\Delta G = -nFE$

If $\Delta G = -ve$, then E_{cell} is +ve.

$$E_{cell} = E^o_{cell} - \frac{RT}{2F}\ln\frac{C_1}{C_2}$$

$$E_{cell} = 0 - \frac{RT}{2F}\ln\frac{C_1}{C_2}$$

$$E_{cell} = \frac{RT}{2F}\ln\frac{C_2}{C_1}$$

So, $C_2 > C_1$.

Thus, $C_2 = \sqrt{2}C_1$ relation is correct.

81. **(a)** $\Delta G^\circ = -nFE^\circ_{cell}$
$= -2 \times (96000) \times 2 \text{ V} = -384000 \text{ J/mol} = -384 \text{ kJ/mol}$

82. **(c)** $E^0_{cell} = \frac{2.303RT}{nF}\log K_C$ or $E^0_{cell} = \frac{0.059V}{n}\log K_C$

$$= \frac{0.059V}{2}\log 10^{16} = 0.4736 \text{ V}$$

83. **(d)** Given that:

$Pt(s) \mid H_2(g, 1\ bar) / HCl(aq) \parallel AgCl(s) / Ag(s) \mid Pt(s)$

$E_{cell} = 0.92$ V

Now, $E_{cell} = E^\circ_{H_2(g)/H^+(aq)} + E^\circ_{AgCl(s)/Ag(s),Cl^-} - \frac{0.06}{n}\log Q$

Cell reaction: $\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$

$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$

Net cell reaction:

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow Ag(s) + H^+(aq) + Cl^-(aq)$$

$$\therefore\quad Q = \frac{[H^+][Cl^-]}{(P_{H_2})^{1/2}}$$

Here, 10^{-6} molal HCl solution is used

$$\text{So}\quad Q = \frac{10^{-6}\times 10^{-6}}{1} = 10^{-12}$$

(assuming molality = molarity)

Now, $0.92 = E^\circ_{AgCl(s)/Ag(s),Cl^-} - \frac{0.06}{1}\log 10^{-12}$

$E^\circ_{AgCl(s)/Ag(s),Cl^-} = 0.92 + [0.06\times(-12)]$

$= 0.92 - 0.72 = 0.20$ V

84. **(c)** From the given data we find Fe^{3+} is strongest oxidising agent. More the positive value of E°, more is the tendency to get oxidized. Thus correct option is (c).

85. **(d)** This is because zinc has higher oxidation potential than Ni, Cu and Sn. The process of coating of iron surface with zinc is known as galvanization. Galvanized iron sheets maintain their lustre due to the formation of protective layer of basic zinc carbonate.

86. **(b)** Magnesium provides cathodic protection and prevent rusting or corrosion.

87. **(b)** In electrochemical cell H_2 has greater tendency to release electrons.

$\therefore$ H_2 is liberated at anode and Cu is deposited at the cathode.

88. **(c)** The given values show that Cr has highest negative value of $E^\circ_{M^{3+}/M^{2+}}$ i.e., Cr is the strongest reducing agent among given metals therefore its oxidation will be easiest.

89. **(d)**

90. **(d)** The metal placed below in electrochemical series does not react with that metal salt solution whose metal is placed above in electrochemical series.

91. **(a)** An oxidising agent with a higher reduction potential will oxidise only reducing agent with a lower reduction potential.

92. **(b)** $E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{right} - E^o_{left}$

$E^o_{cell} = 0.25 - 0.52 = -0.27$V

93. **(a)** The value of $E^\circ_{M^{2+}/M}$ for given metal ions are

$E^\circ_{Mn^{2+}/Mn} = -1.18$ V,

$E^\circ_{Cr^{2+}/Cr} = -0.9$ V,

$E^\circ_{Fe^{2+}/Fe} = -0.44$ V and

$E^\circ_{Co^{2+}/Co} = -0.28$ V.

The correct order of $E^\circ_{M^{2+}/M}$ values without considering negative sign would be

$$Mn^{2+} > Cr^{2+} > Fe^{2+} > Co^{2+}.$$

94. **(d)**

95. **(a)** $E^\circ_{Mn^{2+}/MnO_4^-} = -1.51$ V

$E^\circ_{Cl^-/Cl_2} = -1.36$ V ; $E^\circ_{Cr^{3+}/C_2O_7^{2-}} = -1.33$ V

$E^\circ_{Cr/Cr^{3+}} = +0.74$ V

Since Cr is having highest oxidation potential, Cr is the best reducing agent.

96. **(c)** (i) $\underset{\text{Most stable}}{Al^{3+}} \xrightarrow{E^\circ=-1.66} Al \xleftarrow{E^\circ=+0.55} \underset{\text{Less stable}}{Al^{+}}$

(ii) $\underset{\text{Less stable}}{Tl^{3+}} \xrightarrow{E^\circ=+1.26} Tl \xleftarrow{E^\circ=-0.34} \underset{\text{More stable}}{Tl^{+}}$

Tl^+ has negative electrode potential (E° = –0.34) means, it does not prefer to convert into Tl but reverse must be preferred that's why it is more stable than Tl^{3+} (E° = +1.26). In Al, Al^{3+} is more stable (E° = –1.66) than Al^+ (E° = +0.55) and also from Tl^+ due to more negative value of E°. Therefore, by comparison it confirms that Tl^+ is more stable than Al^+.

97. **(a)** $CH_3OH(\ell) + \frac{3}{2}O_2(g) \to CO_2(g) + 2H_2O(\ell)$

$$\because \quad E^o_{cell} = E^o_{cathode} - E^o_{Anode} = E^o_{O_2/H_2O} - E^o_{CO_2/CH_3OH}$$

$$1.21 = 1.229 - E^o_{CO_2/CH_3OH}$$

$$\Rightarrow \quad E^o_{CO_2/CH_3OH} = 0.019\,V = 19\,mV$$

Fuel cell involves oxidation of methanol which will occur at anode and reduction of O_2 will occur at cathode.

98. **(d)** Fuel cell is used in spaceship and it is type of galvanic cell. It has efficiency of about 70%.

99. **(b)** Mn, Ni and Cd metals used in battery industries.

100. **(b)** H_2SO_4 is regenerated.

Questions Bank

Exercise 3 : PREVIOUS YEARS MCQs

1. **(b)** Higher the charge of the metal cation higher is the molar conductivity. For same charge, higher is solvation lower will be the molar conductivity where $H^{\oplus}$ cation is a exceptional case.

2. **(d)** Anodic Reaction at Anode : $[T\ell_{(s)} \to T\ell^+_{(aq)} + e^-]2$

Reaction at Cathode :

$$Cu^{+2}(aq) + 2e^- \to Cu(s)$$

Overall Redox Reaction

$$2T\ell(s) + Cu^{+2}(aq) \to 2T\ell^+(aq) + Cu(s)$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{\left[T\ell^+\right]^2}{\left[Cu^{+2}\right]}$$

E_{cell} increases by increasing concentration of $[Cu^{+2}]$ ions.

3. **(a)** Reaction occurs at cathode is :

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

In the cathode reaction manganese (Mn) is reduced from the +4 oxidation state to the +3 oxidation state.

4. **(a)** According to the Faraday's law of electrolysis, nF of current is required for the deposition of 1 mol.

According to the reaction,

$$Ni(NO_3)_2 \longrightarrow Ni^{2+} + 2NO_3^-$$

2 F of current deposits = 1 mol

$\therefore$ 0.1 F of current deposits = $\frac{0.1}{2}$ = 0.05 mol

5. **(c)** Molar conductance of solution is related to specific conductance as follows :

$$\wedge_m = \kappa \times \frac{1000}{C} \qquad \text{....(a)}$$

$$\wedge_m = (6.3 \times 10^{-2}\,ohm^{-1}\,cm^{-1}) \times \frac{1000}{(0.1 mol/cm^3)}$$

$= 6.3 \times 10^{-2} \times 10^4\,ohm^{-1}cm^2\,mol^{-1} = 630\,ohm^{-1}\,cm^2\,mol^{-1}$

6. **(a)** $(M \to M^{3+} + 3e) \times 2; (N^{2+} + 2e \to N) \times 3$

Overall reaction : $2M(s) + 3N^{2+}(aq) \to 2M^{3+}(aq) + 3N(s)$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.059}{6}\log\frac{\left[M^{3+}\right]^2}{\left[N^{2+}\right]^3}$$

$$= -0.6 + 0.1 - \frac{0.059}{6}\log\frac{\left(10^{-2}\right)^2}{\left(10^{-1}\right)^3}$$

$$= -0.5 - \frac{0.059}{6}\log 10^{-1} = 0.51\,V$$

7. **(a)** $2H^+ + 2e^- \longrightarrow H_2$

$$E_H(\text{Eq. wt}) = \frac{2}{2} = 1\,g = \frac{22400}{2} = 11200\text{ mL (STP)}$$

$$\text{Total charge passed} = \frac{96500 \times 112}{11200} = 965 \text{ coulomb}$$

$Q = It = 965$ and $t = 965s$.

$$I = \frac{965}{965} = 1\text{amp.}$$

8. **(d)** Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%.

9. **(b)** $W = Zit$

where Z = Electrochemical equivalent

$$\text{Eq. wt. of copper} = \frac{63}{2} = 31.5\,;\ Z = \frac{31.5}{96500}$$

$$W = Zit = \frac{31.5}{96500} \times 1.5 \times 10 \times 60 = 0.2938g$$

10. **(a)** $\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.06 \times 10^{-2} \times 1000}{0.1} = 1.06 \times 10^2$

11. **(c)** Higher the value of reduction potential stronger will be the oxidising hence based on the given values Ag^+ will be strongest oxidizing agent.

12. **(a)** $m = \frac{E \times i \times t}{96500}; \; 2 = \frac{31.75 \times .5 \times t}{96500}$,

$\therefore \quad t = 12157.48$ sec.

13. **(a)** Since concentration of ions is the same hence $E_{cell} = E^{\circ}_{cell}$

14. **(b)** Cl^- is oxidised to Cl_2 at anode.

15. **(a)** Conductivity decreases with decrease in concentration as the number of ions per unit volume that carries the current in a solution decreases on dilution.

16. **(b)** Applying Faraday's second law of electrolysis

$$\frac{\text{wt. of Cu}}{\text{wt. of Al}} = \frac{E_w \text{ of Cu}}{E_w \text{ of Al}}$$

$$E_w \text{ of Cu} = \frac{\text{Atomic wt}}{\text{n factor}} = \frac{63.5}{2}$$

$$E_w \text{ of Al} = \frac{27}{3}$$

$$\therefore \frac{0.4 \times 63.5}{\text{wt of Al}} = \frac{31.75}{9}$$

wt of Al = 7.2 g

$$\text{wt of Al in moles} = \frac{7.2}{27} = 0.27 \text{ mol}$$

17. **(b)** Resistance (R) = 2.5×10^3 ohm

$$\text{Conductivity } (\kappa) = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$\text{Conductivity } (\kappa) = \frac{1.25\text{cm}^{-1}}{2.5 \times 10^3 \text{ohm}}$$

$$= 5 \times 10^{-4} \text{ohm}^{-1}\text{cm}^{-1}$$

$$\text{Molar conductivity } (\Lambda_m) = \frac{\kappa}{C} \times 1000$$

$$\Lambda_m = \frac{5 \times 10^{-4} \text{ohm}^{-1}\text{cm}^{-1}}{0.1 \text{ mol cm}^{-3}} \times 1000$$

$$\Lambda_m = 5 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$$

18. **(b)** Zinc is used for coating iron surface.

Because zinc get oxidized first when comes in contact with moisture and hence iron suface is protected from corosion.

19. **(c)** $\text{Moles of electron} = \frac{\text{Charge}}{F} = \frac{\text{Current} \times \text{Time}}{96500}$

$$\frac{2 \times 20 \times 60}{96500} = 0.02487$$

or 2.487×10^{-2} mol e^-

20. **(b)** 1.2 g mL^{-1}

21. **(b)** S.I Unit of conductivity (κ) is Sm^{-1}

22. **(d)** The reaction involved for lead accumulator during discharging i.e., when cell is in the use are

At anode : $Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+ + 2e^-$

At cathode : $PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Overall reaction : $Pb(s) + PbO_2(s) + 2H^+ + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

23. **(a)** We require nF to deposit 1 mol or 40 g of Ca.

n = 2 (no. of e^- involved)

$\because$ 10 g Ca is deposited by 0.5 F.

24. **(a)** In the cell represented by

$Pb(s) \mid Pb^{2+} (1M) \parallel Ag^+ (1M) \mid Ag(s)$, the

reducing agent is Pb because it readily gets oxidised to Pb^{2+}

25. **(a)** In a dry cell, zinc acts as a negative electrode.

6

Chemical Kinetics

Exercise 1 : WARM-UP

Topic-wise MCQs

1. **(d)**

2. **(d)** $\frac{1}{2}\frac{d[A]}{dt}=\frac{1}{4}\frac{d[B]}{dt}\Rightarrow\frac{d[A]}{dt}=\frac{1}{2}\times\frac{d[B]}{dt}$

$\Rightarrow\quad \frac{1}{2}\times\frac{5\times10^{-3}}{10}=2.5\times10^{-4}\,Ms^{-1}.$

3. **(a)** $\gamma_1A+\gamma_2B\longrightarrow\gamma_3C+\gamma_4D$

Given: $+\frac{d[D]}{dt}=\frac{-3}{2}\frac{d[B]}{dt}$

$\Rightarrow\frac{-1}{2}\frac{d[B]}{dt}=\frac{+1}{3}\frac{d[D]}{dt}$

$\frac{d[B]}{dt}=-2\frac{d[A]}{dt}\Rightarrow-\frac{1}{2}\frac{d[B]}{dt}=\frac{-d[A]}{dt}$

Given, $+\frac{d[D]}{dt}=9\text{ m mol dm}^{-3}s^{-1}$ and

$\frac{+d[C]}{dt}=\frac{20-10}{10}=1\text{ m mol dm}^{-3}s^{-1}$

Therefore, $\frac{+d[C]}{dt}=\frac{1}{9}\times\frac{+d[D]}{dt}\Rightarrow\frac{1}{3}\frac{d[D]}{dt}=\frac{3d[C]}{dt}$

$\Rightarrow\frac{-d[A]}{dt}=-\frac{1}{2}\frac{d[B]}{dt}=\frac{3d[C]}{dt}=\frac{1}{3}\frac{d[D]}{dt}$

Hence, the chemical reaction is $A+2B\longrightarrow\frac{1}{3}C+3D$

Assuming γ_1, γ_2, γ_3 and γ_4 are integers.

$\Rightarrow 3A+6B\longrightarrow C+9D$

Rate of reaction = $\frac{+d[C]}{dt}=1\text{ m mol dm}^{-3}\text{ s}^{-1}.$

4. **(b)** $2\,NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4,$

For forward reaction rate

$=-\frac{1}{2}\frac{dNO_2}{dt}=\frac{dN_2O_4}{dt}=k_1[NO_2]^2$

For backward reaction

$\text{Rate}=-\frac{dN_2O_4}{dt}=\frac{1}{2}\frac{dNO_2}{dt}=k_2[N_2O_4]\cdot$

Rate of disappearance of NO_2 = (Rate of disapperance of NO_2 – Rate of appearence of NO_2)

$=2k_1[NO_2]^2-2k_2[N_2O_4].$

5. **(c)** four times $\therefore$ rate $\propto[B]^2$

6. **(c)** $\frac{k_2}{k_1}=\left[\frac{A_2}{A_1}\right]^n$ Or $2=(8)^n\;\therefore\;n=\frac{1}{3}$

7. **(a)** rate = $K[A]^2$

[A] doubling, rate becomes four time. Hence rate $\alpha[A]^2$

[B] doubling, no effect on the rate. Hence rate $\alpha[B]^0$

$\therefore$ rate = $K[A]^2\,[B]^0$

8. **(c)** Rate = $K\,[A]\,[B]^2$

9. **(d)** $(p+q)=(m+n)$ or $(p+q)\neq(m+n)$

Keeping [B] constant, [A] is made a 4 times, rate also become 4 times. Hence rate α [A]

Keeping [A] constant, [B] is doubled, rate becomes 4 times. Hence rate $\alpha\,[B]^2$

$\therefore$ rate = $K[A]\,[B]^2$

10. **(a)** 0.012 atm min^{-1}

$-\frac{d[N_2O_4]}{dt}=+\frac{1}{2}\frac{d[NO_2]}{dt}$

$-\frac{(0.32-0.50)}{30}=0.006=\frac{1}{2}\frac{d[NO_2]}{dt}$

$\therefore\frac{d[NO_2]}{dt}=0.012\text{ atm min}^{-1}$

11. **(d)** ΔH of reaction

12. **(c)** $\therefore\quad-\frac{1}{4}\frac{d[A]}{dt}=-\frac{d[B]}{dt}=+\frac{1}{2}\frac{d[C]}{dt}=+\frac{d[D]}{dt}$

13. **(a)** $\frac{d[H_2]}{dt}=-0.3\times10^{-14}\,Ms^{-1}$

But Rate $=-\frac{1}{3}\frac{d[H_2]}{dt}\;=+\frac{1}{2}\frac{d[NH_3]}{dt}$

Hence $\frac{d[NH_3]}{dt}=-\frac{2}{3}\frac{d[H_2]}{dt}=-\frac{2}{3}\,(-0.3\times10^{-4})$

$=0.2\times10^{-4}$

14. **(b)** $-\frac{1}{2}\frac{d[A]}{dt}=-\frac{d[B]}{dt}=+\frac{1}{3}\frac{d[C]}{dt}$

15. **(c)** Definition of the rate of reaction

16. **(c)** $xA\rightarrow yB$

$\therefore\quad\frac{-dA}{xdt}=\frac{1}{y}\frac{dB}{dt}\Rightarrow\frac{-dA}{dt}=\frac{dB}{dt}\times\frac{x}{y}$

$\log\left[\frac{-dA}{dt}\right]=\log\left[\frac{dB}{dt}\right]+\log\left(\frac{x}{y}\right)$

Comparing this equation with the equation given in question. We get,

$\log\frac{x}{y}=0.3010\quad\text{or}\quad\log\frac{x}{y}=\log 2$

$\therefore \quad \frac{x}{y} = 2$

$\therefore$ The reaction is of type $2A \rightarrow B$.

Hence, option (c) is correct.

17. **(d)** $2\,H_2(g) + 2\,NO(g) \rightarrow N_2(g) + 2H_2O(g)$

$R_f = K_f\,[NO]^2\,[H_2]$

This means that, for forward reaction the order of reaction w.r.t. [NO] is 2 and that w.r.t. $[H_2]$ is 1.

Assuming the equilibrium expression,

$$K_{eq} = \frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2} = \frac{K_f}{K_b}$$

$$\Rightarrow K_f\,[NO]^2\,[H_2] = K_b \frac{[N_2][H_2O]^2}{[H_2]}$$

At equilibrium, $R_f = R_b$

$$\Rightarrow R_b = K_b \frac{[N_2][H_2O]^2}{[H_2]}$$

Note: In this question, the order of reaction for backward reaction is not given.

18. **(c)** $k = (\text{mol L}^{-1})^{1-n}\ \text{time}^{-1}$. For given reaction $n = 2$.

$\therefore k = \text{mol}^{-1}\ \text{L sec}^{-1}$

19. **(b)** Velocity constant '*k*' is characteristic constant of a reaction and depends only on temperature and catalyst.

20. **(a)** $2A + B \longrightarrow A_2B$

$r_1 = k[A]^2\,[B]$ ...(i)

When, $[A] = [2A]$, $[B] = \left[\frac{B}{2}\right]$

$$r_2 = k[2A]^2\left[\frac{B}{2}\right] = k\,4[A]^2\frac{[B]}{2}$$

$$= k\,2[A]^2[B] = 2r_1 \quad \left(\because r_1 = k[A]^2[B]\right)$$

$\therefore$ Rate of reaction is increased two times.

21. **(a)** Rate $= k[A]^{\circ}$

Unit of k = mol L^{-1} sec^{-1}

22. **(a)** Given $r = k\,[A]^{3/2}\,[B]^{-1/2}$

Order $= 3/2 - 1/2 = \frac{3-1}{2} = \frac{2}{2} = 1$

23. **(a)** The order w.r.t. acetone is 1 because the rate is dependent on the concentration of acetone.

24. **(b)** Given $dx/dt = 2.400 \times 10^{-5}$ mol litre^{-1} sec^{-1}

$k = 3.10 \times 10^{-5}\ \text{sec}^{-1}$ thus, it is a first order reaction.

For first order reaction

$$2N_2O_5 \longrightarrow 2NO_2 + O_2$$

$$\frac{dx}{dt} = k[N_2O_5]$$

or $2.4 \times 10^{-5} = 3.0 \times 10^{-5}\,[N_2O_5]$

or $[N_2O_5] = \frac{2.4 \times 10^{-5}}{3.0 \times 10^{-5}} = 0.8$ mol. litre^{-1}

25. **(c)** $\text{Rate}_1 = k\,[A]^2\,[B]^1$; $\text{Rate}_2 = k\,[2A]^2\,[½B]^2$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2A]^2[½B]^1}{k[A]^2[B]^1} = [2]^2\,[½]^1 = 2^2.2^{-1} = 2^{2-1} = 2$$

26. **(c)** $N_2O \longrightarrow N_2 + \frac{1}{2}O_2$

$\frac{dx}{dt} \propto [N_2O]^1$ *i.e.* order of reaction = 1

27. **(c)** There is no difference between order and molecularity of a reaction.

28. **(d)** $4K = \frac{\text{rate}}{[R]^n} = \frac{M/s}{M^n} = M^{1-n}\,s^{-1}$ when $n = 4$ $K = \text{liter}^3$ $\text{mole}^{-3}\ \text{min}^{-1}$

29. **(c)** time and square of concentration

$$K = \frac{\text{rate}}{[R]^n} = \frac{M/s}{M^n} = M^{1-n}\,s^{-1} \text{ when } n = 3\ M^{-2}\,s^{-1}$$

30. **(b)** $K = \frac{\text{rate}}{[R]^n} = \frac{\text{bar}/s}{\text{bar}^n}$ when $n = 2$ $\quad k = \text{bar}^{-1}\,s^{-1}$

31. **(d)** zero order $K = \frac{\text{rate}}{[R]^n}$ K = rate, when $n = 0$

32. **(c)** moles litre^{-1} sec^1

$$K = \frac{\text{rate}}{[R]^n} = \frac{M/s}{M^n} \qquad n = 0$$

$K = M^{1-n}\,s^{-1} \quad \therefore\ K = M/s$

33. **(d)** $r = K\,[A]^2[B]$

(i) $r = k\,[A]^x\,[B]^y$ (ii) $8r = k\,[2A]^x\,[2B]^y$

(iii) $2r = k\,[A]^x\,[2B]^y$

(iii) $\div$ (i) $\cong 2^y = 2 \therefore y = 1$

(ii) $\div$ (i) $\cong 2^x = 4 \therefore x = 2$

34. **(c)** concentration increased = 10 times

rate increased = 10^2 times

$\therefore$ Order = 2

35. **(d)** $r = k\,[A]^n$

$2r = K\,[A]^n\,16^n$

$$\frac{2r}{r} = \frac{K[A]^n\,16^n}{K[A]^n} \therefore 2 = 16^n \therefore n = \frac{1}{4}$$

36. **(d)** Zero; No I_2 in the rate law equation.

37. **(c)** temperature is changed

38. **(d)** $\frac{1}{6}$ Rate $= k[A]^{1/2}\,[A]^{1/3}\,[c]^1$

$$\therefore \text{Order of reaction } = \frac{1}{2} + \frac{1}{3} + \frac{1}{1} = \frac{11}{6}$$

39. **(c)** It is bimolecular first order reaction since Rate $\propto$ $[N_2O_5]$

40. **(c)** $\text{Rate}_1 = k\,[A]^n\,[B]^m$; $\text{Rate}_2 = k\,[2A]^n\,[½B]^m$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2A]^n[½B]^m}{k[A]^n[B]^m} = [2]^n\,[½]^m = 2^n.2^{-m} = 2^{n-m}$$

41. **(d)** Rate$_1 = k\,[A]^2[B]^3$

when concentrations of both A and B are doubled then

Rate$_2 = k\,[2A]^2[2B]^3 = 32\,k\,[A]^2[B]^3$

$\therefore$ Rate will increase by a factor of 32.

42. **(a)** When concentration A is doubled, rate is doubled. Hence order with respect to A is one.

When concentrations of both A and B are doubled, rate increases by 8 times hence order with respect to B is 2.

$\therefore$ rate = $k\,[A]^1\,[B]^2$

Total order = 1 + 2 = 3

43. **(c)** Order w.r.t. $A_2 = 1$; order w.r.t. $B_2 = 1$

$$\text{Rate} = \frac{1}{2}\frac{d[AB]}{dt} = k_r[A_2][B_2];$$

$$\frac{1}{2}\times\left(2.5\times10^{-4}\right) = k_r(0.1)(0.1)$$

$k_r = 1.25 \times 10^{-2}$

44. **(b)** Slow reaction is the rate determining step.

45. **(d)** In case of (II) and (III), keeping concentration of [A] constant, when the concentration of [B] is doubled, the rate quadruples. Hence, it is second order with respect to B. In case of I & IV, keeping the concentration of [B] constant, when the concentration of [A] is increased four times, rate also increases four times. Hence, the order with respect to A is one. Hence,

Rate = $k\,[A]\,[B]^2$

46. **(c)** As we know that, units of rate constant.

= (unit of conc.)$^{1-n}$ (unit of time)$^{-1}$

= (mol L^{-1})$^{1-n}$ (sec)$^{-1}$

On comparing these units with the given units of rate constant, we get

(mol L^{-1})$^{1-n}$ (sec)$^{-1}$ = L mol^{-1} sec^{-1}

$\Rightarrow$ L^{n-1} mol^{1-n} sec^{-1} = L mol^{-1} sec^{-1}

On comparing the powers, we get

$n - 1 = 1 \Rightarrow n = 2$

So, reaction is of second order.

47. **(d)** If rate = $k[A]^x\,[B]^y\,[C]^z$

From first two given data

$8.08 \times 10^{-3} = k\,[0.2]^x\,[0.1]^y\,[0.02]^z$ .... (i)

$2.01 \times 10^{-3} = k\,[0.1]^x\,[0.2]^y\,[0.02]^z$ .... (ii)

Divide (i) by (ii) we get, $4 = 2^x\,(1/2)^y$

Similarly, from second and third data

$(9)^y\,(9)^z = 3 \qquad 2y + 2z = 1$.

From first and fourth data $4^z = 8 = 2^3$

$2z = 3$. So $z = 3/2,\ y = -1,\ x = 1$

48. **(c)** $t_{1/2} = \dfrac{0.693}{k} \Rightarrow k = \dfrac{0.693}{t_{1/2}}$

$$t = \frac{2.303}{k}\log\frac{[A_0]}{[A]_t} \Rightarrow t = \frac{t_{1/2}}{0.3}\log\frac{[A_0]}{[A]_t}$$

$$83 = \frac{200}{0.3}\log\frac{[A_0]}{[A]_t} \Rightarrow 0.125 = \log\frac{[A_0]}{[A]_t}$$

$$\frac{[A_0]}{[A]_t} = 1.333 \cong \frac{4}{3} \quad \therefore \quad \frac{[A]_t}{[A]_0}\times100 = \frac{3}{4}\times100 = 75\%$$

49. **(b)** $t = \dfrac{1}{k}\ln\left(\dfrac{a}{a-x}\right)$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{30} \Rightarrow 100 = \frac{30}{\ln 2}\ln\left(\frac{1}{w}\right)$$

$\dfrac{1}{w} = 10 \Rightarrow w = 1 \times 10^{-1}$ μg

50. **(d)** $A \rightarrow B$

For first order reaction;

$$k = \frac{2.303}{t}\log\left[\frac{A_0}{A_t}\right] \Rightarrow \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{2}\log\left(\frac{A_0}{A_t}\right)$$

$$\Rightarrow \quad \frac{2.303\times0.3010}{0.3010} = \frac{2.303}{2}\log\frac{A_0}{A_t}$$

$$\log\frac{A_0}{A_t} = 2 \quad \therefore \quad \frac{A_0}{A_t} = 10^2 = 100$$

51. **(a)** As doubling the initial conc. doubles the rate of reaction, order =1

52. **(a)** For a zero order reaction $t_{1/2} = \dfrac{a}{2k}$

53. **(a)** When initial pressure of NO increases by a factor of 2 ($2 \times 20.1 \approx 40$) then initial rate increases by a factor of 4 ($4 \times 0.033 \approx 0.135$). Therefore, order of reaction w.r.t. NO = 2

54. **(b)** $A \rightarrow B$ For a first order reaction

Given $a = 0.4$ mol, $(a - x) = 0.4 - 0.2 = 0.2$

$$k = \frac{2.303}{1}\log\frac{0.4}{0.2} \text{ or } k = 2.303\log 2$$

again $a = 0.6,\quad a - x = 0.6 - 0.3 = 0.3$

$$k = \frac{2.303}{t}\log\frac{0.6}{0.3} \Rightarrow 2.303\log 2 = \frac{2.303}{t}\log 2$$

Hence, $t = 1$ hour

55. **(b)** Given: 75% reaction gets completed in 32 min

$$\text{Thus, } k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{32}\log\frac{100}{(100-75)}$$

$$= \frac{2.303}{32}\log 4 = 0.0433\ \text{min}^{-1}$$

Now we can use this value of k to get the value of time required for 50% completion of reaction

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)} = \frac{2.303}{0.0433}\log\frac{100}{50}$$

$$= \frac{2.303}{0.0433}\log 2 = 16\ \text{min}$$

56. **(c)** $t_{1/4} = \dfrac{2.303}{k}\log\dfrac{1}{3/4} = \dfrac{2.303}{k}\log\dfrac{4}{3}$

$$= \frac{2.303}{k}(\log 4 - \log 3) = \frac{2.303}{k}(2\log 2 - \log 3)$$

$$= \frac{2.303}{k}(2\times0.301 - 0.4771) = \frac{0.29}{k}$$

57. **(b)** Since doubling the concentration of *B* does not change half life, the reaction is of 1st order w.r.t. *B*.

Order of reaction with respect to *A* = 1 because rate of reaction doubles when concentration of *A* is doubled keeping concentration of *B* constant.

∴ Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol^{-1} sec^{-1}.

58. **(a)** $t_{1/2} = 70$ min; for Ist order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{70 \times 60} s^{-1} = \frac{6930}{7 \times 6} \times 10^{-6} s^{-1} = 165 \times 10^{-6} s^{-1}$$

59. **(c)** $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1}$; $\dfrac{120}{240} = \left(\dfrac{4 \times 10^{-2}}{8 \times 10^{-2}}\right)^{n-1}$; $n = 2$

60. **(d)** Since the half life for the decomposition of gas is not dependent on initial concentration, the order of the reaction is one.

61. **(c)** $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1}$; $n = 1 + \dfrac{\log(t_1/t_2)}{\log(a_2/a_1)}$

62. **(c)** $t_{3/4} = \dfrac{2.303}{l} \ell og \dfrac{ao}{ao - ao \times \frac{3}{4}} = \dfrac{2.303}{k} \ell og \dfrac{ao}{ao/4}$

$$= \frac{2.303}{k} \log 4$$

63. **(a)** $t_{1/2} = \dfrac{0.693}{k}$

64. **(d)** $t_{1/2} \alpha C_o$

65. **(c)** $[A] = [A]_o . e^{-kt}$

66. **(b)** $Kt = [Ao] - [A]$

67. **(c)** For Zero order reaction $t = \dfrac{1}{k}\{[A]_o - [A]\}$

But $[A]_o = a$

And when reaction complete $[A] = 0 \therefore t = \dfrac{a}{k}$

68. **(b)** concentration of reactants

69. **(b)** rate of zero order reaction is independent of the concentration of the reacting species

70. **(a)** $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

71. **(d)** Since the slow step is the rate determining step hence if we consider option (A) we find

$$\text{Rate} = k[Cl_2][H_2S]$$

Now if we consider option (B) we find

$$\text{Rate} = k[Cl_2][HS^-] \qquad ...(i)$$

For equation,

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$K = \frac{[H^+][HS^-]}{[H_2S]} \text{ or } [HS^-] = \frac{K[H_2S]}{[H^+]}$$

Substituting this value in equation (i) we find

$$\text{Rate} = k[Cl_2] K \frac{[H_2S]}{H^+} = k' \frac{[Cl_2][H_2S]}{[H^+]}$$

Slow step should involve 1 molecule of Cl_2 and 1 molecule of H_2S only.

Hence, only mechanism (A) is consistent with the given rate equation.

72. **(b)** $A \rightarrow B$ For a first order reaction

Given $a = 0.8$ mol, $(a - x) = 0.8 - 0.6 = 0.2$

$$k = \frac{2.303}{1} \log \frac{0.8}{0.2} \text{ or } k = 2.303 \log 4$$

again $a = 0.9$, $a - x = 0.9 - 0.675 = 0.225$

$$k = \frac{2.303}{t} \log \frac{0.9}{0.225}$$

$$2.303 \log 4 = \frac{2.303}{t} \log 4$$

Hence $t = 1$ hour

73. **(b)**

	N_2O_5	$\rightarrow$	$2NO_2$	+	$\frac{1}{2}O_2$
At t = 0	50		0		0
At t = 50 min	$50 - p_1$		$2p_1$		$\frac{p_1}{2}$

Total pressure at 50 minutes

$$= 50 - p_1 + 2p_1 + \frac{p_1}{2} = 87.5$$

$$\therefore \quad p_1 = \frac{37.5 \times 2}{3} = 25 = \frac{1}{2} \times 50 \text{ mm Hg}$$

This means, 50 min. is half-life.

For 100 minutes, i.e., 2 half lives,

$50 - p_2 = 12.5$

$\therefore \quad p_2 = 37.5$ mm of Hg

Total pressure at 100 minutes

$$= 50 - p_2 + 2p_2 + \frac{p_2}{2} = 50 + \frac{3p_2}{2} = 50 + \frac{3}{2} \times 37.5$$

= 106.25 mm of Hg

74. **(a)** From experiment I and II, it is observed that order of reaction w.r.t. (B) is zero.

From experiment II and III, *x* can be calculated as:

$$\frac{6.93 \times 10^{-3}}{13.86 \times 10^{-3}} = \left(\frac{0.1}{0.2}\right)^x \left(\frac{0.25}{0.3}\right)^y$$

$\because$ Order of reaction w.r.t. B = 0, so y = 0

$$\therefore \quad \frac{6.93 \times 10^{-3}}{13.86 \times 10^{-3}} = \left(\frac{0.1}{0.2}\right)^x$$

$$\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x$$

$x = 1$

Now, Rate $= K[A]^1[B]^o$

or, $6.93 \times 10^{-3} = K[0.1]^1[0.2]^o$

$K = 6.93 \times 10^{-2}$

$$\therefore \quad t_{1/2} = \frac{0.693}{2K} = \frac{0.693}{6.93 \times 10^{-2} \times 2} = 5$$

75. **(c)** For the reaction $2X \rightarrow B$, follow zeroth order

Rate equation is

$Kt = [A]_0 - [A]$

For the half-life; $t = t_{1/2}$ and $[A] = 0.1$

$K\,t_{1/2} = 0.2 - 0.1$

$$K = \frac{0.2 - 0.1}{6} = \frac{0.1}{6}\,\text{M hr}^{-1}$$

$\therefore$ Time required to reach from 0.5 M to 0.2 M = t

$Kt = [A]_0 - [A]$

$$\frac{0.1}{6} \times t = (0.5 - 0.2)$$

$\Rightarrow$ t = 18 hour

76. **(a)** Rate constant of decomposition of $X = 0.05$ μg/year. Unit of rate constant confirms that the decomposition of X is a zero order reaction.

For zero order kinetics,

$[X] = [X]_0 - kt$

$kt = [X]_0 - [X]$

$$t = \frac{[X]_0 - [X]}{k}$$

$$t = \frac{5 - 2.5}{0.05} = \frac{2.5}{0.05} = 50 \text{ years}$$

77. **(d)** $t_{100\%} = \frac{a}{k} = \frac{1}{0.6}\,\text{min} = \frac{1}{0.6} \times 60\text{ sec} = 100\text{ sec.}$

Reaction will be finish in 100 sec., so concentration of B will reach maximum value 2 M after 100 sec.

78. **(b)** Use the formula:

$$t = \frac{2.303}{k}\log\frac{V_0}{V_t} = \frac{1}{k}\ln\frac{V_0}{V_t}$$

$$= \frac{1}{4.5 \times 10^{-2}\,\text{min}^{-1}} \ln\frac{25\text{mL}}{5\text{mL}} = \frac{\log_e 5}{4.5 \times 10^{-2}}\,\text{min}$$

79. **(d)**

$$\begin{array}{lcccc} 2N_2O_5 & \longrightarrow & 4NO_2 & + & O_2 \\ a & & 0 & & 0 \quad t=0 \\ (a-x) & & (2x) & & (x/2) \quad \text{time} = t \end{array}$$

$C_t = C_0 e^{-kt} \Rightarrow (a - x) = a e^{-kt}$

$\Rightarrow \quad x = a - a e^{-kt} \Rightarrow x = a(1 - e^{-kt})$

$[NO_2] = 2x = 2a(1 - e^{-kt})$

80. **(b)** $k = \frac{2.303}{t}\log\frac{a}{(a-x)}$

$(a - x)$ is the concentration left after 100 sec.

$$2.7 \times 10^{-3} = \frac{2.303}{100}\log\frac{0.29}{(a-x)}$$

$$\Rightarrow \quad \frac{0.27}{2.303} = \log\frac{0.29}{(a-x)} \Rightarrow 0.117 = \log\frac{0.29}{(a-x)}$$

$\Rightarrow \quad (a - x) = 0.22$ M.

81. **(b)** $k = \frac{0.693}{45}\text{min}^{-1} = \frac{2.303}{t_{99.9\%}}\log\frac{a}{a - 0.999a}$ or

$$t_{99.9\%} = \frac{2.303 \times 45}{0.693}\log 10^3 = 448\text{ min} \approx 7.5\text{ hrs}$$

82. **(b)** $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log(2) = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$= \frac{E_a}{19.15}(0.0001075)$$

$\Rightarrow \quad E_a = 53441.86\text{ J mol}^{-1} = 53.442\text{ kJ mol}^{-1}$

$\approx 53\text{ kJ mol}^{-1}$

83. **(d)** $k = Ae^{-E_a/RT} \quad \log k = \log A - \frac{E_a}{2.303R}.\frac{1}{T}$

Equation of straight line slope $= \frac{-E_a}{2.303R}$.

84. **(b)** $\frac{r_{100°C}}{r_{10°C}} = 2^{\left(\frac{T_2 - T_1}{10}\right)} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$ (where 2 is temperature coefficient of reaction)

85. **(d)** $\log_{10}\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$T_1 = 300\text{K}, T_2 = 309\text{K}$

$$\log_{10}\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{300} - \frac{1}{309}\right)$$

$$0.3 = \frac{E_a}{2.303 \times 8.3}\left(\frac{9}{300 \times 309}\right)$$

$$E_a = \frac{0.3 \times 2.303 \times 8.3 \times 300 \times 309}{9}$$

$= 59065.04\text{J/mol} = 59\text{ kJ mol}^{-1}$

86. **(b)** $\Delta H = E_{a_f} - E_{a_b} = 0$

87. **(d)** The activation energy depends upon the nature of chemical bonds undergoing rupture during chemical reaction and is independent of enthalpies of reactants and products.

88. **(b)** $k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - E_a/RT$

For $\ln k$ vs $1/T$

$\ln A$ = intercept ; $-E_a/R$ = slope $= -2 \times 10^4$ K

$\therefore \quad E_a = 8.3 \times 2 \times 10^4\text{ J mol}^{-1}$

$= 16.6 \times 10^4\text{ J mol}^{-1}$ or 166 kJ mol^{-1}

89. **(a)** $2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$\log\frac{k_2}{k_1} = \frac{9.0 \times 10^3}{2.303 \times 2}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$\frac{k_2}{k_1} = 1.63;\ k_2 = 1.63k_1;$$

$$\text{Increase in } k_1 = \frac{k_2 - k_1}{k_1} \times 100$$

$$= \frac{1.63k_1 - k_1}{k_1} \times 100 = 63.0\%$$

90. **(c)** $k = Ae^{\frac{-E_a}{RT}} \Rightarrow \ln k = \ln A - \frac{E_a}{RT}$

$$\Rightarrow \log(2 \times 10^{-6}) = \log(4 \times 10^{13}) - \frac{8.3\times10^3}{8.3\times T\times2.3}$$

$$\Rightarrow \log(2) - 6 = 2 \times \log(2) + 13 - \frac{8.3\times10^3}{8.3\times T\times2.3}$$

$$\Rightarrow -19.3 = -\frac{10^3}{T\times2.3} \Rightarrow T = 225 \times 10^{-1}\ \text{K}$$

91. **(c)** Energy activation depends on the nature of the chemical bond being ruptured in the reactant molecule.

92. **(a)** Threshold Energy = Energy of activation + Internal energy

93. **(c)** For the exothermic reaction the energy of products is always less than the reactants. If E_a is the energy of activation for the forward reaction, the energy of activation for backward reaction is $E_a + \Delta H$

94. **(a)** $\text{K} = \text{Ae}^{-\text{E}_\text{a}/\text{RT}} = (6.5\times10^{12}\ \text{s}^{-1})\,\text{e}^{-26000\ \text{K/T}}$

$$\frac{\text{E}_\text{a}}{8.314} = 26000$$

$\Rightarrow$ E_a = 216.164 kJ/mol.

95. **(b)** For 10°C rise of temperature, the rate is almost doubled.

96. **(c)** $\ln k = \ln A - \frac{E_a}{RT}$

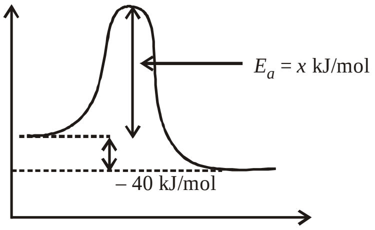
$$\text{Given}: \ln k = 33.24 - \frac{2.0\times10^4}{T}$$

$\therefore$ on comparing $\frac{E_a}{R} = 2.0 \times 10^4$

$\Rightarrow E_a = 2.0 \times 10^4 \times 8.3\ \text{J} = 16.6 \times 10^4\ \text{J} = 166\ \text{kJ}$

97. **(c)** Proper orientation of reactants during collision leads to product.

98. **(a)**



$$\left(\frac{E_{\text{forward}}\ (\text{A}\to\text{B})}{E_{\text{backward}}\ (\text{B}\to\text{A})}\right) = \frac{2}{3} = \frac{x}{-40 + x}$$

$\Rightarrow$ $-80 + 2x = 3x \Rightarrow x = -80$ kJ/mol for forward

For backward = –40 + (–80) = –120 kJ/mol

Because activation energy cannot be negative so, for forward reaction E_a = 80 kJ/mol for backward reaction E_a = 120 kJ/mol.

99. **(b)** $T_1 = 273 + 25 = 298$ K

$T_2 = 273 + 60 = 333$ K

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.3R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\text{or} \quad \log_e\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log_e\frac{2.1\times10^{-2}}{1.5\times10^{-3}} = \frac{E_a}{R}\left(\frac{35}{333\times298}\right)$$

$$\therefore \quad E_a = \frac{298\times333}{35} \times R \times \log_e\frac{21}{1.5}$$

100. **(a)** $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\Rightarrow \log\left(\frac{2.2\times10^{-5}}{2\times10^{-6}}\right)$$

$$= \frac{E_a \times (303 - 287)}{2.303\times2\times10^{-3}\ \text{kcal/mol} - k\times287\times303k}$$

$[T_1 = 273 + 14 = 287k,\ T_2 = 273 + 30 = 303\,k]$

$$\Rightarrow \log 11 = \frac{E_a\times16}{400.542\ \text{kcal/mol}}$$

$\Rightarrow E_a$ = 26 kcal/mol

101. **(d)** $\text{k}_1 = \text{k}_2 \ \therefore\ 10^{18}.\text{e}^{-3000/\text{T}} = 10^{17}.\text{e}^{-2000/\text{T}}$

$$\therefore\ 10.\text{e}^{-3000/\text{T}} = 1.\text{e}^{-2000/\text{T}}$$

$$\therefore\ \ell\text{n}10 - \frac{3000}{\text{T}} = -\frac{2000}{\text{T}}$$

$$\therefore\ 2.303 - \frac{3000}{\text{T}} = -\frac{2000}{\text{T}}$$

$$\therefore\ \text{T} = \frac{1000}{2.303}\text{K}$$

102. **(c)** $\text{K}_1 = \text{K}_2\text{A.e}^{\text{E}_1/\text{RT}};\ \text{K}_1 = \text{A}_1.\text{e}^{-\text{E}_1/\text{RT}};\ \text{K}_2 = \text{A}_2.\text{e}^{-\text{E}_2/\text{RT}}$

$$\frac{\text{K}_1}{\text{K}_2} = \frac{\text{A}_1}{\text{A}_2} \times \text{e}^{(\text{E}_2-\text{E}_1)/\text{RT}} = \text{A.e}^{(2\text{E}_1-\text{E}_1)/\text{RT}} = \text{A.e}^{\text{E}_1/\text{RT}}$$

$$\therefore\ \text{K}_1 = \text{K}_2.\text{A.e}^{\text{E}_1/\text{RT}}$$

103. **(a)** $\ell\text{og}\frac{\text{K}_2}{\text{K}_1} = \frac{\text{Ea.DT}}{2.303\text{RT}_2\text{T}_1}$

$$= \frac{9000\times5}{2.303\times2\times300\times295} = 0.1104$$

$$\ell\text{og}\frac{\text{K}_2}{\text{K}_1} = 0.1104\quad \frac{\text{K}_2}{\text{K}_1} = 1.289\quad \text{K}_2 = \text{K}_1 \times 1.289$$

104. **(c)** $\ell og\frac{K_2}{K_1}=\frac{Ea}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

$$\ell og\frac{0.0693}{0.0231}=\frac{Ea}{2.303\times 8.3}\left(\frac{320-300}{300\times 320}\right)$$

$$\ell og3=\frac{Ea}{1.901}\left(\frac{20}{96000}\right)\ Ea=43.\,84$$

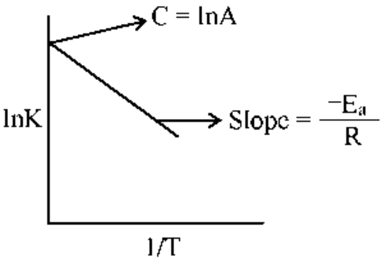
105. **(d)** Activation energy and frequency factor.
106. **(a)** increasing the temperature.
107. **(d)** $\Delta H = Ea^r - Ea^r - 30 = 70 - Ea^r \therefore Ea^r = 100$
108. **(a)** $\Delta H = Ea^r - Ea^r \therefore +5 = 15 - Ea^r \therefore Ea^r = 10$
109. **(c)** more than ΔH
110. **(a)** $E_f < E_r$
111. **(c)** Bimolecular
112. **(b)** Threshold Energy – Energy of the reactants
113. **(a)** an increase in the number of activated molecules
114. **(a)** Slow
115. **(c)** Activation energy is always Positive
116. **(c)** Collision frequency
117. **(d)** threshold energy.
118. **(a)** According to Arrhenius Theory,

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

straight line graph
$y = mx + c$

$$\text{slope (m)} = -\frac{E_a}{R}$$

Intercept (c) = ln A



$$\text{Slope (m)} = -\frac{E_a}{R}$$

$$\frac{E_a}{R} - = -10^3\,K$$

$E_a = 8.314 \times 10^3\ JK^{-1}\ mol^{-1}\ K$

$$E_a = \frac{8.3214\times 10^3}{10^3}Jmol^{-1}\ [1kJ = 10^3\ J]$$

$E_a = 8.314\ kJ\ mol^{-1}$

119. **(b)** $K_1 = 3.46 \times 10^{-2}$
$T_1 = 298k$
$K_2 = ?$
$T_2 = 350$
$E_a = 50.1\ kJ\ mol^{-1}$
$R = 8.314\ JK^{-1}\ mol^{-1}$

According to Arrhenius theory,

$$\log\frac{K_2}{K_1}=\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\log\frac{K_2}{3.46\times 10^{-2}}=\frac{50.1\times 10^3}{2.303\times 8.314}\left[\frac{1}{298}-\frac{1}{350}\right]$$

$$\log\frac{K_2}{3.46\times 10^{-2}}=1.30$$

$$\frac{K_2}{3.46\times 10^{-2}}=10^{1.30}=20$$

$K_2 = 3.46 \times 10^{-2} \times 20$
$K_2 = 69.03 \times 10^{-2}$
$\therefore\ K_2 = 0.69\ s^{-1}$

120. **(d)** According to Arrhenius theory.
$K = A \times e^{-E\ /RT}$

$$\log\frac{K_2}{K_1}=\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Given,
$K_1 = x,\quad T_1 = 300$
$K_2 = 2x\quad T_2 = 310$

$$\log\frac{2x}{x}=\frac{E_a}{2.303\times 8.3}\left[\frac{1}{300}-\frac{1}{310}\right]$$

$$E_a=\frac{\log 2\times 2.303\times 8.3\times 300\times 310}{10}$$

$E_a = 53.49\ kJ\ mol^{-1}$.

Exercise 2 : ACCELERATOR

Topic-wise MCQs

1. **(b)** Average rate $=\frac{-\Delta[R]}{\Delta t}$.
2. **(d)** For reversible reaction, the forward rate of reaction decreases as the concentration of the reactant decreases. Simultaneously, the backward rate of reaction increases as the concentration of the product increases.
3. **(a)** To understand the chemical reaction completely the rate of reaction and factors controlling the rate are equally important with the thermodynamics.
4. **(b)** $r = k\,[X]\,[Y]^0 = k\,[X]$

Using I and II:

$$\frac{4\times 10^{-3}}{2\times 10^{-3}}=\left(\frac{L}{0.1}\right)\Rightarrow L=0.2$$

Using I and III:

$$\frac{M\times 10^{-3}}{2\times 10^{-3}}=\frac{0.4}{0.1}\Rightarrow M=8$$

$$\frac{M}{L}=\frac{8}{0.2}=40$$

5. **(a)** If we write rate of reaction in terms of concentration of NH_3 and H_2, then

Rate of reaction $= \frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

So, $\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

6. **(b)** The curve Y shows the increase in concentration of products with time.

7. **(c)** $K = \frac{2.303}{40}\ell og\frac{0.1}{0.025}$

$= 0.03466\ \text{min}^{-1}$

Rate $= [A]^1 = 0.03466 \times 0.01 = 3.466 \times 10^{-4}\ \text{M min}^{-1}$

8. **(b)** Average velocity $= -\left[\frac{\text{Change in concentration}}{\text{Change in time}}\right]$

$= -\left[\frac{C_2 - C_1}{t_2 - t_1}\right]$

$= -\frac{[0.03 - 0.04]}{[2400 - 0]}$

$= \frac{0.01}{2400} = 4.167 \times 10^{-6}$

9. **(a)** rate of reaction $= \frac{\text{Change in concentration}}{\text{Change in time}} = \frac{|x - y|}{100}$

10. **(a)** $A + 2B \rightarrow 3C + 2D$

$-\frac{dA}{dt} = -\frac{1}{2}\frac{dB}{dt} = \frac{1}{3}\frac{dC}{dt} = \frac{1}{2}\frac{dD}{dt}$

Rate of disappearance of $B = -\frac{dB}{dt} = x \times 10^{-2}$

Rate of reaction $= \left(-\frac{1}{2}\frac{dB}{dt}\right) = -\frac{1}{2}x \times 10^{-2}$

Rate of appearance of $C = \frac{dC}{dt} = -\frac{3}{2}\frac{dB}{dt}$

$= -\frac{3}{2} \times x \times 10^{-2}$

$\therefore$ Ratio of reaction : Rate of appearance

$-\frac{x}{2} \times 10^{-2}\ :\ -\frac{3}{2} \times x \times 10^{-2}$

1 : 3

11. **(d)** The reaction involving two different reactant can never be unimolecular.

12. **(a)** For a zero order reaction.

rate $= k[A]^o$ i.e. rate $= k$

hence unit of k = M.sec^{-1}

For a first order reaction.

rate $= k\,[A]$

k = M.sec^{-1}/M = sec^{-1}

13. **(b)** The value of rate constant can be increased only by increasing the temperature.

14. **(b)** $O_3 \xrightarrow{\text{Fast}} O_2 + O;\ O + O_3 \xrightarrow{\text{Slow}} 2O_2$

$k = \frac{[O_2][O]}{[O_3]}$ (I) Rate $= k'\,[O_3][O]$ put [O] from (I)

$r = \frac{k'[O_3]K[O_3]}{[O_2]} = k[O_3]^2[O_2]^{-1}$

Intermediates are never represented in rate law equation.

15. **(d)** Overall order = sum of orders w.r.t each reactant.

Let the order be x and y for G and H respectively

Exp.No.	**[G]mole litre^{-1}**	**[H]mole litre^{-1}**	**rate (mole litre^{-}time^{-1})**
1	a	b	r
2	$2a$	$2b$	$8r$
3	$2a$	b	$2r$

$\because$ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant *i.e.*, rate $\propto$ [G]

$\therefore$ $x = 1$

From (2) and (3), $y = 2$

$\therefore$ Overall order is 3.

16. **(c)** From 0 to 1h, $N_t = N_0e^t$

When drug is administered bacterial growth is given by,

$\frac{dN}{dt} = -5N^2$

So, at t = 1 h, $N_t = eN_0$

Integrating the differential equation,

$\int_{eN_0}^{N}\frac{dN}{N^2} = -5\int_1^t dt$

$\frac{1}{N} - \frac{1}{eN_0} = 5(t-1) \Rightarrow \frac{N_0}{N} - \frac{1}{e} = 5N_0(t-1)$

$\frac{N_0}{N} = 5N_0t + \left(\frac{1}{e} - 5N_0\right)$

The above equation is similar to straight line equation with positive slope.

Thus $\frac{N_0}{N}$ increases linearly with t.

17. **(d)**

18. **(b)** Both order and molecularity of a reaction are always the same.

19. **(d)** For Zero order reaction $t_{1/2}\,\alpha\,C_o$

20. **(c)** The rate is not depend upon the reactant present in excess

21. **(b)** $2^n = 4$ $3^n = 9$ $\therefore n = 2$

22. **(b)** $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$

23. **(c)** mole^{-1} litre sec^{-1}

24. **(a)**

$r_1 = k[A]^n[B]^m$

Now A is doubled & B is halved in concentration

$\Rightarrow$ $r_2 = k2^n[A]^n.\frac{[B]^m}{2^m}$

$$r_2 = k[A]^n [B]^m . 2^n . \left(\frac{1}{2}\right)^m$$

$$\text{Now } \frac{r_2}{r_1} = 2^n \left(\frac{1}{2}\right)^m \Rightarrow \frac{r_2}{r_1} = 2\,(n\text{-}m)$$

25. **(b)** Before applying medicine

$$\frac{dA}{dt} = k[A] \text{ (First order Rate law)}$$

$$\frac{A}{A_0} = \frac{N}{N_0} = e^{kt}$$

After applying medicine

Active Bacteria → Inactive Bacteria
(A) (I)

$$r = -\frac{dA}{dt} = k[A]^2 \qquad \text{(Rate law)}$$

$y = kx^2$ Parabola

26. **(a)** $\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A+A$

$\text{Rate} = k_2 A_2 [A][B_2]$ .... (1) (from slow step)

$$\Rightarrow \left(\frac{k_1}{k_{-1}}\right) = K_{eq} = \left(\frac{[A]^2}{[A_2]}\right)$$

$$\Rightarrow \quad [A] = \sqrt{\frac{k_1}{k_{-1}}} \cdot \sqrt{[A_2]}$$

Substituting in (1); we get

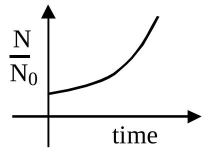
$$\text{Rate} = k_2 \sqrt{\frac{k_1}{k_{-1}}} \cdot [A_2]^{1/2} \cdot [B_2]$$

$$\therefore \text{ Order} = 1 + \frac{1}{2} = \left(\frac{3}{2}\right) = 1.5$$

27. **(d)** Because no. of bacteria initial = N_0
and No. of bacteria at any time t = N
Since bacterial growth is given as

$$N = N_0 e^{Kt}$$

Where K = growth constant for bacterial growth



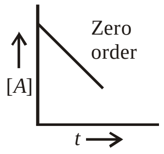
28. **(d)** $t_{1/2} \propto \frac{1}{a^2}$

We know that $t_{1/2} \propto \frac{1}{a^{n-1}}$

i.e. $n = 3$

Thus, reaction is of 3rd order.

29. **(a)** Plots of conc. [*A*] *V*s time, *t*



30. **(a)** Given initial concentration (a) = 2.00 M; Time taken (t) = 200 min and final concentration ($a - x$) = 0.15 M.
For a first order reaction rate constant,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{200} \log \frac{2.00}{0.15}$$

$$= \frac{2.303}{200} \times (0.301 + 0.824) = 1.29 \times 10^{-2} \text{ min}^{-1}.$$

$$\text{Further}, \ (t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{1.29 \times 10^{-2}} = 53.72 \text{ min}.$$

31. **(a)** Rewriting the given data for the reaction

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$$

Actually this reaction is autocatalyzed and involves complex calculation for concentration terms.

We can look at the above results in a simple way to find the dependence of reaction rate (i.e., rate of disappearance of Br_2). From data (1) and (2) in which concentration of CH_3COCH_3 and H^+ remain unchanged and only the concentration of Br_2 is doubled, there is no change in rate of reaction. It means the rate of reaction is **independent of concentration of Br_2**. Again from (2) and (3) in which ($CH_3CO\ CH_3$) and (Br_2) remain constant but H^+ increases from 0.05 M to 0.10 *i.e.* doubled, the rate of reaction changes from 5.7×10^{-5} to 1.2×10^{-4} (or 12×10^{-5}), thus it also becomes almost doubled. It shows that rate of reaction is directly proportional to $[H^+]$. From (3) and (4), the rate should have doubled due to increase in conc of $[H^+]$ from 0.10 M to 0.20 M but the rate has changed from 1.2×10^{-4} to 3.1×10^{-4}. This is due to change in concentration of CH_3COCH_3 from 0.30 M to 0.40 M. Thus the rate is directly proportional to $[CH_3\ COCH_3]$. We now get

$$\text{rate} = k\,[CH_3COCH_3]^1[Br_2]^0[H^+]^1$$
$$= k\,[CH_3COCH_3][H^+].$$

32. **(b)** 42 s

$$Ao \xrightarrow{t_{1/2}} \frac{Ao}{2} \xrightarrow{t_{1/2}} \frac{Ao}{4} \xrightarrow{t_{1/2}} \frac{Ao}{8} \therefore 3 \times t_{1/2}$$

33. **(b)** For a zero order reaction : Rate = $K[A]^0 = K$
Thus, the rate does not change with concentration.
Therefore, I is of zero order reaction.
For the integrated rate law of zero order : $C = -kt + C_0$
Thus, the graph II is for a zero order reaction.
For a first order reaction:-

$$t = \frac{2.303}{K} \log \frac{[R]_0}{[R]} \text{ or } \log \frac{[R]_0}{[R]} = \frac{K}{2.303} t$$

Thus, III is a graph for a first order reaction.

34. **(a)** In graph (i), ln [Reactant] vs time is linear with positive intercept and negative slope. Hence it is 1st order. In graph (ii), [Reactant] vs time is linear with positive intercept and negative slope. Hence, it is zero order.

35. **(b)** For zero order reaction,
rate, $r = k[R]^\circ$

$$\Rightarrow \text{rate} = \frac{-d[R]}{dt} = k \times 1 \Rightarrow \quad d[R] = k\,dt$$

$\Rightarrow \quad [R] = -kt + R_0$

where R_0 is the concentration of reactant at time $t = 0$.
Thus, [R] decreases with time t.

36. **(a)** For first order reaction

$$k = \frac{1}{t}\ln\left(\frac{P_\circ}{P}\right) \Rightarrow \quad \text{In}\left(\frac{P_\circ}{P}\right) = kt \quad \Rightarrow \quad \ln\left(\frac{P}{P_\circ}\right) = -kt$$

On comaring with straight line equation $y = mx$
$k = \text{slope} = 3.465 \times 10^4$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{3.465 \times 10^4} = 2 \times 10^{-5}\,s$$

37. **(d)** From first order reaction,

$$\ln\frac{a}{a-x} = Kt$$

$\ln a - \ln(a-x) = Kt$
$\ln(a-x) = \ln a - Kt$
$y = c - mx$
C(intercept) = ln a
m (slope) = –K
\ given,
C = ln a
or, ln a = –2.303
2.303 log a = –2.303
log a = –1

$\therefore \quad \boxed{a = 10^{-1}}$

again, $-K = -(10)^{-2}$

$\boxed{K = 10^{-2}}$

38. **(d)** $A_t = A_0 e^{-kt}$ where $A_t = (a - x)$ = conc. of reactant remained after time = t
$A_0 = a$ = Initial concentration of reactant when $t = 0$

39. **(b)** $t_{1/2} \alpha\ a^{1-n}$

40. **(b)**

41. **(a)**

42. **(b)**

43. **(c)** $100\% \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25\% \therefore T = 2 \times t_{1/2}$

$$= \frac{T}{2} = 30\,\text{min}$$

44. **(c)** 500 s

$$\frac{M}{10} \xrightarrow{t_{1/2}} \frac{M}{20} \xrightarrow{t_{1/2}} \frac{M}{40} \xrightarrow{t_{1/2}} \frac{M}{80} \xrightarrow{t_{1/2}} \frac{M}{180}$$

$\therefore \quad T \cong 3 \times t\ t_{1/2}$ to $4 \times t_{1/2} \cong 450$ to 600 s

45. **(d)** $Ct = Co \times \left(\frac{1}{2}\right)^{t/t_{112}}$

$$Ct = Co \times \left(\frac{1}{2}\right)^{60/15}, \; Ct = Co \times \frac{1}{16}$$

46. **(a)** $T = n \times t_{1/2}\ n = \frac{96}{24} = 4$

$$\therefore \text{Amount left} = \frac{a}{2^n} = \frac{10}{2^4} = \frac{10}{16} = 0.63$$

47. **(b)** $K = \frac{2.303}{1.386 \times 60 \times 60}\ell og\frac{a}{a - 0.75a}$
$= 2.8 \times 10^{-4}\,S^{-1}$

48. **(a)** For Zero order reaction

$$K = \frac{[A]_o}{2t_{1/2}} = \frac{2}{2 \times 1} = 1\text{mol } L^{-1}hr^{-1}$$

$$t = \frac{[A]_o - [A]}{K} = \frac{0.50 - 0.25}{1} = 0.25hr$$

49. **(a)** $K = \frac{2.303}{t}\ell og\frac{P_o}{P_t} \therefore 3.38 \times 10^{-5} = \frac{2.303}{600}\ \ell og\frac{500}{P_t}$

$$\ell og\frac{500}{P_t} = 0.0088 \text{ or } \frac{500}{P_t} = 1.021 \text{ or } P_t = 490 \text{ atm}$$

50. **(d)** According to given conditions t_1 and t_2 can be given as

$$t_1 = t_{\frac{1}{4}} = \frac{1}{k}\ln\frac{A_0}{A_0} = \frac{1}{k}\ln 4$$

$$t_2 = t_{\frac{1}{8}} = \frac{1}{k}\ln\frac{A_0}{A_0} = \frac{1}{k}\ln 8$$

$\therefore$ Ratio t_1/t_2 will be given by

$$\frac{t_1}{t_2} = \frac{\ln 4}{\ln 8} = \frac{2\ln 2}{3\ln 2} = \frac{2}{3}$$

51. **(c)**

	$A(g) \rightarrow$	$B(g)\ +$	$C(g)$
$t = 0$	P^o	0	0
$t = t$	$P^o - x$	x	x
$t = \infty$	0	P^o	P^o

$$P_t = P^o + x \Rightarrow x = P_t - P^o = P_t - \frac{P_\infty}{2}$$

$$P_\infty = 2P^o \Rightarrow P^o = \frac{P_\infty}{2}$$

$$k = \frac{1}{t}\ell n\frac{P^o}{P^o - x}$$

$$k = \frac{1}{t}\ell n\frac{P_\infty}{2(P_\infty - P_t)}$$

52. **(c)**

	$A(g) \longrightarrow$	$2B(g)\ +$	$C(g)$
$t = 0$	P_0		
$t \to \infty$	0	$2P_0$	P_0

$P_\infty = 3P_0 = 240$
$P_0 = 80$ mm of Hg

$$kt = \ln\left(\frac{P_\infty - P_0}{P_\infty - Pt}\right)$$

$$k\times 10 = \ln\left(\frac{240-80}{240-160}\right)$$

$$k = \frac{\ln 2}{10} = 0.0693\,\text{min}^{-1}$$

$\therefore$ Option (c) is incorrect

53. **(b)** The graph given is for 1st order reaction

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]} \Rightarrow k = \frac{2.303}{25}\log\frac{[50]}{[10]}$$

$$k = \frac{2.303}{25}\log 5 = \frac{2.303\times 0.7}{25}s^{-1}$$

$$= \frac{2.303\times 0.7}{25} = \frac{2.303}{t}\log\frac{50}{2.5} \Rightarrow \frac{1.699}{25} = \frac{2.303}{t}\log 20$$

$$t = \frac{1.301\times 25\times 2.303}{0.699} = 46.46\,\text{s} \approx 47\,\text{s}$$

54. **(c)** $t_{1/2} = \propto [A]_0 \Rightarrow$ Order = zero

$$t_{1/2} = \frac{A_0}{2k} \Rightarrow \text{Slope} = \frac{1}{2k} = 76.92$$

$$k = \frac{1}{2\times 76.92}$$

$$[A]_{10} = -kt + A_0 = -\frac{1}{2\times 76.92}\times 10 + 2.5 = 2.435$$

$= 2435\times 10^{-3}$ mol/L

55. **(c)** For zero order reaction :

$$\text{Half life} = \frac{[A]_o}{2k} \Rightarrow 60\text{min} = \frac{2}{2k} \Rightarrow k = \frac{1}{60}\text{M/min}$$

$$\text{Now, } [A]_t = [A]_o - kt \Rightarrow t = \frac{[A]_o - [A]_t}{k}$$

$$= \frac{0.5-0.25}{1/60} = 15\text{ min}$$

56. **(d)** Half life of A = 10 min

Half life of B = 40 min

$[A]_0 = 8[B]_0$ (given)

$$\Rightarrow [A]_0 = 8[B]_0 \xrightarrow{10\text{ min}} 4[B]_0 \xrightarrow{10\text{ min}} 2[B_0]$$

$$\xrightarrow{10\text{ min}} [B_0] \xrightarrow{10\text{ min}} \frac{[B]_0}{2}$$

$$\Rightarrow [B_0] \xrightarrow{40\text{ min}} \frac{[B]_0}{2}$$

Therefore, 40 min. is the time required for concentration to be same for both the reactants A and B.

57. **(d)** $\frac{t_2}{t_1} = \left(\frac{C_1}{C_2}\right)^n$ and n = 1

$C_o = 16$ mg/mL

$t_1 = ?, C_1 = 8$ mg/mL

$t_2 = 12, C_2 = 4$ mg/mL

$$\Rightarrow t_1 = \frac{t_2 X C_2}{C_1} = \frac{12\times 4}{8} = 6$$

58. **(b)** $r_1 = k[A]^1[B]^1$

$$r_1 = k\left[\frac{n_A}{V}\right]^1\left[\frac{n_B}{V}\right]^1$$

By Reducing the volume to 1/3 of its original volume, the concentration of rectants will becomes 3 times.

$$r_2 = k\left[\frac{3n_A}{V}\right]^1\left[\frac{3n_B}{V}\right]^1$$

$\boxed{r_2 = 9r_1}$ Rate will become 9 times to its initial rate.

59. **(c)**

(A) $t_{1/2} \propto \frac{1}{A_0^{n-1}}$ $\qquad \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{(A_0)_2^{n-1}}{(A_0)_1^{n-1}}$

$$\frac{200}{100} = \left(\frac{0.025}{0.100}\right)^{n-1} \Rightarrow 2 = \left(\frac{1}{4}\right)^{n-1}$$

$$\Rightarrow \frac{1}{4}\times 2 = \left(\frac{1}{4}\right)^n \Rightarrow 2 = 4^n \Rightarrow n = \frac{1}{2}\text{ (order)}$$

(B) $t_{1/2} \propto \sqrt{A_0}$

$$\frac{200}{t_{1/2}} = \frac{(1)^{-1/2}}{(0.1)^{-1/2}} = \frac{(0.1)^{1/2}}{(1)^{1/2}} \quad \text{when } A_0 = 1\text{ M}$$

$t_{1/2} = 200\sqrt{10}$ min

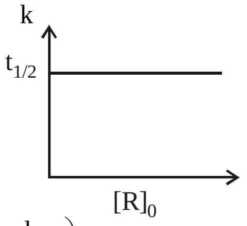
(C) The order would change to 0.769 if the concentration was 0.500 instead of 0.100. Thus, C is not correct.

(D) $\frac{200}{t_{1/2}} = \frac{(0.1)^{1/2}}{(1.6)^{1/2}}$ $\qquad$ when $A_0 = 1.6$ M

$t_{1/2} = 800$ min

60. **(d)** For first order reaction $t_{1/2} = \frac{\ln 2}{k}$

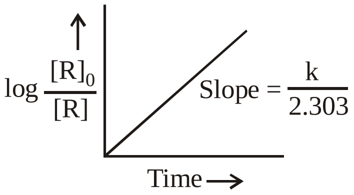
$t_{1/2}$ is independent of $[R]_0$



For first order reaction

$$k = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$$

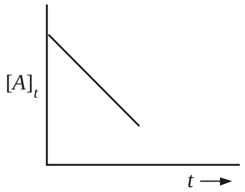
$$\log\frac{[R]_0}{[R]} = \frac{1}{2.303}kt\ ;\ \log\frac{[R]_0}{[R]} = \left(\frac{k}{2.303}\right)\times t$$



61. **(b)** For zero order reaction : $A \rightarrow P$

$$\text{Rate} = k \Rightarrow \frac{[A]_t - [A]_0}{t} = k$$

Thus, concentration $\propto t$ and rate is constant.



62. **(a)** Given : $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$

t = 0	0.6	0	0
t = 100s	0.6 – y	y	y/2

$$P_{Total} = (0.6 - y + y + \frac{y}{2}) = 0.6 + \frac{y}{2}$$

As given in question,

$k = 4.606 \times 10^{-2}\ sec^{-1}$

$$kt = \ln \frac{0.6}{0.6-y} = 2.303 \log \frac{0.6}{0.6-y}$$

$$4.606 \times 10^{-2} \times 100 = 2.303 \log \frac{0.6}{0.6-y} \Rightarrow y = 0.594$$

$$\Rightarrow P_{Total} = 0.6 + \frac{0.594}{2} = 0.897\ atm = 897 \times 10^{-3} atm$$

Thus, $x = 897 \times 10^{-3}$ and answer is 897.

63. **(c)** Nuclear phenomenon independent of temperature. Decay constant is a nuclear property.

64. **(c)** Rate constant remain same even change in concentration of reactant.

65. **(a)** For first reaction,

$$Kt = \ln \frac{[R_0]}{[R]}$$

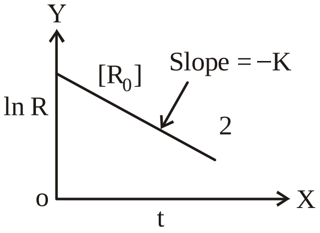
$Kt = \ln R_0 - \ln R$

$\Rightarrow \ln R = \ln R_0 - Kt$

$\Rightarrow y = C + mx$

Slope = –K

Intercept = $\ln R_0$



66. **(a)** For zero order reaction

$$t_{1/2} = \frac{[A]_0}{2K}$$

$[A]_0 = 4\ mol\ L^{-1}$, $t_{1/2} = 0.5$ hr

$$0.5 = \frac{4}{2K}\ \ K = \frac{4}{2 \times 0.5} = 4\ mol\ L^{-1} Hr^{-1}$$

Zero order intigrated rate equation

$$[A]_t = [A]_0 - Kt$$

$$t = \frac{2.0 - 1.0}{4} = \frac{1.0}{4} = \frac{1}{4}$$

67. **(b)** For first order reaction,

Initial pressure = 200 mm

Final pressure = 250 mm

Time = 20 minutes

	$A(g) \longrightarrow$	$B(g) +$	$C(g)$
t = 0	200	0	0
t = 20	200 – x	x	x

$P_t = P_A + P_B + P_C$

$250 = 200 - x + x + x$

$x = 50$

at 20 mint pressure become = 200 – 50 = 150.

$$Kt = 2.303 \log \frac{P_o}{P_t}$$

$$K = \frac{2.303}{20} \log \frac{200}{150}$$

$K = 0.013818$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.013818} = 50.16$$

68. **(b)** Half life is independent of initial concentration of the reactant, so it is a first order reaction.

$$Kt = \ln \frac{[R_0]}{[R]} \Rightarrow Kt = 2.303 \log \frac{[R_0]}{[R]}$$

So graph ‘2’ is not the correct for this reaction.

69. **(a)** For a first order reaction, the time taken is given by:–

$$t = \frac{2.303}{k} \log \left(\frac{A_0}{A} \right)$$

Where, t = time taken

k = rate constant

A_0 = initial concentration of reactant

A = concentration of reactant at time t

$t_{1/2}$ = half time

$$\text{for } t_{1/2} = \frac{2.303}{k} \log \left(\frac{A_0}{\frac{A_0}{2}} \right)$$

$$t_{1/2} = \frac{2.303}{k} \log 2 \qquad \text{...(i)}$$

$$\text{for } t_{3/4} = \frac{2.303}{k} \log \left(\frac{A_0}{\frac{A_0}{4}} \right)$$

$$t_{3/4} = \frac{2.303}{k} \log 4 \qquad \text{...(ii)}$$

Dividing equation (ii) by equation (i)

$$\frac{t_{3/4}}{t_{1/2}} = \frac{\frac{2.303}{k} \log (2)^2}{\frac{2.303}{k} \log 2} = \frac{\frac{2.303}{k} 2 \log (2)}{\frac{2.303}{k} \log 2} = 2$$

70. **(c)** For a 1st order reaction :

$$kt = 2.303\log\frac{[A]_0}{[A]}$$

Where, k = rate constant

t = time taken

$[A]_0$ = initial concentration of reactant

$[A]$ = concentration of reactant at time 't'

Now, for $t = 75$ min

$$[A] = \frac{[A]_0}{8}$$

$$\therefore\quad k = \frac{2.303}{15}\log\left(\frac{[A]_0}{\frac{[A]_0}{8}}\right)$$

$$\therefore\quad k = \frac{2.303}{75}\log(8)$$

$$\therefore\quad k = \frac{2.303}{75}\times 3\log 2$$

$$\text{hence, } k = \frac{2.303}{75}\times 3\times 0.30$$

$$\text{Now, for } t = t^{1/2} = \text{half life } [A] = \frac{[A]_0}{2}$$

$$\therefore\quad t^{1/2} = \frac{2.303\log 2}{\frac{2.303}{75}\times 3\times 0.30}$$

$$\text{so, } t^{1/2} = \frac{2.303\times 0.30}{\frac{2.303}{75}\times 3\times 0.30} = \frac{75}{3} = 25$$

71. **(d)** $A \rightarrow$ Product

rate = $K[A]$ (1st order reaction)

$0.2 = K\times 0.02$

$K = 10$

For x

$0.4 = 10[x]$

$$x = \frac{0.4}{10} = 0.04$$

For y $1.0 = 10[y]$

$$y = \frac{1}{10} = 0.1$$

Ratio x : y

$$\frac{x}{y} = \frac{0.04}{0.1} = \frac{4}{10} = \frac{2}{5}$$

72. **(b)** For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

73. **(b)** For a reversible reaction,

$\Delta H = E_a$ (forward) $- E_a$ (backward)

$\Delta H = 150 - 260 = -110\ \text{kJ mol}^{-1}$

74. **(c)** We know that the activation energy of chemical reaction is given by formula = $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$, where k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore, activation energy of chemical reaction is depends on rate constant at two different temperatures.

75. **(b)** According to Arrhenius equation

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

76. **(b)** Arrhenius equation

$$k = A.e^{-E_a/RT} \quad \Rightarrow \ln K = \ln A - \frac{E_a}{RT}$$

$$\text{slope} = \frac{-E_a}{R}$$

so, activation energy of reaction can be determined from the slope of $\ln k$ vs $\frac{1}{T}$

77. **(d)** Arrhenius equation :

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

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

$$\Rightarrow \ln k = \ln A - \left(\frac{E_a}{R\times 10^3}\right)\times\frac{10^3}{T}$$

$$\text{Slope of graph} = \frac{-E_a}{R\times 10^3} = \frac{-10}{5}$$

$$E_a = 2R\times 10^3\ \text{J} = 2R\ \text{kJ}$$

78. **(a)** $k = Ae^{-E_a/RT}$

Taking ln both sides;

$$\ln k = \frac{-E_a}{RT} + \ln A\ ,\quad y = mx + c$$

$$\text{Slope} = \frac{E_a}{R} = \frac{20}{5} \Rightarrow E_a = 4R = 8\ \text{cal/mol}$$

79. **(a)** As per Arrhenius equation $(k = Ae^{-E_a/RT})$, the rate constant increases exponentially with temperature.

80. **(d)** $k_f = A_f\ e^{-E_f/RT}$ and $k_b = A_b\ e^{-E_b/RT}$

$$\text{We know that } K_{eq} = \frac{k_f}{k_b} \Rightarrow K_{eq} = \frac{A_f}{A_b}e^{-(E_f - E_b)/RT}$$

$$\Rightarrow \ln K_{eq} = \ln\frac{A_f}{A_b} - \frac{(E_f - E_b)}{RT}$$

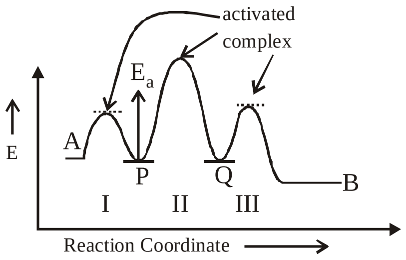
$$\Rightarrow \ln K_{eq} = \frac{-\Delta H}{R}\left(\frac{1}{T}\right) + \ln\frac{A_f}{A_b}$$

Comparing this equation with y = mx + c

$$m = \frac{-\Delta H}{R} = +ve$$

Thus, $\Delta H < 0$ or reaction is exothermic.

81. **(b)** Step II with highest activation energy is rate Determining Step.
No. of activated complex = 3



Number of intermediates = 2

82. **(a)** $$\ln k = \ln A - \frac{E_a}{10^3 RT} \times 10^3 = \ln A + \frac{10^3}{T}\left[-\frac{E_a}{10^3 R}\right]$$

From the graph,

$$\frac{-E_a}{10^3 \times R} = -18.5\,;\, E_a = 153.735 = 154 \text{ kJ/mol}$$

83. **(a)** Arrhenius equation is, $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

$$\text{Given : Slope} = -10000 = \frac{-E_a}{2.303R}$$

$$\because \log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{10^{-4}}{10^{-5}} = 10000\left[\frac{1}{500} - \frac{1}{T_2}\right]$$

$$\Rightarrow 1 = 20 - \frac{10000}{T_2} \Rightarrow T_2 = \frac{10000}{19} = 526.3 \approx 526 \text{ K}$$

84. **(c)**

85. **(c)** With increase in temperature, the number of collision per unit volume per second increases.

86. **(a)** Catalyst provides an alternative reaction pathway which has lower energy of activation than that of the reaction without catalyst.

87. **(a)** The collosion frequency increases. As a result, probability of product formation increases.

88. **(c)** Proper orientation of reactants during collision leads to product.

89. **(c)** Applicable to bimolecular reactions.

90. **(c)** With the increase in temperature the fraction of molecules having energy equal to threshold energy or more increases.

91. **(b)** For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

92. **(c)** We know that the activation energy of chemical reaction is given by formula = $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$, where k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore, activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

93. **(a)** $k = A\,e^{-Ea/RT}$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

For graph between log k with $\frac{1}{T}$

$$|\text{Slope of curve}| = \frac{E_a}{2.303R}$$

From given graph :

Magnitude of slope ⇒ (2) > (1) > (3)

Hence $Ea_2 > Ea_1 > Ea_3$

94. **(a)** $A_2 + B_2 \rightleftharpoons 2AB$

$E_f = 180 \text{ kJ mol}^{-1}$

$E_b = 200 \text{ kJ mol}^{-1}$

$\Delta H = E_f - E_b = -20 \text{ kJ mol}^{-1}$

In presence of catalyst :

$E_f = 180 - 100 = 80 \text{ kJ mol}^{-1}$

$E_b = 200 - 100 = 100 \text{ kJ mol}^{-1}$

Catalyst does not change ΔH or ΔG of a reaction.

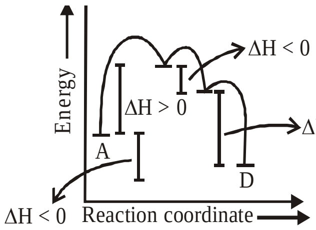
Catalyst only reduces activation energy of the reaction.

95. **(c)** Arrhenius equation holds true for elementary as well as complex reactions.

Unit of A is same as unit of k. Rate of reaction is high if activation energy is low.

A and E_a are temperature independent.

96. **(a)** A net release of heat is observed in the process.



97. **(c)** Activation energy of forward reaction = $E_1 + E_2$

Energy of product > Energy of reactant

$$\text{Stability} \propto \frac{1}{\text{Energy}}$$

98. **(d)** $$\log K = \log A - \frac{E_a}{2.303RT} \quad ...(i)$$

$$\text{Given,}\ \log K = 7.14 - \frac{1 \times 10^4 \text{K}}{T} \quad ...(ii)$$

Comparing equation (i) and (ii) we get

$$\frac{E_a}{2.303RT} = \frac{10^4 \text{K}}{T}$$

$\therefore\ E_a = 10^4 \times 2.303 \times 8.3\ \text{J mol}^{-1} = 191.1 \times 10^3\ \text{J mol}^{-1}$

$E_a = 191.1\ \text{kJ mol}^{-1}$.

99. **(c)** The Arrhenius equation expressed as

$$K = A\exp\left(-\frac{E_a}{RT}\right)$$

Taking log both side

$$\ln K = \ln A - \frac{E_a}{R}\cdot\frac{1}{T}$$

y-axis = $m \times x$-axis

$$\text{Slope} = m = -\frac{E_a}{R}$$

$E_a = 2 \times 10^4 \text{K} \times \text{R}$

$E_a = 2 \times 10^4\ \text{K} \times 8.3\ \text{JK}^{-1}\ \text{mol}^{-1}$

$E_a = 16.6 \times 10^4\ \text{J mol}^{-1}$

$$E_a = 16.6 \times 10^4 \times \frac{1}{1000}$$

$= 166\ \text{kJ mol}^{-1}$

100. **(b)** $E_a = 25 - 10 = 15\ \text{kJ mol}^{-1}$

$|\Delta H| = |5 - 10| = 5\ \text{kJ mol}^{-1}$

Exercise 3 : PREVIOUS YEARS MCQs

1. **(b)** increase four times
2. **(d)** According to given conditions t_1 and t_2 can be given as

$$t_1 = t_{\frac{1}{4}} = \frac{1}{k}\ln\frac{A_0}{A_0} = \frac{1}{k}\ln 4$$

$$t_2 = t_{\frac{1}{8}} = \frac{1}{k}\ln\frac{A_0}{A_0} = \frac{1}{k}\ln 8$$

$\therefore$ Ratio t_1/t_2 will be given by

$$\frac{t_1}{t_2} = \frac{\ln 4}{\ln 8} = \frac{2\ln 2}{3\ln 2} = \frac{2}{3}$$

3. **(c)** $t_{1/4} = \frac{2.303}{k}\log\frac{1}{3/4} = \frac{2.303}{k}\log\frac{4}{3}$

$$= \frac{2.303}{k}(2\times 0.301 - 0.4771) = \frac{0.29}{k}$$

4. **(c)** For first order reaction, $k = \frac{0.693}{t_{1/2}}$

where k = rate constant

$t_{1/2}$ = half life period = 480 sec.

$$\therefore\ k = \frac{0.693}{480} = 1.44 \times 10^{-3}\ \text{sec}^{-1}$$

5. **(b)** For a reversible reaction,

$\Delta H = E_a\,(\text{forward}) - E_a\,(\text{backward})$

$\Delta H = 150 - 260 = -110\ \text{kJ mol}^{-1}$

6. **(b)** For zero order reaction,

$$\text{rate, } r = k[\text{R}]^\circ \Rightarrow \text{rate} = \frac{-d[R]}{dt} = k \times 1$$

$\Rightarrow\ d[\text{R}] = k\,dt \quad \Rightarrow \quad [R] = -kt + R_0$

where R_0 is the concentration of reactant at time $t = 0$.

Thus, [R] decreases with time t.

7. **(b)** For zero order reaction,

$$\text{rate, } r = k[\text{R}]^\circ \Rightarrow \text{rate} = \frac{-d[R]}{dt} = k \times 1$$

$\Rightarrow\ d[\text{R}] = k\,dt \quad \Rightarrow \quad [R] = -kt + R_0$

where R_0 is the concentration of reactant at time $t = 0$.

Thus, [R] decreases with time t.

8. **(d)** $k = Ae^{-E_a/RT} \quad \log k = \log A - \frac{E_a}{2.303R}\cdot\frac{1}{T}$

Equation of straight line slope = $\frac{-E_a}{2.303R}$.

9. **(c)** $t_{1/4} = \frac{2.303}{k}\log\frac{1}{3/4} = \frac{2.303}{k}\log\frac{4}{3}$

$$= \frac{2.303}{k}(\log 4 - \log 3) = \frac{2.303}{k}(2\log 2 - \log 3)$$

$$= \frac{2.303}{k}(2\times 0.301 - 0.4771) = \frac{0.29}{k}$$

10. **(c)** $N_2O \longrightarrow N_2 + \frac{1}{2}O_2$

$\frac{dx}{dt} \propto [N_2O]^1$ *i.e.* order of reaction = 1

11. **(c)** For a first order reaction,

$$t = \frac{2.303}{k}\log\frac{[A]_o}{[A]}$$

for 99% completion of the reaction,

$$t = \frac{2.303}{k}\log\frac{100}{100-99}$$

$$t = \frac{2.303}{k}\log 10^2 \Rightarrow t = \frac{4.606}{k}$$

12. **(d)** none of the above
13. **(d)** It is a second order reaction, first order both w.r.t $S_2O_8^{2-}$ and I^-.

$\therefore\ r = k[S_2O_8^{2-}][I^-]$

All other options are of first order reaction.

14. **(c)** $\frac{k_2}{k_1} = \frac{Ae^{-E_{a_2}/RT}}{Ae^{-E_{a_1}/RT}} = e^{(E_{a_1} - E_{a_2})/RT}$

$$2.303\log\frac{k_2}{k_1} = \frac{E_{a_1} - E_a}{RT} = \frac{(83.314 - 75)\times 10^3}{8.314\times 500} = 2$$

$$\log k_2 = \frac{2}{2.303} = 0.868$$

Taking Antilog

$k_2 = 7.38$

15. **(b)** halved rate" = k [A] $[B]^2$ rate " = k [2A] $\left[\frac{B}{1}\right]^2$

$$= \frac{1}{2}k[A][B]^2$$

$$\therefore \quad x'' = \frac{1}{2}x'$$

16. **(c)** $t_{1/2}$ is independent of initial concentration.

$\therefore \quad t_{1/2} \propto a^o$.

17. **(d)** $A \longrightarrow B, \Delta H = -10 \text{ kJ mol}^{-1}$

It is an exothermic reaction,

$E_{a(b)} = E_{a(f)} - (\Delta H)$

$= 50 - (-10) = 60$ kJ

18. **(b)** $8 \times V_1 = k[A]^2[B] = x V_2 = k[2A]^2[2B] \therefore V_2 = 8x$

19. **(c)** $\frac{-1}{2}\frac{d[SO_2]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt}$

$$\therefore \quad \frac{d[SO_3]}{dt} = \frac{-2d[O_2]}{dt}$$

20. **(c)** Acc to Arrhenius equation.

$$K = Ae^{-E_a/RT}$$

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

$$\log k = \log A - \frac{E_a}{2.303\,R} \times \frac{1}{T}$$

$$y = mx + C$$

$$y = \log k;\ x = \frac{1}{T};\ \text{Slope} = \frac{-E_a}{2.303\,R}$$

$$m = \frac{-E_a}{2.303\,R}$$

21. **(a)** Pseudo first order reaction e.g., inversion of cane sugar is an example of

$$\underset{\substack{\text{Sucrose}\\(\text{Cane sugar})}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The concentration of water remains constant

22. **(c)** Variation of rate constant k with temperature T(K) is given by Arrhenius equation.

$$k = Ae^{-E_a/RT} = \frac{A}{e^{Ea/RT}} \quad \text{...(i)}$$

23. **(a)** Given, $k = 7 \times 10^{-4}\ s^{-1}$, $[A]_0 = 0.08$ M

$$t_{1/2} = \frac{0.693}{k} = \frac{0.0693}{7 \times 10^{-4} s} = 990\,s$$

24. **(a)** $t_{1/2} = \frac{0.693}{k}$

25. **(b)** For reaction, $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

$$-\frac{1}{2}\frac{\Delta[SO_2]}{\Delta t} = \frac{-\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t}$$

So, average rate of reaction is written as

$$-\frac{\Delta[O_2]}{\Delta t}.$$

7

Elements of Groups 16, 17 and 18

Exercise 1 : WARM-UP

Topic-wise MCQs

1. **(b)** Oxygen is the second most electronegative element.

2. **(d)** Ionisation potential decreases down the group.

3. **(a)** On moving left to right in period electronegativity increases and decreases down the group.

$$F > O > Cl > Br$$

4. **(a)** Reactivity follows the order F > Cl > Br > I

5. **(b)** Ionization potential of inert gases is highest in periodic table due to stable electronic configuration.

6. **(a)** Ionisation energy decreases as we move away from nucleus due to less electrostatic attraction between electrons and nucleus

7. **(c)** Ar is the most abundant in atmosphere.

8. **(d)** Due to weak van der Waal's forces, He has lowest boiling point.

9. **(d)** He was observed in the spectrum of the sun.

10 **(d)** Xe forms maximum compounds hence, it is most reactive.

11. **(b)** Noble gases exhibit low chemical activity

12. **(b)** At 2.2 K, liquid helium can flow.

13. **(d)** Electron gain enthalpy for noble gases is positive and it becomes less positive with increase in size of atom.

Value of electron gain enthalpy

$He - 48\ kJ\ mol^{-1}$, $Ne - 116\ kJ\ mol^{-1}$

Ar, $Kr - 96\ kJ\ mol^{-1}$, $Xe - 77\ kJ\ mol^{-1}$

Hence, Ne has highest positive electron gain enthalpy.

14. **(c)** Solubility increases from He to Rn.

15. **(c,d)** Noble gases have low boiling point and low melting point because of

(i) weak van der Waal's interactions and,

(ii) weak dispersion forces.

Hence, option (c) and (d) both are the correct answer.

16. **(b)** H_2O has exceptionally high b.p. due to hydrogen bonding.

17. **(a)** Acidity increases as we go down the group.

18. **(d)** S-H bond is weaker than, O–H bond. Hence, H_2S will furnish more H^+ ions

19. **(d)** All hexafluorides of group 16 elements are gaseous in nature.

20. **(d)** $2Ag_2O\,(s) \rightarrow 4Ag\,(s) + O_2\,(g)$

$2Pb_3O_4\,(s) \rightarrow 6PbO\,(s) + O_2\,(g)$

$2PbO_2\,(s) \rightarrow 2PbO\,(s) + O_2\,(g)$

21. **(a)** Mn_2O_7 is an acidic oxide. BaO and Na_2O are basic oxides while N_2O is a neutral oxide.

22. **(a)** SnO_2 is an amphoteric oxide because it reacts with acids as well as with bases to form corresponding salts.

$SnO_2 + 2H_2SO_4(conc) \longrightarrow Sn(SO_4)_2 + 2H_2O$

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

23. **(c)** It is present as S_8 molecules.

24. **(c)** S_2 is paramagnetic. It contains two unpaired electrons in the antibonding π^* orbital.

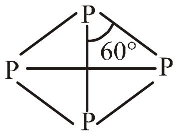
25. **(c)** On going down the group, bond dissociation enthalpy of the hydrides of oxygen family decreases. Therefore, thermal stability also decreases.

26. **(a)** The weakning of M—H bond with increase in size of M (where M = S, Se, Te) explains the acid character of hydrides.

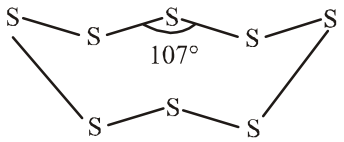
27. **(a)** Water molecule is significantly more polar than the other group 16 hydride molecules so the attraction between $H^{\delta+}$ and $O^{\delta-}$ between water molecules is stronger than the attraction of $H^{\delta+}$ and $E^{\delta-}$ between other group 16 hydride molecules.

28. **(b)** All hydrides excepts H_2O possess reducing property with increases in the order $H_2S < H_2Se < H_2Te$.

29. **(c)**



Strained ring



Crown Structure

30. **(d)** On moving down the group from S to Te, the boiling point of hydrides increases due to increase in van der waal force of attraction. But H_2O has highest boiling point due to presence of hydrogen bonding.

Hence, the increasing order of boiling point of group 16 hydrides is given as : $H_2S < H_2\,Se < H_2\,Te < H_2O$

Thus, H_2S has lowest boiling point while H_2O has highest boiling point.

31. **(d)** Bond energy decreases from Cl to I.

32. **(d)** Oxidising power decreases down the group.

33. **(d)** Due to hydrogen bonding, HF is a liquid.

34. **(b)** Except ionisation potential, other factors are true to explain the oxidising (strong) behaviour of F_2.

35. **(b)** On moving from top to bottom of halogen group the bond dissociation energy of hydrogen halides decreases and so the heat of formation of halogen acids also decreases.

36. **(c)** Volatile character; HCl > HBr > HI > HF

37. **(c)** The H–X bond strength decreases from HF to HI. *i.e.* HF > HCl > HBr > HI. Thus, HF is most stable while HI is least stable. The decreasing stability of the hydrogen halide is also reflected in the values of dissociation energy of the H–X bond.

H – F	H – Cl	H – Br	H – I
$135\,\text{kcal mol}^{-1}$	$103\,\text{kcal mol}^{-1}$	$87\,\text{kcal mol}^{-1}$	$71\,\text{kcal mol}^{-1}$

38. **(d)** HCl acid at 25° C is a gas and polar in nature.

39. **(d)** In gaseous state, HCl is covalent in nature, while in aqueous solution it ionises to give H^+ and $\overset{-}{Cl}$ ions.

40. **(d)** H_2O, HF and NH_3 have hydrogen bonding as the intermolecular forces while HCl has weaker dipole-dipole interaction.

Thus, HCl has the lowest boiling point.

Among H_2O, HF, and NH_3 H_2O has the highest boiling point due to extensive network of hydrogen bonds.

Among NH_3 and HF, HF forms stronger hydrogen bonds due to very high electronegativity of fluorine.

Thus, the order of boiling point will be :-

$HCl < NH_3 < HF < H_2O$

41. **(d)** The oxidizing power decreases down the group.

42. **(c)** The products X and Y are HIO_3 and HCl respectively,

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$

Iodic acid

43. **(a)** Mixture of (He + O_2) is used for asthma patient.

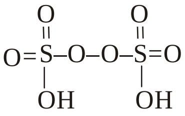
44. **(b)** Thermal decomposition of O_3 is exothermic.

Ozone is diamagnetic in nature (due to presence of paired electron) and both the O – O bond length are equal. It has a bent structure.

45. **(a)** $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$

46. **(a)** In SO_3, sp^2 hybridisation is for Sulphur atom.

47. **(b)**

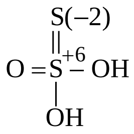


$$O=\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}=O$$

Peroxodisulphuric acid

$(H_2S_2O_8)$

48. **(a)** Sulphur have a general tendency to form two double bond.



$$O=\overset{\overset{S(-2)}{\|}}{\underset{\underset{OH}{|}}{\overset{+6}{S}}}-OH$$

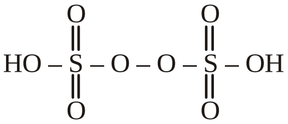
$H_2S_2O_3$

49. **(c)** $HO.SO_2OH + 2PCl_5 \rightarrow ClSO_2Cl + 2POCl_3 + 2HCl$

Sulphuryl chloride

50. **(b)** Conc. H_2SO_4 is a strong dehydrating agent due to which carbohydrates becomes charred on reaction with conc. H_2SO_4 acid.

51. **(b)**

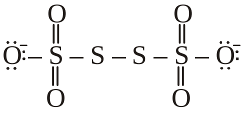


$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Peroxodisulphuric acid

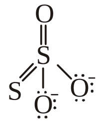
52. **(b)** Oleum is $H_2S_2O_7$.

53. **(a)**



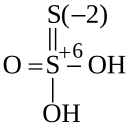
$$\ddot{\underset{..}{O}}{}^{-}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\ddot{\underset{..}{O}}{}^{-}$$

$S_4O_6^{2-}$



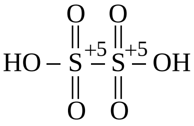
$S_2O_3^{2-}$

54. **(a)** Sulphur have a general tendency to form two double bond.



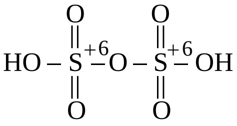
$$O=\overset{\overset{S(-2)}{\|}}{\underset{\underset{OH}{|}}{\overset{+6}{S}}}-OH$$

$H_2S_2O_3$



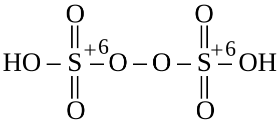
$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+5}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+5}{-}OH$$

$H_2S_2O_6$



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+6}{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+6}{-}OH$$

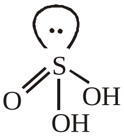
$H_2S_2O_7$



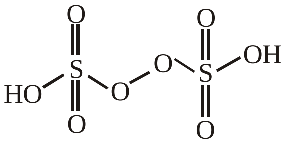
$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+6}{-}O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\overset{+6}{-}OH$$

$H_2S_2O_8$

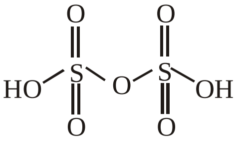
55. **(d)**



(H_2SO_3)
Sulphurous
acid



$(H_2S_2O_8)$
Peroxodisulphuric
acid



$H_2S_2O_7$
Pyrosulphuric
acid

56. **(c)** Peroxysulphuric acid (Peroxydisulphuric acid) = $H_2S_2O_8$.

Pyrosulphuric acid = $H_2S_2O_7$

$\Rightarrow$ Sum of O-atoms = 8 + 7 = 15

57. **(a)** $H_2\overset{+6}{S}O_4 + \overset{+6}{S}O_3 \rightarrow H_2S_2O_7\,(\text{oleum})$

$\Rightarrow$ Sum of oxidation states

= 6 + 6 = 12

58. **(d)** $O_3(g) + 2I^-(aq) + H_2O(l) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$

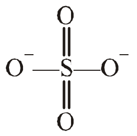
59. **(a)** Preparation of H_2SO_4 from iron pyrite (FeS_2):

$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$ and from S: $S + O_2$ ’ $\rightarrow SO_2$

60. **(c)** $H_2SO_4 + SO_3$ ’$\rightarrow H_2S_2O_7$

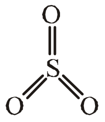
61. **(c)**

(i) SO_4^{2-} :



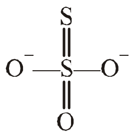
Average bond order = 6/4 = 1.5

(ii) SO_3 :



Average bond order = 6/3 = 2

(iii) $S_2O_3^{2-}$:



Average bond order = 4/3 = 1.33

Correct sequence of bond order is

$SO_3 > SO_4^{2-} > S_2O_3^{2-}$

62. **(c)** MnO_2 and $KMnO_4$ with conc HCl give Cl_2.

63. **(b)** $6NaOH + 3\overset{0}{Cl_2} \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$

64. **(d)** $2K\overset{+7}{Mn}O_4 + 16HCl \rightarrow 2\overset{+2}{Mn}Cl_2 + 2KCl + 8H_2O + 5Cl_2$

O.S of Mn changes from +7 to +2 hence reduction occurs and Cl_2 is formed.

65. **(b)** $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

66. **(d)** $3Ca(OCl)_2 \rightarrow Ca(ClO_3)_2 + 2CaCl_2$

It is autooxidation and disproportionation.

67. **(b)** Chlorine water loses its yellow colour on standing because in the presence of light a mixture of hypochlorous acid (HOCl) and hydrochloric acid are fomed.

$$H_2O + Cl_2 \longrightarrow HOCl + HCl$$

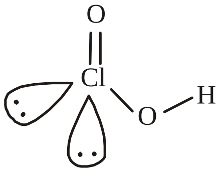
68. **(d)** $Na\overset{+1}{Cl}O \longrightarrow Na\overset{+5}{Cl}O_3 + 2Na\overset{-1}{Cl}$ All statements are correct as evident from the reaction

69. **(d)** As the oxidation state of the central halogen atom increases, the halogen-oxygen bond becomes more and more covalent. As a result, the thermal stability of the oxoacid increases. Thus, $HClO_4$ is most stable to heat, whereas HClO is least stable to heat.

70. **(d)** Interhalogen compounds are not highly volatile.

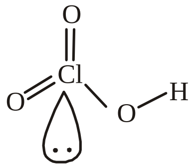
71. **(d)** Number of Cl = O bonds

$HClO_2$



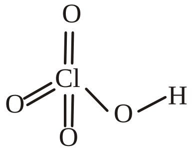
Chlorous acid

$HClO_3$



Chloric acid

$HClO_4$



Perchloric acid

72. **(d)** The stability of oxides of halogens decreases in the order I > Cl > Br

The stability of oxides of iodine is greater than those of chlorine and bromine. Iodine oxygen bond is stable due to greater polarity of the bond while the stability of the chlorine oxygen bond is due to multiple bond formation involving *d*-orbitals of the chlorine atom. Bromine being in between, lacks both these characteristics. Thus the stability of oxides of halogens decreases as mentioned above.

73. **(c)** AB_5 species have square pyramidal structures.

Hence, BrF_5, IF_5 and ClF_5.

74. **(b)** Br_2 + Excess $F_2 \rightarrow Br\ F_5$

[Hint: Due to high reactivity of BrF_5, it absorbs moisture from surrounding resulting into formation of $HBrO_3$]

75. **(c)** $SiCl_4$

1. Hydrolysis of $P_4\,O_{10} \rightarrow$

   $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

   H_3PO_4 and P_4O_{10} are not solid under standard conditions.

2. Hydrolysis of $F_2 \rightarrow$

   $2F_2 + 2H_2O \longrightarrow 4HF + O_2$

   HF is a liquid or gas and O_2 is a gas

3. Hydrolysis of $SiCl_4 \rightarrow$

   $SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$

SiO_2 is a solid and HCl is a gas

Hydrolysis of Azide ion

Azide ion does not hydrolyse under normal conditions.

76. **(a)** $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

77. **(c)** $Ti + 2I_2 \rightarrow TiI_4 \xrightarrow{\Delta} Ti + 2I_2$ (van Arkel)

$I_2 + H_2O$ fi $IO^- + 2H^+ + I^-$

78. **(b)** The shape of XeO_3 is Trigonal Pyramidal.

79. **(b)** $XeOF_4$ is square pyramidal.

80. **(b)** XeF_4 is planar.

81. **(a)** In XeO_3 the hybridisation is sp^3.

82. **(b)** $XeF_4 + H_2O \rightarrow 2HF + XeOF_2$

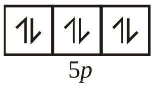
83. **(d)** $XeF_4 + H_2O \rightarrow XeO_2F_2 + 4HF$

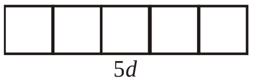
84. **(c)** He has a diffusing property through rubber, glass or plastics.

85. **(d)** The products of the concerned reaction react each other forming back the reactants.

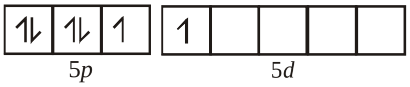
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF \cdot$$

86. **(c)** $2XeF_6 + SiO_2 \rightarrow SiF_4 + 2XeOF_4$

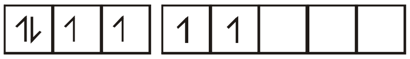
87. **(b)** $Xe = [Kr]4d^{10}5s^2$ 


G.S.

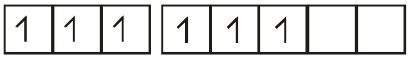
In first excited state, Xe can form XeF_2

Xe = 

In second excited state, Xe can form XeF_4

Xe = 

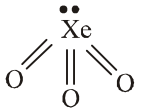
In third excited state, Xe can form XeF_6

Xe = 

Hence, xenon can combine with only even number of fluorine atoms.

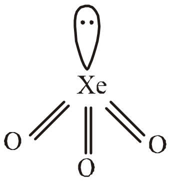
88. **(a)** $XeF_6 + H_2O$ ’→ $XeO_3 + 6HF$

$$H = \frac{1}{2}(V + M - C + A)$$



$$= \frac{1}{2} \times 8 = 4 \Rightarrow sp^3 \text{ hybridisation}$$

89. **(a)** $6\,XeF_4 + 12\,H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$



pyramidal

90. **(b)** Xenon forms three binary fluorides XeF_2, XeF_4 and XeF_6 by direct reaction of elements under appropriate conditions.

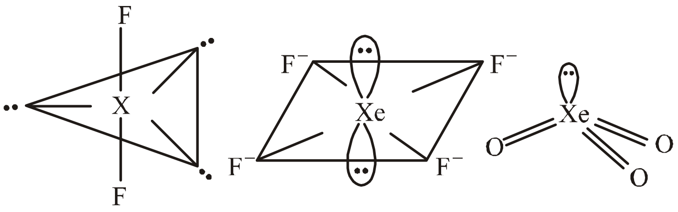
$$Xe(g) + 2F_2(g) \xrightarrow{873\,K,\ 7bar} XeF_4(s)$$

(1 : 5 ratio)

91. **(a)** Xe forms fluorides of even number of fluorine atoms. This is so because the promotion of one, two or three electrons from the 5p- orbital will result in two, four or six half-filled orbitals and this will give XeF_2, XeF_4 or XeF_6 respectively.

92. **(d)** $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

93. **(d)**

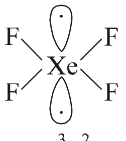


XeF_2 (sp^3d) XeF_4 (sp^3d^2) XeO_3 (sp^3)

94. **(b)** $XeF_4 + SbF_5 \longrightarrow \underset{\text{Cation}}{[:\overset{..}{Xe}F_3]^{\oplus}}\ \underset{\text{Anion}}{[SbF_6]^-}$

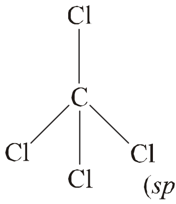
Hybridisation	sp^3d (Xe)	sp^3d^2 (Sb)
Geometry:	Trigonal bipyramidal	octahedral
Shape:	T-shaped	octahedral

95. **(c)** XeF_4 is sp^3d^2 hybridised and due to presence of 2 lone pair of electrons its shape is square planar.



sp^3d^2

CCl_4 is sp^3 hybridised due to 4 bonds. Its geometry is sigma.



$(sp)^3$

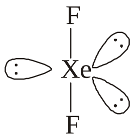
96. **(d)**

(d) Helium has lowest boiling point among all the noble gases. Due to minimum van der Waal's force of attraction.

(a) $Xe(g) + 3F_2(g) \xrightarrow[60-70\,bar]{573\,k} XeF_6(s)$

(b) Ar used in electric bulbs.

(c) 3 lone pairs are present in XeF_2.



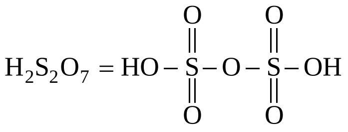
(sp^3d) Linear

97. **(d)** $Xe + F_2 \xrightarrow[60-70\text{ bar}]{573\,K} XeF_6$ (1:20)

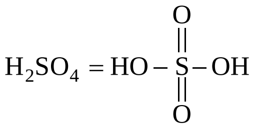
98. **(c)** In $KMnO_4$ manganese is already present in its highest possible oxidation state *i.e.* +7. So no further oxidation is possible.

99. **(b)**

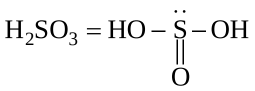
100. **(c)** Number of π-bonds



$$H_2S_2O_7 = HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$



$$H_2SO_4 = HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH \quad 2$$



$$H_2SO_3 = HO-\overset{\cdot\cdot}{\underset{\underset{O}{\|}}{S}}-OH \quad 1$$

101. **(c)** $6NaOH + 4S \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

102. **(b)** H_2S

103. **(a)** H_2Te

104. **(c)** In liquid state BrF_3 dissociates into BrF_2^+ and BrF_4^- ions most easily.

105. **(a)** ICl_7. The hybridisation is $\frac{1}{2}(7+7+0-0) = 7\ (sp^3d^3)$

106. **(c)** $2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$

107. **(d)** MnO_2 or $KMnO_4$ with conc. HCl give Cl_2.

108. **(d)** Interhalogen compounds are not highly volatile.

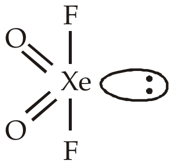
109. **(a)** Since the electronegativity of halogens follow the order Cl > Br > I the strength of acids follow the order HClO > HBr > HIO.

110. **(b)** $HSO_4^- - e^- \rightarrow HSO_4 \rightarrow H_2S_2O_8 \rightarrow S_2O_8^{2-}$

111. **(d)** $K_2Cr_2O_7 + \text{conc.}HCl \rightarrow Cl_2$

112. **(a)** $2\overset{-}{Br} + Cl_2 \rightarrow Br_2 + 2\overset{-}{Cl}$. Chlorine is more oxidising is nature

113. **(d)** XeO_2F_2 has trigonal bipyramidal geometry, but due to presence of lone pair of electrons on equitorial position, its actual shape is see-saw.



114. **(c)** Hybridisation of XeF_4 is sp^3d^2 and structure is square planar

115. **(b)** $XeOF_4$ square pyramidal.

116. **(b)** $XeF_4 + H_2O \rightarrow 2HF + XeOF_2$

117. **(b)** $2KClO_3 \rightarrow 2KCl + 3O_2$

118. **(c)**

119. **(b)**

120. **(d)**

Exercise 2 : ACCELERATOR

Topic-wise MCQs

1. **(c)** Air is liquified by making use of the joule-Thompson effect (cooling by expansion of the gas) Water vapour and CO_2 are removed by solidification. The remaining major constituents of liquid air i.e., liquid oxygen and liquid nitrogen are separated by means of fractional distillation (b.p. of O_2 = –183°C : b. P. of N_2 = – 195.8°C)

2. **(c)** Due to greater tendency for catenation, sulphur shows property of polyanion formation to a greater extent.

For example, in polysulphides such as $S_3^{2-}, S_4^{2-}, S_5^{2-}$

3. **(c)** Outer electronic configuration of Cl atom

$= 3s^2 3p_x^2 p_y^2 p_z^1$

Outer electronic configuration of Cl^- ion $= 3s^2 3p_x^2 p_y^2 p_z^2$

Hence Cl^- has 4 unshared pair of electrons.

4. **(d)** We know that positive ion is always smaller and negative ion is always larger than the corresponding atom. Therefore the correct order of the size is $I^- > I > I^+$

5. **(c)** Iodine is a molecular solid as weak van der Waal's forces are present between its molecules.

6. **(b)**

7. **(b)**

(a) $\Delta_{eg}H(Cl) < \Delta_{eg}H(F)$
(–349) (–333) Correct

(b) $\Delta_{eg}H(Se) < \Delta_{eg}H(S)$
(–195) (–200) Incorrect

(c) $\Delta_{eg}H(I) < \Delta_{eg}H(At)$
(–296) (–270) Correct

(d) $\Delta_{eg}H(Te) < \Delta_{eg}H(Po)$
(–190) (–174) Correct

8. **(c)** Fluorine is most electronegative element in periodic table and exhibits O.S. value of –1 only.

9. **(c)** The electron gain enthalpy order for halogens is

$Cl > F > Br > I$

Due to small size of fluorine the extra electron to be added feels more electron-electron repulsion. Therefore fluorine has less value for electron affinity than chlorine.

10. **(c)**

11. **(b)** Polarizibility of noble gases increases down the group because of increase of distance of electrons from nucleus. Thus He (first member of group) is least polarized.

12. **(b)**

13. **(a)**

14. **(a)**

15. **(a)** Rn because it is radioactive element obtained by the disintegration of radium

$${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_{2}He^{4}$$

16. **(b)**

17. **(b)**

18. **(c)** Argon is used in high temperature welding and other operations which require a non-oxidising atmosphere and the absence of nitrogen.

19. **(b)** Neon gives a distinct reddish glow when used in either low-voltage neon glow lamps or in high voltage discharge tube.

20. **(a)** As size increases, van der Waal's forces of attraction between noble gas atoms also increases. Consequently, ease of their liquefaction increases.

21. **(d)** Electron gain enthalpy for noble gases is positive and it becomes less positive with increase in size of atom.

Value of electron gain enthalpy

He – 48 kJ mol^{-1}, Ne – 116 kJ mol^{-1}

Ar, Kr – 96 kJ mol^{-1}, Xe – 77 kJ mol^{-1}

Hence, Ne has highest positive electron gain enthalpy.

22. **(c)** Helium is twice as heavy as hydrogen it is inflammable but not lighter than hydrogen. Helium has the lowest melting and boiling point of any element which makes liquid helium an ideal coolant for many extremely low temperature application such as super conducting magnet and cryogenic research where temperature close to absolute zero are needed. He is used in gas cooled atomic reactors as a heat transfer agent.

23. **(c)**

Element	$\Delta_{eg}H$ **[kJ / mol]**
He	+48
Ne	+116
Kr	+96
Xe	+77

24. **(a)** Instantaneous dipole-induced dipole forces are most responsible in allowing xenon gas to liquify.

25. **(b)** As we move down the group, the melting and boiling points show a regular increase due to corresponding increase in the magnitude of their van der Waals forces of attraction as the size of the atom increases.

26. **(d)** As the size of anion (M) increases M – H bond strength decreases, so release of H^+ becomes easier. Thus H_2Te is most acidic because size of Te is highest.

27. **(c)** SO_2 is highly soluble in water and therefore cannot be collected over water.

28. **(b)** H - S bond is weaker than H—O bond due to large size of S. Moreover due to high electronegativity of oxygen it forms hydrogen bond in H_2O.

29. **(d)** H_2O is liquid but H_2S is a gas. This can be attributed to the presence of intermolecular hydrogen bonding in case of H_2O.

30. **(d)** Oxidation state of sulphur varies from – 2 to + 6 in its various compounds.

31. **(a)** The first member of a group exhibits anomalous behaviour and shows different physical and chemical properties than the rest of the elements due to smallest size and highest electronegativity.

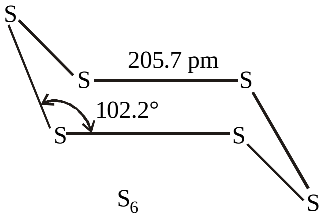
e.g. Oxygen is diatomic while other members are poly atomic.

32. **(a)** Bond dissociation energy of E–H bond in hydrides of group 16 follows the order:

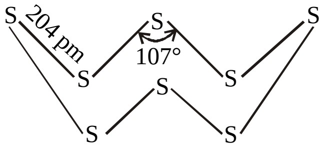
$H_2O > H_2S > H_2Se > H_2Te$

33. **(a)** At room temperature, water is liquid and has boiling point 373 K due to hydrogen bonding. Whereas H_2S is a gas and it has no hydrogen bonding. Hence boiling point of H_2S is less than 300 K (boiling point of H_2S is –60°C).

34. **(a)** The S_6 molecule has a chair-form hexagon ring with the approx same bond length as that in S_8, but with some what smaller bond angles, i.e., bond lengths are approx. same but bond angles are different.



S_6



S_8

35. **(c)** Selenium oxide (SeO_2) is colourless solid.

36. **(b)** $H_2O < H_2S < H_2Se < H_2Te$ (Boiling point)

$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$ (Acidic nature)

$HF < HCl < HBr < HI$ (Acidic nature)

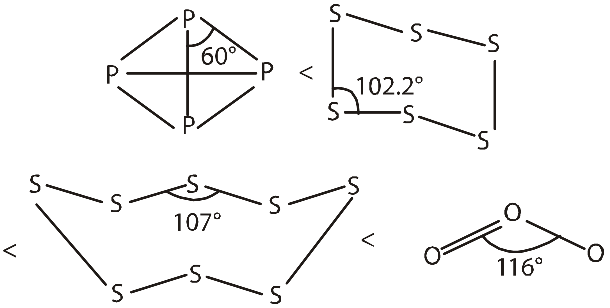
$H_2Te < H_2Se < H_2S < H_2O$ (Bond angle)

37. **(d)** Among S and Te, S will be more stable in +6 state than in +4 state due to inert pair effect.

That is why SO_2 is the strongest reducing agent.

38. **(d)** Increasing order of bond angles :-

$P_4 < S_6 < S_8 < O_3$.



39. **(c)** The H–X bond strength decreases from HF to HI. i.e. HF > HCl > HBr > HI. Thus HF is most stable while HI is least stable. The decreasing stability of the hydrogen halide is also reflected in the values of dissociation energy of the H–X bond

H – F	H – Cl	H – Br	H – I
135 kcal mol^{-1}	103 kcal mol^{-1}	87 kcal mol^{-1}	71 kcal mol^{-1}

40. **(b)** $\underset{\text{(cold \& dil)}}{Cl_2 + 2NaOH} \rightarrow NaCl + NaClO + H_2O$

$\underset{\text{(hot \& conc.)}}{3Cl_2 + 6NaOH} \rightarrow 5NaCl + NaClO_3 + 3H_2O$

41. **(d)** As the oxidation state of the central halogen atom increases, the halogen-oxygen bond becomes more and more covalent. As a result the thermal stability of the oxoacid increases. Thus, $HClO_4$ is most stable to heat, whereas HClO is least stable to heat.

42. **(a)** Longer bond length means weaker bond energy i.e. less bond dissociation energy or more reactivity. Larger the size of anion more will be bond length thus the order of reactivity is HI > HBr > HCl.

43. **(a)** The order of bond energy is

$Cl-Cl > F-F > Br-Br > I-I$

The small value of bond energy in F_2 than Cl_2 (anomaly) is due to smaller size of F atom which leads to inter-electronic repulsions.

44. **(a)** Fluorine, like other halogens has seven electrons is the valence shell. Since it is the most electronegative element, therefore, it readily accepts one electron to acquire the stable electronic configuration of the nearest noble gas. Therefore, like other halogens, it also *exhibits an oxidation state of* –1.

Further, since fluorine is the most electronegative element and does not have d-orbitals is its valence shell, therefore, it cannot expand its octet and hence does not show positive oxidation states. On the other hand, other halogens have d-orbitals and, therefore, can expand their octets and thus show positive oxidation states of +1, +3, +5 and +7 in addition to oxidation state of –1.

45. **(c)** Br_2 reacts with NaI only to get I_2.

$2NaI + Br_2 \rightarrow 2NaBr + I_2$

46. **(c)** MI > MBr > MCl > MF. As the size of the anion decreases covalent character also decreases.

47. **(d)** Since all the halogens have a strong tendency to accept electrons. Therefore halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine.

48. **(c)** From the given options we find option (a) is correct. The oxidising power of halogens follow the order $F_2 > Cl_2 > Br_2 > I_2$. Option (b) is incorrect because it in not the correct order of electron gain enthalpy of halogens.

The correct order is $Cl_2 > F_2 > Br_2 > I_2$. The low value of F_2 than Cl_2 is due to its small size.

Option (c) is incorrect. The correct order of bond dissociation energies of halogens is

$Cl_2 > Br_2 > F_2 > I_2$.

49. **(a)** Bond energy of F_2 less than Cl_2 due to lone pair-lone pair repulsions and small size of fluorine.

$\therefore$ Bond energy order $Cl_2 > Br_2 > F_2 > I_2$

50. **(a)** Generally, bond energy $\propto \dfrac{1}{\text{Bond length}}$

So, bond energy order is : C–F > C–Cl > C–Br > C–I

51. **(c)** Due to strong H-bonding between HF molecules. HF has highest boiling point among the hydrogen halides.

52. **(b)** $I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$

Chlorine oxidises iodine to iodic acid. So statement b is incorrect.

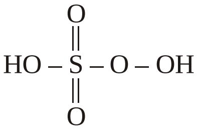
53. **(c)** Boiling point of hydrogen halides are

HF > HI > HBr > HCl

HF have hydrogen bond so its boiling point is high and molecular mass increases hence boiling point of other halide increases.

54. **(c)** Oleum is $H_2S_2O_7$ (H_2SO_4+ SO_3) which is obtained by dissolving SO_3 in H_2SO_4 and is called fuming sulphuric acid.

55. **(d)** Caro's acid is H_2SO_5 which contains one S – O – OH peroxy linkage. It is also known as permonosulphuric acid.



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

56. **(a)** $\underset{\text{Thiosulphate}}{2S_2O_3^{-2}} + I_2 \rightarrow \underset{\text{Tetrathionate}}{S_4O_6^{-2}} + 2I^-$

57. **(d)** Hypo ($Na_2S_2O_3$) is used in photography. It is used during fixing of image. It dissolves AgBr that has not been affected by light during exposure leaving metallic silver (Ag) as such

$$AgBr + \underset{\text{Hypo}}{2Na_2S_2O_3} \longrightarrow \underset{\text{Soluble complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

58. **(a)** Sodium thiosulphate is a reducing agent. It is used in volumetric titration (Iodimetry) to reduce I_2 to I^-.

$$\underset{\text{Sod. thiosulphate}}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{\text{Sod. tetrathionate}}{Na_2S_4O_6} + 2NaI$$

59. **(c)** Ozone layer is beneficial to us, because it stops harmful ultraviolet radiations from reaching the earth.

60. **(b)** At anode : $2OH^- \rightleftharpoons H_2O + \frac{1}{2}O_2$

61. **(c)** $X = Na_2SO_3$

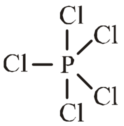
$$\underset{(X)}{SO_3^{2-}} + H_2SO_4 \rightarrow [H_2SO_3] \rightarrow H_2O + \underset{(Y)}{SO_2}$$

$$SO_2 + 2NaOH \rightarrow \underset{(X)}{Na_2SO_3} + H_2O$$

$$\underset{(X)}{Na_2SO_3} + \underset{(Y)}{SO_2} + H_2O \rightarrow \underset{(Z)}{2NaHSO_3}$$

62. **(c)**

$$\begin{tikzcd} SO_2\,(g) + Cl_2\,(g) \arrow[r] & \underset{(A)}{SO_2Cl_2\,(g)} \arrow[d, "P_4"] \\ & \underset{(B)}{PCl_5} + SO_2 \end{tikzcd}$$



Shape of B is Trigonal bipyramidal (TBP)

Hydrolysis of B :

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow \underset{\text{(Phosphoric acid)}}{H_3PO_4} + 3HCl$$

PCl_5 is a yellowish white powder and in solid state exists as an ionic solid.

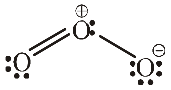
PCl_5 has three equatorial P–Cl bonds which are equivalent while the two axial bonds are longer than equatorial bonds.

63. **(d)** $Fe_2O_3.xH_2O$

In the contact process for the manufacturer of sulfuric acid [H_2SO_4] the arsenic purifier is crucial to remove arsenic impurities from the sulfur dioxide (SO_2) gas before it enters the catalytic converter. The arsenic purifier typically contain a mass of ferric oxide (Fe_2O_3) or other suitable materials. Which effectively adsorb arsenic compounds.

64. **(a)** Ozone has a central oxygen atom that forms a single bond and a double bond.

Thus, it has one lone pair and other oxygen atoms have two and three respectively.

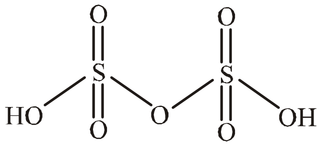


⇒ Total number of lone pairs = 6

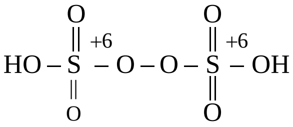
Total number of bond pairs = 3

⇒ Ratio = 6 : 3 or 2 : 1

65. **(c)** The S-O-S bond is present in disulphuric or pyrosulphuric acid that has the formula $H_2S_2O_7$.



66. **(c)** The structure of Peroxydisulphric acid is:-



$$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|\,+6}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|\,+6}}{S}}-OH$$

Oxidation states of s-atoms = +6 and + 6 Number of

S– OH bonds = 2.

67. **(d)** Bleaching action of chlorine is due to oxidation in presence of moisture.

$Cl_2 + H_2O \rightarrow HCl + HClO$

$HClO \rightarrow HCl + O$

Colouring matter + | O | → Colourless matter

68. **(c)** A stronger oxidising agent (Cl_2) displaces a weaker oxidising agent (Br_2) from its salt solution.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

69. **(a)** Due to absence of reaction between marble and bromine.

70. **(b)** $H_2O + \overset{0}{Br_2} \longrightarrow \overset{+1}{HOBr} + \overset{-1}{HBr}$

Thus here oxidation number of Br increases from 0 to +1 and also decreases from 0 to –1. Thus it is oxidised as well as reduced.

71. **(d)** $I_2 + \underset{\text{(Conc)}}{10HNO_3} \longrightarrow \underset{\text{Periodic acid}}{2HIO_3} + 10NO_2 + 4H_2O$

72. **(d)** $\underset{+1}{HOCl} < \underset{+3}{HOClO} < \underset{+5}{HOClO_2} < \underset{+7}{HOClO_3}$

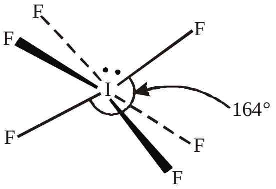
In case of oxyacids of similar element as the oxidation number of the central atom increases, strength of acid also increases.

73. **(b)** ClO_2 contains 7 + 12 i.e. 19 valence electrons which is an odd number, i.e., there is (are) free electron(s). Hence it is paramagnetic in nature.

74. **(b)** $HClO_4$ is the strongest acid amongst all because the oxidation state or Cl is maximum (+7).

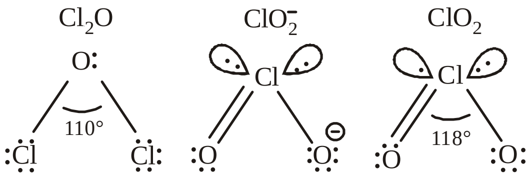
75. **(a)** The structure of IF_6^- is distorted octahedral

This is due to presence of a "weak" lone pair.



76. **(c)** The correct order of increasing bond angle is

$Cl_2O < ClO_2^- < ClO_2$

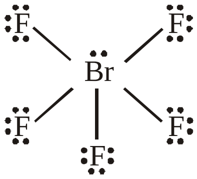


* In ClO_2^- there are 2 lone pairs of electrons present on the central chlorine atom. Therefore the bond angle in ClO_2^- is less than 118° which is the bond angle in ClO_2 which has less number of electrons on central chlorine atom.

77. **(d)** Chlorine reacts with excess of ammonia to produce ammonium chloride and nitrogen.

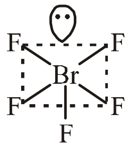
$$3Cl_2 + 8NH_3\,(\text{excess}) \longrightarrow 6NH_4Cl + N_2$$

78. **(b)** The molecular geometry of BrF_5 is square pyramidal with asymmetric charge distribution on the central atom.

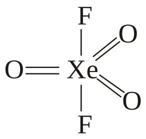


79. **(a)** $Br_2 + F_2\,(\text{excess}) \longrightarrow BrF_5$

Structure of BrF_5 is

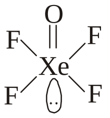


80. **(a)** Structure of XeO_3F_2



So, bond pairs = 5, π bonds = 3 lone pairs = 0

81. **(c)** In $XeOF_4$, Xe is sp^3d^2, hybridised having 5 bond pairs and 1 lone pair respectively.



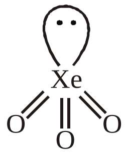
$XeOF_4$

Square pyramidal

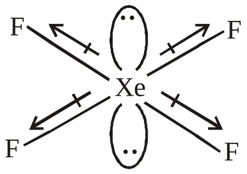
(sp^3d^2)

82. **(b)** The hybridization of XeO_3F_2 is sp^3d and its structure is trigonal bipyramidal in which oxygen atoms are situated on the plane and the fluoride atoms are on the top and bottom.

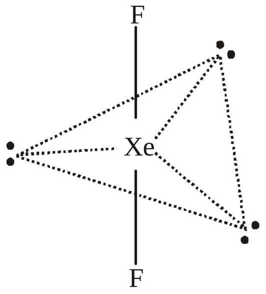
83. **(b)** The shape of XeO_3F_2 is trigonal Pyramidal.



84. **(b)** XeF_4 has zero dipole moment. It has square planar structure due to which the bond moments of Xe – F cancel each other.

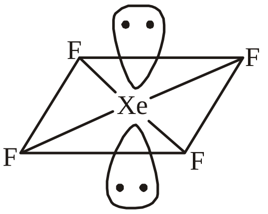


85. **(c)** XeF_2:



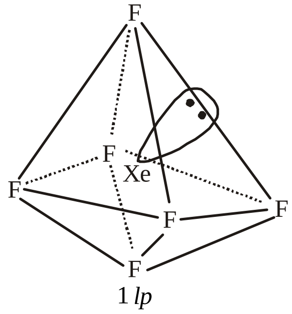
3 *lp*

XeF_4:



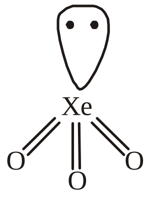
2 *lp*

XeF_6:



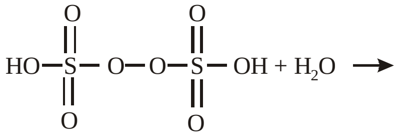
1 *lp*

XeO_3 :



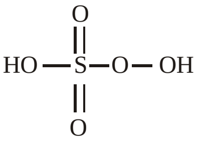
1 *lp*

86. **(c)**



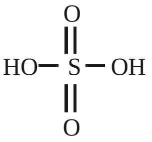
$$HO-\overset{O}{\underset{O}{S}}-O-O-\overset{O}{\underset{O}{S}}-OH + H_2O \longrightarrow$$

peroxodisulphuric acid



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

+



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

peroxomonosulphuric acid

sulphuric acid

87. **(a)** $2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$ HBr is oxidised to Br_2

88. **(a)** In H_2SO_4, the S atom is present in its highest oxidation state of +6. Hence H_2SO_4 can act an oxidant only by gain of electrons

89. **(d)**

$$3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

90. **(a)** $2KBr + 3H_2SO_4 \rightarrow 2KHSO_4 + SO_2 + Br_2 + 2H_2O$

91. **(d)** Ozone is an allotrope of oxygen.

92. **(a)** $3O_2 \xrightarrow{UV} 2O_3$

93. **(a)** $3Cl_2 + 2NaI \rightarrow 2NaCl + I_2$

I_2 gives violet colouration in $CHCl_3$.

$$5Cl_2 + 6H_2O + I_2 \rightarrow \underset{\text{Colourless}}{HIO_3} + 10HCl$$

94. **(c)** $2F_2 + \underset{\text{(Hot, conc.)}}{4NaOH} \rightarrow 4NaF + 2H_2O + O_2$

$2F_2 + 2H_2O \rightarrow 4HF + O_2$

$Cl_2 + \underset{\text{(cold, dil.)}}{2NaOH} \rightarrow NaCl + NaClO + H_2O$

$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HCl + O_2$

95. **(c)** $2F_2\,(g) + 2H_2O\,(l) \rightarrow 4H^+\,(aq) + 4F^-\,(aq) + O_2\,(g)$

$Cl_2\,(g) + 2H_2O\,(l) \rightarrow HCl\,(aq) + HOCl$

96. **(b)**

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

97. **(c)** $Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2}O_2$

Hydrogen has more affinity for chlorine.

99. **(c)** Helium is obtained during radioactive decay.

99. **(b)** Xe is also known as stranger gas.

100.(c) $(CH_3COO)_2Pb + H_2S \rightarrow PbS + 2CH_3COOH$

$$PbS + 4H_2O_2 \rightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$$

Exercise 3 : PREVIOUS YEARS MCQs

1. **(b)** Order of reactivity of halogens: $Cl_2 > Br_2 > I_2$

But the interhalogen compounds are generally more reactive than halogens (except F_2), since the bond between two dissimilar electronegative elements is weaker than the bond between two similar atoms, i.e, X – X.

2. **(b)** F < Cl < Br < I : Covalent radius → Size increases down the group.

Irregularity in electron affinity, as Cl has more electron affinity than F due to larger size and less repulsion.

Cl > F > Br > I : Electron affinity

$F^- < Cl^- < Br^- < I^-$: Ionic radius → Ionic size increases down the group

F > Cl > Br > I : Ionisation enthalpy → Decreases down the group

3. **(a)** TeO_2 primarily behave as an oxidizing agent. Because in TeO_2 tellurium is present in +4 oxidation state thus, it has tendency to accept electrons. TeH_2 is acidic in nature as Te – H bonds are unstable hence TeH_2 can act as an acid.

4. **(d)** Fluorine does not show variable oxidation state as it is the most electronegative element and shows only –1 state.

5. **(b)** The key step in the manufacture of H_2SO_4 is catalytic oxidation of SO_2 with O_2 to give SO_3 in presence of V_2O_5.

6. **(d)** V_2O_5 catalyses the oxidation of SO_2 in the manufacture of H_2SO_4.

7. **(d)** Xe has 8 e^- in its valence shell.

8. **(c)** $Cl_2 + NaOH \rightarrow NaCl + NaClO + H_2O$

[cold and dilute]

9. **(c)** Chlorinated water is yellow in colour on standing reaction occurs

$Cl_2 + H_2O \rightarrow HCl + HOCl$

10. **(c)** $Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow 2HCl + S + Na_2SO_4$

11. **(d)**

(i) The first ionization energy of xenon (1, 170 kJ mol^{-}) is quite close to that of dioxygen (1,180 kJ mol^{-1}).

(ii) The molecular diameters of xenon and dioxygen are almost identical.

Based on the above similarities Barlett (who prepared $O_2^+[PtF_6]^-$ compound) suggested that since oxygen combines with PtF_6, so xenon should also form similar compound with PtF_6.

12. **(d)** $K_2Cr_2O_7 + \text{conc.}\, HCl \rightarrow Cl_2$

13. **(c)** Nitric oxide (pollutant) act as an homogeneous catalyst in the conversion of oxygen to ozone, since at very high concentration in air it converts into NO_2 which generate free oxygen atom.

14. **(a)** Nitric oxide

15. **(c)** In the preparation of sulphuric acid (H_2SO_4) by lead chamber process, mixture containing SO_2 air and NO is treated with steam (H_2O). In this reaction, NO acts as a catalyst.

$$2SO_2 + \underset{\text{(from air)}}{O_2} + 2H_2O + \underset{\text{Catalyst}}{[NO]} \longrightarrow 2H_2SO_4 + \underset{\text{Catalyst}}{[NO]}$$

16. **(b)** Argon is the most abundant noble gas in the atmosphere.

17. **(a)** No compound of Ar has yet been reported with F_2.

18. **(b)** Oxygen being more electronegative, will be best oxidising agent among given options.

19. **(b)** Electron gain enthalpy becomes less negative on moving from chlorine to iodine. However, negative electron gain enthalpy of fluorine is less than that of chlorine due to small sized of fluorine atom. It has very high inter electronic repulsion in the relatively small 2*p* orbitals. Hence, incoming electron experience less attraction from the nucleus.

$\therefore$ Chlorine has the highest value of electron gain enthalpy.

20. **(a)** Octahedral sulphur (rhombic or α-sulphur) is the most stable allotrope of sulphur.

21. **(d)** The highest oxidation state exhibited by group 17 elements is + 7.

22. **(c)** S_2 is paramagnetic. It contains two unpaired electrons in the antibonding π^* orbital

23. **(c)** See oxy acids of sulphur

24. **(a)** $2H_2S + O_2 \rightarrow 2H_2O + 2S$

25. **(c)** O_2 is paramagnetic and O_3 is diamagnetic

26. **(c)** Fluorine always –1

27. **(c)** Oxy acids having higher + O.S for halogen are more stronger in nature . Hence the order

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

8

Transition and Inner Transition Elements

Exercise 1 : WARM-UP

Topic-wise MCQs

1. **(a)** $_{78}Pt = [Xe]\ 4f^{14}5d^9\ 6s^1$ (Exceptional electronic configuration)

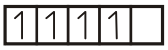
2. **(b)** $Cr\ (24) = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6, 3d^5, 4s^1$

3. **(b)** $Zn^+ = [Ar]3d^{10}4s^1, Fe^{2+} = [Ar]3d^6 4s^0,$

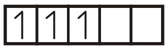
$Ni^+ = [Ar]3d^8 4s^1,\ \ Cu^+ = [Ar]3d^{10}4s^0;$

Fe^{2+} contains maximum number of unpaired electrons.

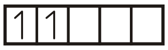
4. **(a)** Os shows maximum oxidation state of + 8.

5. **(c)** $Mn^{3+} = [Ar]3d^4 = [Ar]$ 

Number of unpaired electrons = 4

$Cr^{3+} = [Ar]3d^3 = [Ar]$ 

No. of unpaired electrons = 3

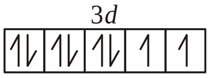
$V^{3+} = [Ar]3d^2 = [Ar]$ 

No. of unpaired electrons = 2

6. **(b)** Atomic no. of Ni = 28

Ni (Ground state) = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$

$Ni^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^0$



∴ It has 2 unpaired electrons

7. **(c)** Due to completely filled *d*-orbitals, these metals are not considered as transition metals.

8. **(b)** Since reduction potential of fluorine is highest, transition metals exhibit highest oxidation state with fluorine.

9. **(b)** $_{30}Zn$ and $_{80}Hg$ have their *d*-orbitals completely filled so they do not show any variable valency.

10. **(a)** Fe because it easily gets oxidised in moist air.

$$Fe \xrightarrow[H_2O/H^+]{air} \underset{Rust}{Fe_2O_3.xH_2O}$$

11. **(b)** $Cr = 3d^54s^1$; half-filled d-orbital

$Cu = 3d^{10}4s^1$; completely-filled d-orbital

12. **(a)** Highest O.S. by Mn (+7)

13. **(d)** The minimum oxidation state in transition metal is equal to the number of electrons in 4*s* shell and the maximum oxidation state is equal to the sum of the 4*s* and 3*d* electrons.

$Ti = [Ar]\ 3d^24s^2$

Hence, minimum oxidation state is +2 and maximum oxidation state is +4. Thus, the common oxidation states of Ti are +2, +3 and +4

14. **(d)** $(n-1)d^5ns^2$ attains the maximum O.S. of + 7.

15. **(c)** Due to absence of unpaired electrons, Zn has the lowest enthalpy of atomization.

16. **(c)** Rhenium oxide has conductivity similar to copper.

17. **(b)** $_{24}Cr, _{26}Fe, _{27}Co, _{25}Mn, _{21}Sc$

Electonic configuration

$Cr: [Ar]3d^5 4s^1, Fe: [Ar]3d^6 4s^2,\ Co: [Ar]3d^7 4s^2,$

$Mn: [Ar]3d^5 4s^2,\ Sc: [Ar]3d^1 4s^2$

Configuration of ions

$Cr^{3+}[Ar]3d^3 \qquad Fe^{3+}[Ar]3d^5$

$Co^{3+}[Ar]3d^6 \qquad Mn^{2+}[Ar]3d^5$

$Sc^{3+}[Ar]3d^0$

Fe^{3+}, Mn^{2+} have same electronic configuration

18. **(a)** In reactivity series, Cu lies below hydrogen and it is least electropositive among the given metals.

19. **(d)** The substances which are strongly attracted by magnetic field and show permanent magnetism even in absence of magnetic field are ferromagnetic e.g., Co, Fe, Ni.

20. **(c)** Zn, Cd and Hg are non typical transition elements because they have complete d-orbitals.

21. **(d)** The catalyst used in manufacturing polyethylene is known Ziegler-Natta catalyst. It is a mixture of $TiCl_4$, $Al(C_2H_5)_3$ or $Al(CH_3)_3$ works at 333 – 343K at pressure 6 - 7 atm pressure in a hydrocarbon solvent.

22. **(a)** In Cr^{3+} number of unpaired e^- = 3. Electronic configuration of $Cr^{3+} = 1s^22s^22p^63s^23p^63d^3$.

23. **(d)** Zr^{+4}(4d) Hf^{+4}(5d) series-size almost same due to lanthanoid contraction.

24. **(a)** Transition elements form coloured ions due to *d*-*d* transitions. In the presence of ligands, there is splitting of energy levels of *d*-orbitals. They no longer remain degenerated. So, electronic transition may occur between two *d*-orbitals. The required amount of energy to do this

is obtained by absorption of light of a particular wavelength in the region of visible light.

25. **(c)** The transition metals and their compounds are used as catalysts. Because of the variable oxidation states, they may form intermediate compound with one of the reactants. These intermediate provides a new path with low activation energy.

26. **(d)** Most of the transition metal compounds (ionic as well as covalent) are coloured both in the solid state and in aqueous solution in contrast to the compounds of s and *p*-block elements due to the presence of incomplete *d*-subshell.

27. **(a)** 40 elements are present in *d*-block.

28. **(d)** Sc does not show variable valency because of only one electron in 3*d*-subshell : $[Ar]3d^1 4s^2$.

29. **(c)** Zn, Cd, Hg or group 12 have full d^{10} configuration and hence are not regarded as transition metals.

30. **(c)** Cerium (Ce) belongs to lanthanide series and is member of inner-transition metals.

31. **(c)** If non metal is added to the interstital site, the metal becomes less malleable due to formation of covalent bond between metal and non metal.

32. **(c)** V has the highest enthalpy of atomization.

33. **(d)** For chromium ion +3 oxidation state is most stable.

34. **(d)** The electronic configuration of different species given in the question are

$_{22}Ti^{2+}$: $1s^2\,2s^2\,p^6\,3s^2\,p^6\,d^2$
$_{23}V^{3+}$: $1s^2\,2s^2\,p^6\,3s^2\,p^6\,d^2$
$_{24}Cr^{4+}$: $1s^2\,2s^2\,p^6\,3s^2\,p^6\,d^2$
$_{25}Mn^{5+}$: $1s^2\,2s^2\,p^6\,3s^2\,p^6\,d^2$

35. **(d)** V^{2+} – violet, V^{3+} – green, V^{4+} – blue,
Fe^{2+} – green, Fe^{3+} – yellow

36. **(d)** Sc^{3+} : $1s^2, 2s^2p^6, 3s^2p^6d^0, 4s^0$; no unpaired electron.
Cu^+ : $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^0$; no unpaired electron.
Ni^{2+}: $1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^0$; unpaired electrons are present.
Ti^{3+} : $1s^2, 2s^2p^6, 3s^2p^6d^1, 4s^0$; unpaired electron is present
Co^{2+} : $1s^2, 2s^2p^6, 3s^2p^6d^7, 4s^0$; unpaired electrons are present
So from the given options the only correct combination is Ni^{2+} and Ti^{3+}.

37. **(a)** Mn^{2+} – 5 unpaired electrons; Fe^{2+} – 4 unpaired electrons
Ti^{2+} – 2 unpaired electrons; Cr^{2+} – 4 unpaired electrons
Hence, maximum no. of unpaired electron is present in Mn^{2+}. Magnetic moment ∝ number of unpaired electrons

38. **(d)** Ti^{4+} ($3d^0$) and Zn^{2+} ($3d^{10}$) are colourless.

39. **(a)** Strongest oxidising agent have highest reduction potential value.

$$E^\circ_{Mn^{3+}/Mn^{2+}} = 1.51\text{ V (highest)}$$

40. **(b)** Colour of transition metal ion salt is due to d-d transition of unpaired electrons of d-orbital. Metal ion salt having similar number of unpaired electron in d-orbitals shows similar colour in aqueous medium.

V^{4+} : $[Ar]3d^1$	↑				
Cu^{2+} : $[Ar]3d^2$	↑↓	↑↓	↑↓	↑↓	↑

Number of unpaired electrons = 1.

41. **(d)** Magetic moment $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons $\sqrt{15} = \sqrt{n(n+2)}$ $\therefore n = 3$

42. **(d)** Ni^{3+} : $[Ar]\,3d^7$; Mn^{3+} : $[Ar]\,3d^4$
Fe^{3+} : $[Ar]\,3d^5$; Co^{3+} : $[Ar]\,3d^6$

43. **(b)** $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

44. **(d)** Ni and Co are used as catalyst.

45. **(a)** Very high ionisation energy and weak metallic bond.

46. **(c)** Only Cu in its +2 oxidation state is able to oxidizes the I^- to I_2

47. **(c)** $M^{2+} \rightarrow 23e^-$; $+2e^-$ (M should be Mn)

$3d^5 4s^2$ $\quad \mu = \sqrt{5(5+2)} = \sqrt{35} = 5.9$

48. **(a)** In Sc^{3+} there is/are no unpaired electrons. So the aqueous solution of Sc^{3+} will be colourless.

49. **(b)** + 8 oxidation state is observed in Osmium.

50. **(a)** Os and Sc
Os = 22.60 g/cm^3
Sc = 3.01 g/cm^3

51. **(c)** Magnetic moment $\mu = \sqrt{n(n+2)}$BM

$1.73 = \sqrt{n(n+2)}$ $\therefore$ n = 1, it has one unpaired electron hence electronic configuration is $[Ar]3d^1$ and electronic configuration for Z = 22 is $[Ar]\,3d^2\,4s^2$. Hence charge on Ti is +3.

52. **(a)**

	Cu	>	Ni	>	Zn	>	Sc
Density in (g cm^{-3})	8.92		8.90		7.14		2.99

53. **(a)** Paramagnetic nature ∝ number of unpaired electron

Metal ion	**d-electrons**					**Number of unpaired e$^-$**
Cu^{2+}	↑↓	↑↓	↑↓	↑	↑	2
V^{2+}	↑	↑	↑			3
Cr^{2+}	↑	↑	↑	↑		4
Mn^{2+}	↑	↑	↑	↑	↑	5

Hence, increasing order of paramagnetic nature is,
$Cu^{2+} < V^{2+} < Cr^{2+} < Mn^{2+}$

54. **(b)** $Cu^{2+}\,[Ar]3d^9$; $Ti^{4+}\,[Ar]3d^0$; $Co^{2+}\,[Ar]3d^7$;

$Fe^{2+}\,[Ar]3d^6$ 1,3,4 are coloured ions.

55. **(a)** $V^{2+} = [Ar]3d^3$; $Cu^{2+} = [Ar]\ 3d^9$; $Fe^{2+} = [Ar]\ 3d^6$
$Zn^{2+} = [Ar]3d^{10}$; $Fe^{3+} = [Ar]\ 3d^5$; $Ti^{3+} = [Ar]\ 3d^1$
$Ni^{+3} = [Ar]\ 3d^7$; $Co^{3+} = [Ar]\ 3d^6$; $Cu^+ = [Ar]\ 3d^{10}$
Thus, Zn^{2+}, Fe^{2+}, Co^{3+} and Cu^+ can have zero magnetic moment, due to even number of electrons that can get paired in a complex.

56. **(a)** Many of transition metals are sufficiently electropositive to react with dilute acid in order to produce hydrogen gas. But those having lower standard reduction potential are not able to liberate H_2 from dilute acid

57. **(c)** All the oxides of Fe(FeO, Fe_2O_3 and Fe_3O_4) are basic in nature.

58. **(d)** Sc electronic configuration = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^1$ to form the oxide Sc have to remove 2 electrons from its d and s-orbital. It will form a very unstable configuration. Sc only shows +3 oxidation state and make inert gas configuration.

59. **(a)** $_{24}Cr = [Ar]\ 3d^5 4s^1$; $_{25}Mn = [Ar]\ 3d^5 4s^2$
$_{26}Fe = [Ar]\ 3d^6\ 4s^2$; $_{27}Co = [Ar]\ 3d^7\ 4s^2$
Due to half-filled *d*-orbital in Mn^{2+}, it is most stable.

60. **(a)** The outermost electronic configuration of Fe is
$Fe = [Ar]\ 3d^6\ 4s^2$; $Fe^{2+} = [Ar]\ 3d^6\ 4s^0$
Since Fe^{2+} has 4 unpaired electrons, it is paramagnetic in nature.
$Zn = [Ar]\ 3d^{10}\ 4s^2$ —— no unpaired e^-
$Hg^{2+} = [Ar]\ 4f^{14}\ 5d^{10}$ —— no unpaired e^-
$Ti^{4+} = [Ar]\ 3d^0\ 4s^0$ —— no unpaired e^-

61. **(a)** The ionisation energies increase with increase in atomic number. However, the trend is some irregular among *d*-block elements. On the basis of electronic configuration, the
Zn : $3d^{10}\ 4s^2$; Fe : $3d^6\ 4s^2$
Cu : $3d^{10}\ 4s^1$; Cr : $3d^5\ 4s^1$
IE_1 follows the order : Zn > Fe > Cu > Cr

62. **(c)** Solid potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride gives orange red vapours of a volatile oily liquid CrO_2Cl_2.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{chromyl chloride}}{2CrO_2Cl_2}$$

63. **(c)** In acid medium

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

(O.S. of Mn changes form +7 to +2)

64. **(b)** $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{dark green}}{2K_2MnO_4} + 2H_2O$

65. **(a)** The green colour appears due to the formation of Cr^{3+}ion

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

66. **(a)** $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

67. **(b)** Hydrated copper sulphate $CuSO_4 . 5H_2O$ is blue in colour, because the ligand (water) molecules facilitates *d*-*d*- transition. Anhydrous copper sulphate $CuSO_4$ is colourless. In the absence of ligand (water) molecules, splitting of *d*-orbitals is not possible. Hence, *d*-*d* transition is not possible. Hence, option (b) is correct.

68. **(c)**

69. **(b)** In neutral or faintly alkaline medium thiosulphate is quantitatively oxidized by $KMnO_4$ to SO_4^{2-}

$$8KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 3K_2SO_4 + 8MnO_2 + 3Na_2SO_4 + 2KOH$$

70. **(c)** In laboratory, manganese (II) ion salt is oxidised to permanganate ion in aqueous solution by peroxodisulphate.

$$2Mn^{2+} + \underset{\text{peroxodisulphate ion}}{5S_2O_8^{2-}} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

71. **(a)** $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

Hence, CrO_4^{2-} ion is obtained.

72. **(b)** Chromate and dichromate ions both are interconvertible due to pH change.

$$Cr_2O_7^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} 2CrO_4^{2-}$$

73. **(c)** Al is concentrated by leaching.

74. **(a)** Sphalarite ore containing metal zinc. This impure metal is evaporated to obtain the pure metal by distillation.

75. **(d)** $SiO_2 + CaO \longrightarrow \underset{\text{(slag)}}{CaSiO_3}$

It is related to the extraction of iron.

76. **(b)** Bauxite is a chief ore of Al that is concentrated by leaching. Haematite is concentrated by magnetic separation and zinc blende and calamine are concentrated by froth floatation process.

77. **(b)** Cr is present in +6 oxidation state. In both of chromate (CrO_4^{2-}) and dichromate ions $(Cr_2O_7^{2-})$
i.e. d^0-configuration. So, d-d transition is absent in them.
The yellow colour of CrO_4^{2-} and orange colour of $Cr_2O_7^{2-}$ is due to charge transfer of oxygen to vacant *d*-orbital of metal Cr (VI).

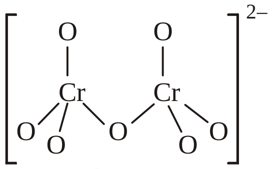
78. **(c)** The term chromic acid is usually used for a mixture made by adding concentrated sulphuric acid to dichromate.

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + H_2Cr_2O_7$$

$$K_2Cr_2O_7 + 4H_2O_2 \rightarrow CrO_5 + 5H_2O$$

79. **(c)** In the extraction of iron using blast furnace to remove impurity SiO_2 is used and limestone i.e. $CaCO_3$ chemical is added to the ore.

80. **(d)**



Dichromate ion

There are six equivalent Cr — O bonds and one Cr — O — Cr bond.

81. **(a)** The given reaction is cyanide leaching which can be used for metals like Ag and Au.

Levigation is the process of grinding of an ore into fine powder.

Froth floatation is used for sulphides of Fe, Pb, etc and is a physical process.

Liquation is used for purifying metals by partially heating them.

82. **(c)**

83. **(b)** In neutral or faintly alkaline medium, iodide ion is oxidised to iodate as:

$$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + \underset{\text{Iodate ion}}{IO_3^-}$$

84. **(b)** By van Arkel method for refining Zr and Ti

85. **(d)**

$$8\overset{+7}{Mn}O_4^- + 3S_2O_3^{-2} + H_2O \rightarrow 8\overset{+4}{Mn}O_2 + 6SO_4^{-2} + 2OH^-$$

Change in oxidation state of Mn is from +7 to +4 i.e., 3

86. **(d)** Potassium permangnate on heating at 513 K gives potassium manganate (K_2MnO_4) and its colour is green.

$$2KMnO_4 \xrightarrow[513K]{\Delta} \underset{\text{Green}}{K_2MnO_4} + \underset{\text{Black}}{MnO_2} + O_2$$

In K_2MnO_4, manganese oxidation state is +6 and hence, it has one unpaired electron and paramagnetic.

87. **(c)** $\underset{\text{Flux}}{CaO} + \underset{\text{Gangue}}{SiO_2} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$

88. **(b)** Copper matter is composed of copper sulphite Cu_2S and (Iron Sulphide) FeS.

89. **(c)** $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

This reaction is self reduction.

90. **(c)**

$$\underset{\substack{\text{(Almost black}\\\text{crystal)}}}{2K\overset{+7}{Mn}O_4} \xrightarrow{\Delta} \underset{\substack{\text{(Water soluble}\\\text{Green solvent)}}}{K_2\overset{+6}{Mn}O_4} + \underset{\substack{\text{(Water insoluble}\\\text{Black residue)}}}{\overset{+4}{Mn}O_2} + O_2\uparrow$$

$Mn^{6+}(3d^1 4s^0) \rightarrow$ Paramagnetic; $Mn^{4+}(3d^3 4s^0)$ $\rightarrow$ Paramagnetic

91. **(a)**

92. **(d)** Calcination involves heating it removes the volatile matter which escapes leaving behind the metal oxide:

$$Fe_2O_3 . x\,H_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + x\,H_2O(g)$$

93. **(b)**

$$MnO_2 \xrightarrow[\text{air / }KNO_3]{\text{Fusion with KOH,}} \underset{(A)}{K_2MnO_4} \xrightarrow[\substack{\text{oxidation in alkaline}\\\text{medium}}]{\text{electrolytic}} \underset{(B)}{KMnO_4}$$

94. **(b)** Distillation is a process that can be used to separate a pure liquid from a mixture of liquids. It works when the liquids have different boilings points.

95. **(d)**

96. **(b)** $Na_2Cr_2O_7$ is hygroscopic.

97. **(c)** I^- is converted to IO_3^- by neutral or faintly alkaline MnO_4^- as shown below.

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

98. **(d)** Deacon's process is used for the manufacture of chlorine in this process.

$$4HCl + O_2 \xrightarrow[723k]{CuCl_2} 2Cl_2 + 2H_2O.$$

99. **(a)** Mond process is used for refining of nickel. van Arkel method is used for refining zirconium or titanium. Zone refining method is used for producing semiconductor and other metals of very high purity eg., germanium, silicon, boron, gallium and indium.

100. **(d)** $PbCrO_4$ + NaOH (hot excess) $\rightarrow$ $[Pb(OH)_4]^{-2} + Na_2CrO_4$

The product is dianionic complex with coordination number four.

101. **(a)** Pyrolusite (It is MnO_2)

102. **(b)** $CuSO_4.5H_2O$

In $K_2Cr_2O_7$ and K_2CrO_4, the Cr is in +6 oxidation state and hence contain no '*d*' electron.

In $KMnO_4$, Mn is in +7 oxidation state and this also do not contain any '*d*' electrons.

They exhibit colour due to charge transfer spectra and not due to d-d transistion.

103. **(a)** The permanganate ion has an intense purple colour. Mn(+VII) has a d^0 configuration. So the colour arises from charge transfer and not from d-d spectra.

104. **(b)**

105. **(a)** $4Au + 8CN^-(aq) + 2H_2O(aq) + O_2(g)$

$$\longrightarrow \underset{(A)}{4[Au(CN)_2]^-} + 2H_2O$$

$$\xrightarrow{Zn(s)} \underset{(B)}{2[Zn(CN)_4]^{2-}} + 2Au$$

106. **(c)** Atomic radius of Zr (Z = 40) is 160 pm, while
Atomic radius of Hf (Z = 72) is 169 pm.

107. **(a)** $_{57}La = [Xe]5d^1\,6s^2$
$_{58}Ce = [Xe]4f^1\,5d^1\,6s^2$
+II and +III oxidation states are common for lanthanum. Ce and other lanthanides do not show +II oxidation state often.

108. **(b)** The correct order of ionic radii :-

$$\underset{(86\ Pm)}{_{70}Yb^{3+}} < \underset{(91)}{_{66}Dy^{3+}} < \underset{(96)}{_{62}Sm^{3+}} < \underset{(101)}{_{59}Pr^{3+}}$$

This order can be explained on the basis of lanthanide contraction due to which the atomic and ionic radii decrease steadily.

109. **(b)** $Nd(60) = [Xe]\,4f^4\,5d^0\,6s^2$
$Nd^{2+} = [Xe]\,4f^4\,5d^0\,6s^0$

110. **(c)** Both Eu^{+2} and Yb^{+2} tends to acquire common oxidation state of +3 by loosing 1 electron and becomes highly stable.

111. **(c)** Elements Np and Pu both show maximum oxidation state of 7.

112. **(d)** $Ce \rightarrow [xe]4f^1 5d^1\,6s^2$; $Ce^{4+} \rightarrow [Xe]$
$Yb \rightarrow [xe]4f^{14} 6s^2$; $Yb^{2+} \rightarrow [Xe]4\,f^{14}$
$Lu \rightarrow [xe]4f^{14} 5d^1\,6s^2$; $Lu^{3+} \rightarrow [Xe]4\,f^{14}$
$Eu \rightarrow [xe]4f^7\,6s^2$; $Eu^{2+} \rightarrow [Xe]4\,f^7$

113. **(d)**

114. **(a)** $4f$ orbital is nearer to nucleus as compared to $5f$ orbital therefore, shielding of $4f$ is more than $5f$.

115. **(c)**

116. **(c)** On going from left to right in lanthanoid series ionic, size decreases *i.e.*,
$Ce^{3+} > Tb^{3+} > Er^{3+} > Lu^{3+}$.

117. **(c)** Europium (Eu)
Atomic No. - 63
Electronic configuration - $[Xe]4f^7 6s^2$
It shows only +2 and +3 oxidation state.

118. **(b)** The lanthanide contraction relates to atomic as well as M^{3+} radii in which the regular decrease in the size of lanthanoid ion from La^{3+} to Lu^{3+} are found.

119. **(a)** Lanthanum is the first element of Lanthanide series so size decreases with increase in atomic number so La has the largest atomic radii.

120. **(b)** Ce-lanthanide, Cs-alkali metal, C*f*-actinide, Ca-alkaline earth metal.

Exercise 2 : ACCELERATOR
Topic-wise MCQs

1. **(c)** Due to unpaired d-electrons.

2. **(d)** The first ionization energies of Ti, V, Cr and Mn are 656, 650, 652 and 717 kJ/mole respectively. I.E. increase in a period from L → R hence, manganese has maximum first ionisation potential.

3. **(b)**

4. **(d)** $Fe^{3+} = [Ar]\,3d^5$

5. **(c)** Chromium Cr ($Z = 24$) $\Rightarrow [Ar]\,3d^4 4s^2$
$\therefore$ Common positive oxidation state of Cr are from +2 to + 6.
Where +3 and +6 are the most stable oxidation states.

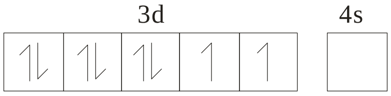
6. **(b)** $_{26}Fe = [Ar]\,3d^6 4s^2$. Third ionisation results into stable d^5 configuration.

7. **(b)** Bronze is a mixture of Cu + Sn.

8. **(c)** Cu^+ ion is colourless.

9. **(d)** Scandium always shows +3 oxidation state, hence it form colourles conpounds.

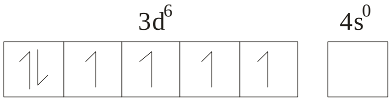
10. **(a)** Elements or ions containing unpaired electrons are paramagnetic.
$_{28}Ni = [Ar]\,3d^8 4s^2$; $Ni^{2+} = [Ar]\,3d^8\,4s^0$



Because Ni^{2+} have 2 unpaired electrons in 3d subshell therefore it is paramagnetic.

11. **(c)** Ions having unpaired electrons are coloured.

12. **(d)** $Fe_{(26)} \Rightarrow 3d^6\,4s^2$



4 unpaired e^-

13. **(c)**

Metal ion	Colour
Fe^{2+}	green
Cu^{2+}	blue
Fe^{3+}	yellow
V^{3+}	green

14. **(a)**

15. **(a)**

Metal	**Valence shell Electronic configuration**	**Unpaired electron**	**Magnetic moment** $(\mu = \sqrt{n(n+2)})$
Cr^{3+}	$3d^3 4s^0$	3	$\mu = \sqrt{15} = 3.87$
Cu^{3+}	$3d^9 4s^0$	1	$\mu = \sqrt{3} = 1.73$
CO^{3+}	$3d^6 4s^0$	4	$\mu = \sqrt{24} = 4.90$
Fe^{2+}	$3d^6 4s^0$	4	$\mu = \sqrt{24} = 4.90$

16. **(b)** $MnF_4 \Rightarrow +4$ state $\Rightarrow [Ar]3d^3$
$MnF_3 \Rightarrow +3$ state $\Rightarrow [Ar]3d^4$ (Strongest O.A)
$MnF_2 \Rightarrow +2$ state $\Rightarrow [Ar]3d^5$
For $n = 4$,

$$\therefore \quad \mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89 = 5$$

17. **(d)** The Cr^{+3}/Cr^{+2} reduction potential is negative because Cr^{+3} is more stable than Cr^{+2} due to its half filled t_2g orbitals in an octahedral crystal field. This means Cr^{+2} readily oxidized to Cr^{+3} making Cr^{+2} a strong reducing agent.

18. **(c)** $Cr^+ - 4s^0\, 3d^5$
$Mn^{2+} - 4s^0\, 3d^5$

So, the outermost electronic configuration will be same in case of Cr^+ and Mn^{2+}.

19. **(c)** Cu is present in brass, bronze and german silver.

20. **(a)** The element having atomic number 26 is Fe.

$Fe\,(26) = 3d, 4s^2 \Rightarrow Fe^{2+} = 3d^6$

In aqueous solution, it exists as $[Fe(H_2O)_6]^{2+}$ which is high spin complex due to weak field nature of H_2O ligand.
So, total no. of unpaired electrons = 4

$\mu = \sqrt{4(4+2)}$ BM $= \sqrt{24} = 4.8$ BM

21. **(a)**

22. **(a)** Such ions, which have unpaired electrons exhibit colour and paramagnetic behaviour.
$Cu^{2+} - 3d^9$ (one unpaired e^-)
$Cr^{3+} - 3d^3$ (three unpaired e^-)
$Sc^+ - 3d^2$ (two unpaired e^-)

23. **(b)**

24. **(a)** General electronic configuration of valence shell of Gr oup 12 elements: $(n-1)d^{-10}ns^2$

25. **(c)** The melting point of metals are higher for heavier elements. Thus, the order of melting points will be W > Mo > Cr.

26. **(c)** In all other compounds
$CuCl_2 \rightarrow [Cu^{2+}] \Rightarrow [Ar]3d^9$
$CuCl \rightarrow [Cu^+] \Rightarrow 3d^{10}\, 4s^0$
$ScCl_3 \rightarrow [Sc^{3+}] \Rightarrow 3d^0 4s^0$
$TiCl_4 \rightarrow [Ti^{4+}] \Rightarrow 3d^0 4s^0$
$CuCl_2$ contains one unpaired electron.
Hence, it is coloured compound.

27. **(c)** Magnetic moment is directly proportional to number of unpaired electrons in the atom.

Ion	**Unpaired electrons**
Fe^{3+}	5
Mn^{4+}	3
Ni^{2+}	2
V^{4+}	1

28. **(c)** V_2O_5 is amphoteric

29. **(d)** Cr^{+3} due to presence of unpaired electrons.

30. **(a)** Magnetic moment = $\sqrt{n(n+2)}$ = 5.92 i.e., n = 5
Number of unpaired electrons in $Mn^{2+} = 5$
Number of unpaired electrons in $Ti^{3+} = 1$
Number of unpaired electrons in $Cr^{3+} = 3$
Number of unpaired electrons in $Cu^{2+} = 1$
Thus Mn^{2+} have magnetic moment = 5.92 BM.

31. **(d)**

32. **(c)** In set Cu^{2+}, Fe^{2+}, Co^{2+}, all the ions have unpaired d-electrons. Hence, they are all coloured ions.
$Cu^{2+} \rightarrow [Ar]3d^9\, 4s^0$
$Fe^{2+} \rightarrow [Ar]3d^6\, 4s^0$
$Co^{2+} \rightarrow [Ar]3d^7\, 4s^0$

33. **(b)**

34. **(b)** Both have 3 unpaired electrons.

35. **(a)** The +7 oxidation state of Mn is not represented in simple halides but MnO_3F is known.

36. **(d)** Catalytic activity of transition elements is due to their variable oxidation states and to form complexes.

37. **(b)** Interstitial compounds retain metallic conductivity.

38. **(b)** $V^+ = 3d^3 4s^1$, $Cr^+ = 3d^5$, $Mn^+ = 3d^5 4s^1$, $Fe^+ = 3d^6 4s^1$
Clearly, IE_2 of Cr will be highest as Cr^+ has exactly half filled *d*-subshell.

39. **(c)** Metallic bond made by elements with d^5 configuraiton can be stronger (Cr) or weaker (Mn) than that with d^3 configuration (V).

40. **(d)** The ions with unpaired electrons are coloured and those with paired electrons are colourless

$$\underset{(\text{No. of } e^-\text{s} = 28)}{Zn^{2+}} = 1s^2\, 2s^2p^6\, 3s^2 3p^6 3d^{10}$$

$$\underset{(\text{No. of } e^-\text{s} = 21)}{Cr^{3+}} = 1s^2\, 2s^2p^6\, 3s^2 3p^6 3d^3$$

$$\underset{(\text{No. of } e^-\text{s} = 26)}{Ni^{2+}} = 1s^2\, 2s^2p^6\, 3s^2 3p^6 3d^8$$

Thus Zn^{2+}, Cr^{3+} and Ni^{2+} have zero, 3 and 2 unpaired electrons respectively.

41. **(a)** In a period on moving from left to right, ionic radii decreases. So order of cationic radii is
$Cr^{2+} > Mn^{2+} > Fe^{2+} > Ni^{2+}$

42. **(c)** The melting points of the transition element first rise to a maximum and then fall as the atomic number increases; manganese have abnormally low melting point.

43. **(c)** Standard electrode potential value for M^{3+}/M^{2+} is Cr > Fe > Mn.

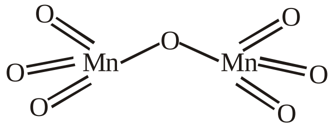
Magnetic moment $(\mu) = \sqrt{n(n+2}$

n = no. of unpaired electron.
So $Mn^{2+} = 3d^5 = 5$ unpaired election
$Cr^{2+} = 3d^4 = 4$ unpaired electron
$Fe^{2+} = 3d^6 = 4$ unpaired electron
So, $Mn^{2+} > Cr^{2+} \approx Fe^{2+}$

$$\overset{(+5)}{VO_2^+} < \overset{(+6)}{Cr_2 O_7^{2-}} < \overset{(+7)}{Mn O_4^-}$$

Mn^{+7} have highest oxidation state then Cr^{+6} and V^{+5} so it is act as strongest oxidising agent.
First ionisation enthalpy Ti > Cr > V

44. **(c)** In manganese heptoxide, there are 6, Mn = o bonds.



45. **(a)** In the extraction of iron from haematite (Fe_2O_3) is first reduced to Fe_3O_4 and then to FeO.

$FeO + CO \rightarrow Fe + CO_2$

$C + CO_2 \rightarrow 2CO$

$$\underset{(Flux)}{CaO} + \underset{\substack{(x)\\(gangue)}}{SiO_2} \rightarrow \underset{\substack{(y)\\slag}}{CaSiO_3}$$

46. **(c)** Due to d^5 configuration, Mn has exactly half filled *d*-orbitals. As a result the electronic configuration is stable which means 3*d* electrons are more tightly held by the nucleus and this reduces the delocalization of electrons resulting in weaker metallic bonding.

47. **(b)** $KMnO_4$ is an oxidising so it can oxidise SO_2 readily.
$KMnO_4 + SO_2 \rightarrow Mn^{2+} + SO_3$
NO_2 is strong oxidising agent, CO_2 is neither oxidising agent nor reducing agent.

48. **(b)** $Fe_2O_3 + 3C \longrightarrow 2\,Fe + 3CO$

Lime stone $(CaCO_3)$ is added as a flux and sulphur, silicon and phosphorus are oxidixed and passed into the slag.

49. **(d)** In Deacon's process, chlorine (Cl_2) gas is produced by catalytic oxidation of hydrogen chloride

$4HCl + O_2(o) \rightarrow 2Cl_2(g) + 2H_2O$

Thus X is Cl_2

Chloride react with iodine and water to form iodic acid

$5Cl_2 + I_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$

50. **(b)** $CrO_3 + 2NaOH \rightarrow Na_2CrO_4 + H_2O$

51. **(a)** $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 3I_2 + 7H_2O + 2\,Cr^{3+}$
oxidation state of Cr is +3.

52. **(d)** $3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + \underset{green}{2Cr^{+3}} + H_2O$

53. **(b)** This method is used for removing gangue from sulphide ores. In this process a suspension of the powdered ore is made with water. Collectors & froth stabilisers are added to it. Collectors like pine oils, fatty acids enhance non wettability of the mineral particles and froth stabilisers like cresols, aniline stabiline the froth.

54. **(b)** The iron obtained from blast furnance contain about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn).

This is known as pig iron.

55. **(c)** Composition of German silver is Zinc (35%)

Copper 50%

Nickel (15%)

Composition of brass

Zinc (30%) and Copper (–70%) and some quantity of Nickel (Ni).

Therefore, iron (Fe) is not common to German silver and brass.

56. **(b)** H_2 is not a very strong reducing agent.

57. **(a)** **Mond's Process :**

$$Ni\,(s)\,(impure) + 4\,CO \xrightarrow{\Delta} Ni\,(CO)_4\,(g) \xrightarrow{\Delta} Ni\,(s)\,(pure) + 4\,CO$$

Van Arkel process :

$$Zr + 2I_2 \xrightarrow{\Delta} ZrI_4 \xrightarrow{\Delta} Zr + 2I_2$$

58. **(d)** Zone refining method is useful for producing semiconductor grade metals of high purity.

59. **(d)** In acidic medium,

$$5Fe^{2+} + 8H^+ + \overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

x = 5 moles of Ferrous ion

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

y = 6 moles of Ferrous ion

Than, x + y = 5 + 6 = 11.

60. **(c)** $Zn + \underset{Conc.}{NaOH} \rightarrow \underset{Sodium\ zincate}{Na_2ZnO_2} + \underset{Hydrogen}{H_2}$

Thus in this reaction hydrogen gas is produced when zinc is treated with concentrated NaOH.

61. **(b)** Roasting involves an ore in the presence of air to convert it into its oxide.

62. **(a)** $2MnO_4^- + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-}$

63. **(b)** In neutral or weakly alkaline solution oxidation state of Mn changes by 3 unit

$$\overset{+7}{Mn}O_4^{-1} \rightarrow \overset{+4}{Mn}O_2$$

64. **(a)** In VO_2^+, V is in +3 oxidation state.

$Cr_2O_7^{2-}$ Cr is in +6 oxidation state.

MnO_4^- Mn is in +7 oxidation state.

Oxidising power means substance have more tendency to accept electron. Mn is in highest oxidation state so it have more oxidising power. So correct is:

$$MnO_4^- > Cr_2O_7^{2-} > VO_2^+$$

65. **(b)** $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

$Na_2Cr_2O_7$

$+2 + 2x - 14 = 0$

$2x - 12 = 0$

$x = +6$

66. **(d)** Leaching is based on the principle of relative/selective solubility to concentrate an ore from its impurities.

e.g., in Al_2O_3 ore from bauxite.

67. **(d)** Levigation or gravity separation is the process of separating the light impure particles from the heavier ore particles by washing in current of water.

68. **(c)** In Acidic medium

$$\overset{+6}{Cr_2}O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

In basic medium

$$\overset{+6}{Cr_2}O_7^{2-} + 2OH^- \rightarrow 2\overset{+6}{Cr}O_4^{2-} + H_2O$$

Oxidation state of Cr in CrO_4^{2-}

$\Rightarrow x + 4(-2) = -2 \Rightarrow x = +6$

69. **(b)** Copper matter is composed of copper sulphite Cu_2S and (Iron Sulphide) FeS.

70. **(c)** $4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + O_2 + H_2O + 3H_2O$

71. **(d)** In Mond process nickel is heated in a steam of carbon monoxide forming a volatile complex.

${}_{28}Ni\,[Ar] = 3d^8\,4s^2$

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$$

Two unpaired electron.

72. **(c)**

73. **(a)** $2K_2CrO_4 + 2HNO_3 \longrightarrow K_2Cr_2O_7 + 2KNO_3 + H_2O$

74. **(d)** In Neutral or faintly alkaline solutions

Oxidation of iodide to iodate

$$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$$

75. **(b)** $HgCl_2$ compound is easily volatile. They are insoluble in water and soluble in acids.

76. **(b)** In acidic medium hydrogen sulphide is oxidised, sulphur being precipitated

$H_2S \longrightarrow 2H^+ + S^{2-}$

$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

77. **(c)** Balanced equation is

$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow$

$K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

5 mole H_2S required 2 mol of $KMnO_4$

1 mol H_2S required $\frac{2}{5} = 0.4$ mol of $KMnO_4$

78. **(c)** $SO_3^{2-} + H_2SO_4 \longrightarrow SO_4^{2-} + SO_2 + H_2O$

$$5SO_2 + 2KMnO_4 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$\therefore$ Oxidation state of Mn in $MnSO_4$ is + 2.

79. **(b)** Zone refining method is used for semiconductors that are B, In, Ge, Si and Ga.

80. **(b)** In the blast furnace reduction of iron oxides take place at different temperature ranges.

At 900 – 500K

$FeO + CO \longrightarrow Fe + CO_2$

$C + CO_2 \longrightarrow 2CO$

$CaO + SiO_2 \longrightarrow CaSiO_3$ (slag)

81. **(d)** $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{-3+} + 7H_2O$

82. **(a)** $\underset{(X)}{2KMnO_4} \xrightarrow{513K} \underset{(Y)}{K_2MnO_4} + MnO_2 + \underset{gas}{O_2}$

$$MnO_2 + 4NaCl + \underset{Conc.}{4H_2SO_4} \rightarrow MnCl_2 + 4NaHSO_4 + \underset{\substack{(Z)\\ \text{Pungent gas}}}{Cl_2} + 2H_2O$$

83. **(b)** $\overbrace{\overset{+6}{Cr_2}O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr}^{ox}{}^{3+} + 7H_2O$

84. **(c)** HCl, HNO_3 oxidised on reation with acidified $KMNO_4$.

85. **(d)** When the yellow solution (sodium chromate) is acidified with dilute sulphuric acid and adding small amount of amyl alcohol and 10%, H_2O_2, the organic layer turns blue and confirms the formation of chromium pentoxide. The oxidation state of Cr in chromium pentoxide is +6.

$$CrO_4^{2-} + 2H^+ + 2H_2O \longrightarrow \underset{\substack{\text{Chromium}\\ \text{pentoxide}}}{CrO_5} + 3H_2O$$

86. **(b)**

(i) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(ii) $2MnO_4^- + I^- + H_2O \longrightarrow 2MnO_2 + \underset{Y}{IO_3^-} + 2OH^-$

Hence, (X) and (Y) are respectively I_2 and IO_3^-

87. **(c)** $SO_2 + \text{dil. } H_2SO_4 \rightarrow \underset{(X)}{SO_3(g)}$

$$SO_3 + K_2Cr_2O_7 \xrightarrow[H_2SO_4]{\text{dil.}} \underset{\substack{\text{(Green)}\\(Y)}}{Cr_2(SO_4)_3}$$

88. **(d)** $8MnO_4^- + 3S_2O_3^{2-} + H_2O \xrightarrow[\text{alk.solution}]{\text{neutral or}}$

$$8MnO_2 + 6SO_4^{2-} + 2OH^-$$

89. **(b)** During electrolytic refining of copper impure copper is used as anode and pure copper is used as cathode.

90. **(d)**

	Complex	Nature of ligand	Metal oxidation state	Configuration after splitting	Unpaired electron	Magnetic moment $(\mu_1 = \sqrt{n(n+2)})$
I.	$[Fe(CN)_6]^{4-}$	Strong Field	Fe^{2+}	$t_{2g}^6 e_g^0$	0	0
II.	$[MnCl_4]^{2-}$	Weak Field	Mn^{2+}	$e_g^2 t_{2g}^3$	5	5.91
III.	$[Mn(CN)_6]^{4-}$	Strong Field	Mn^{2+}	$t_{2g}^2 e_g^0$	1	1.73
IV.	$[Cr(NH3)_6]^{3+}$	Strong Field	Cr^{3+}	$t_{2g}^3 e_g^0$	3	3.87

Order of magnetic moment is II > IV > III > I

91. **(d)** Chemical reaction occurring in blast furnace related to the extraction of iron from haematite are:-

(i) $3Fe_2O_3 + Co \longrightarrow 2Fe_3O_4 + CO_2$

(ii) $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$

(iii) $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

92. **(b)** Ytterbium shows +2 oxidation state with diamagnetic nature due to $4f^{14}6s^2$ configuration.

93. **(a)** Gd (Z = 64) $\Rightarrow 4f^7\,5d^1\,6s^2$

$Gd^{3+} = 4f^7$

Gd^{3+} is stable due to the presence of exactly half-filled 4*f*-subshell.

94. **(b)** Cerium exists in two different oxidation states +3 and +4.

$Ce^{4+} + e^- \rightarrow Ce^{3+} \quad E^0 = +1.61\text{ V}$

It shows, Ce^{4+} prefer to gain electron and acts as a strong oxidising agent.

95. **(a)**

(A) $(NH_4)_2\,[Ce(NO_3)_6]$

$_{58}Ce = [Xe]\ 4f^2 5d^0 6s^2$

$Ce^{4+} = 4f^0$ (diamagnetic)

(B) $Gd(NO_3)_3$

$_{64}Gd = [Xe]4f^7 5d^1 6s^2$

$Gd^{3+} = 4f^7$

$\mu = \sqrt{7(7+2)} = \sqrt{63}$ B.M.

(C) $Eu(NO_3)_3$

$_{63}Eu = [Xe]4f^7 5d^0 6s^2$

$Eu^{3+} = 4f^6$

$\mu = \sqrt{6(6+2)} = \sqrt{48}$ B.M.

Order of spin only magnetic moment is

(B) > (C) > (A)

96. **(b)** As a result of lanthanoid contraction, change in ionic radii on going from elements of 4*d* to 5*d* transition series is very small. Thus, chemical properties of 4*d* and 5*d* series of transition elements are similar.

97. **(a)** $_{62}Sm : 4f^6 6s^2$; $_{64}Gd : 4f^7 5d^1 6s^2$; $_{63}Eu : 4f^7 6s^2$; $_{65}Tb : 4f^9 6s^2$; $_{61}Pm : 4f^5 6s^2$

98. **(d)** All members do not show +4 oxidation state.

99. **(b)** $Ce^{3+} = [Xe]\,4f^1$; $Ce^{4+} = [Xe]4f^0$

100. **(a)** The energy difference between 5f and 6d orbitals is less than that between 4f and 5d orbitals. The penultimate and anti-penultimate orbitals of lanthanoids and actinoids are respectively (4f and 5d) and (5f and 6d). Removal of electrons from anti-penultimate shell of actinoid (5f) is easy compare to that from lanthanoid (4f).

Hence actinoids show a large number of oxidation states.

Exercise 3 : PREVIOUS YEARS MCQs

1. **(c)** Mn_2O_7 is acidic, V_2Os is amphoteric adn GrO is basic

2. **(b)** Impure metal is made the anode and a solution containing a salt of the same metal is used as an electrolyte

3. **(d)**

Mineral	**Metal**
Calamine	Zinc
Chalcocite	Copper
Chalcopyrite	Copper
Siderite	Iron

4. **(c)** Zinc has compeletely filled orbirtals $(Ar)3d^{10}\,4s^2)$

Hence, among the given elements, Zn has highest ionization enthalpy

5. **(d)** $_{71}Lu: [Xe]4f^{14}5d^16s^2$

$Lu^{3+}: [Xe]\,4f^{14}$

6. **(d)** $Fe^{2+} \rightarrow$ Green colour

$Fe^{3+} \rightarrow$ Yellow colour

7. **(a)** $Ce = [Xe]\,4f^1\,5d^1\,6s^2$

$Ce^{3+} = [Xe]\,4f^1\,5d^0$

$Ce^{4+} = [Xe]\,4f^0\,5d^0$ (Noble gas configuration)

Ce^{3+} get easily oxidised to Ce^{4+} by acheiving noble gas configuration.

8. **(a)** $V = 3d^3\,4s^2$; $V^{2+} = 3d^3 = 3$ unpaired electrons

$Cr = 3d^5\,4s^1$; $Cr^{2+} = 3d^4 = 4$ unpaired electrons

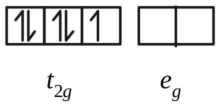
$Mn = 3d^5 4s^2$; $Mn^{2+} = 3d^5 = 5$ unpaired electrons

$Fe = 3d^6\,4s^2$; $Fe^{2+} = 3d^6 = 4$ unpaired electrons

Hence the correct order of paramagnetic behaviour

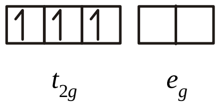
$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

9. **(d)** d^5 —— strong ligand field



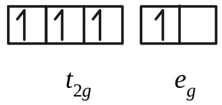
$\mu = \sqrt{n(n+2)} = \sqrt{3} = 1.73$ B.M.

d^3— in weak as well as in strong field



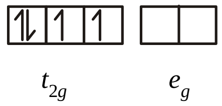
$\mu = \sqrt{3(5)} = \sqrt{15} = 3.87$ B.M.

d^4– in weak ligand field



$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89$

d^4– in strong ligand field



$\mu = \sqrt{2(4)} = \sqrt{8} = 2.82.$

10. **(d)** In $Cu^+[Ar]3d^{10}$ there is no unpaired electron, $Cu^{2+}[Ar]3d^9$ contains one unpaired electron hence coloured.

11. **(a)**

Ion	Valence shell electronic configuration
Eu^{2+}	$4f^7$
Pm^{2+}	$4f^5$
Ce^{2+}	$4f^2$
Gd^{2+}	$4f^75d^1$

Due to stable half filled 4f orbitals, Eu^{2+} will be most stable.

12. **(b)** Sc^{2+} has one unpaired e^- in its *d*-orbital.

13. **(b)** The oxidation state in both (lanthanide and actinide) is +3. The property of actinide are very similar to those of lanthanide when both are in +3 state.

14. **(b)** The required equation is

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + \underset{\text{nascent oxygen}}{5[O]}$$

$$2Fe(C_2O_4) + 3H_2SO_4 + 3[O] \longrightarrow Fe_2(SO_4)_3 + 2CO_2 + 3H_2O$$

O required for 1 mol. of $Fe(C_2O_4)$ is 1.5, 5O are obtained from 2 moles of $KMnO_4$

$\therefore$ 1.5 [O] will be obtained from $= \frac{2}{5} \times 1.5 = 0.6$ moles of $KMnO_4$.

15. **(c)** $K_2Cr_2O_7 + 3SO_2 + 4H_2SO_4 \rightarrow$

$$K_2SO_4 + Cr_2(SO_4)_3 + 3SO_3 + 4H_2O$$

O.N.of chrominum changes from +6 to +3

16. **(b)** In lanthanides, there is poorer shielding of 5 *d* electrons by 4 *f* electrons resulting in greater attraction of the nucleus over 5 *d* electrons and contraction of the atomic radii.

17. **(a)** $K_2CrO_4 \longrightarrow 2K^+ + CrO_4^{2-}$

$K_2Cr_2O_7 \longrightarrow 2K^+ + Cr_2O_7^{2-}$

Both ions contain – 2 charge.

18. **(d)** La $(OH)_3$ (Z = 57) is the most basic hydroxide due to lanthanide contration.

19. **(c)** Ti^{4+}, Cu^{1+} are colourless compound

Ti : [Ar] $4s^2 3d^2$ Cu : [Ar] $4s^1 3d^{10}$

Ti^{4+} : [Ar] $4s^0\ 3d^0$ Cu^{1+} : [Ar] $4s^0\ 3d^{10}$

20. **(d)** Zirconium (Zr) with atomic number 40 and Hafnium (Hf) with atomic number 72 belongs to period 5th and 6th respectively.

21. **(a)** Oxidation state of Mn in MnO_4^{2-} is +6.

Mn (+6) = $1s^2\ 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^1, 4s^0$

Hence, manganate ion MnO_4^{2-} is paramagnetic due to presence of unpaired electron. Also, MnO_4^{2-} is green in colour.

22. **(d)** When lanthanoids (Ln) are heated with sulphur, then Ln_2S_3 are formed.

23. **(a)** By the action of concentrated sulphuric acid, sodium chromate gets converted into sodium dichromate in the manufacture of potassium dichromate.

24. **(d)** For scandium (Z = 21)electronic configuration is $4s^2 3d^1$. After the removal of 3 electrons; (Sc^{3+}), acquires a stable configuration $(4s^0 d^0)$.

Hence, it forms colourless compounds.